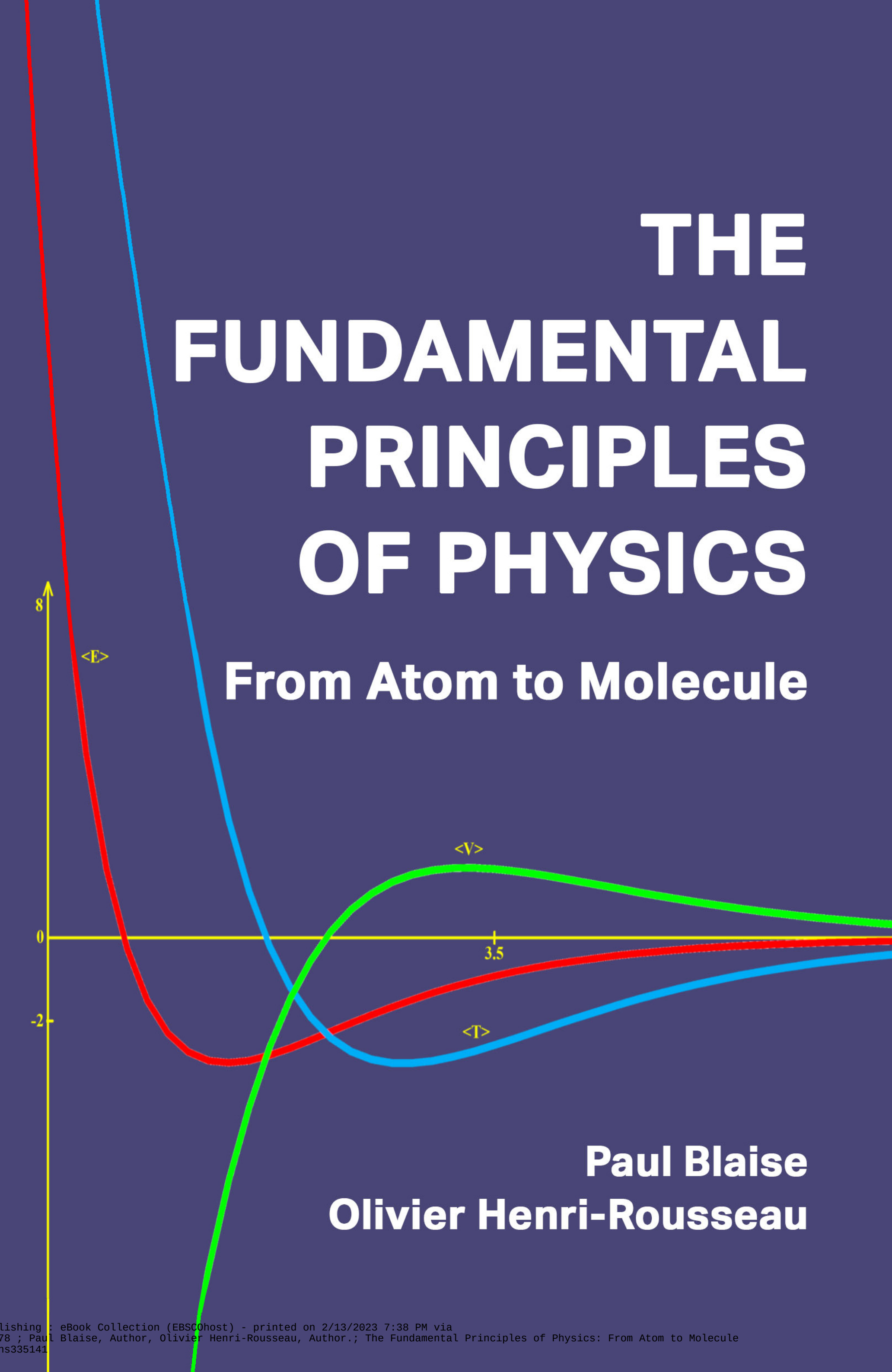

THE FUNDAMENTAL PRINCIPLES OF PHYSICS

From Atom to Molecule

Paul Blaise
Olivier Henri-Rousseau

The Fundamental Principles of Physics

The Fundamental Principles of Physics:

From Atom to Molecule

By

Paul Blaise and Olivier Henri-Rousseau

Cambridge
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The Fundamental Principles of Physics: From Atom to Molecule

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The Constituents of Matter

The Wave-Like and Corpuscular Nature of Light

PREFACE

The book by Profs. Paul Blaise and Olivier Henri-Rousseau entitled "The Fundamental Principles of Physics: From Atom to Molecule" presents in an illustrative, didactic and attractive way current knowledge in the area of molecular physics at the basic and advanced level for undergraduate science students.

The book is composed of eight chapters describing constituents of matter, the wave and corpuscular nature of light and matter, quantization of energy in the hydrogen atom, semi-classical and quantum models of the hydrogen atom, Lewis and MO models of chemical bond and chemical reactivity and molecular orbitals in electrocyclic reactions.

The material is presented in an attractive and illustrative way. The book contains photos of eminent scientists and well designed figures. Most of the chapters end with well prepared tutorials containing problems to be solved and answers.

This book is a valuable source of knowledge in molecular physics at the undergraduate level and is recommended to students of physics, chemistry and molecular science.

Prof. Dr. hab. Marek J. Wójcik
Jagiellonian University
Krakow, Poland

FOREWORD

This book corresponds to an introductory course on the structure of matter for students in the first years of their physical sciences degrees. Starting from the fundamental constituents of matter and highlighting their mutual interactions, it gradually leads to a more precise idea of what an atom or molecule is by using theories that seek to reproduce the experimental behaviors of matter while remaining within the commonly accepted scientific framework. The aim of this course is therefore to awaken in physical science students an acknowledgement of the complexity of reality, as well as the methods used to achieve some understanding of the world around us. To this end, since the beginning of the 20th century physics has possessed a powerful theoretical tool to understand certain aspects and behaviors of matter: quantum theory, which uses quantum mechanics. However, being aware of the difficulties in understanding quantum theory that can arise in the minds of students, we have often insisted on the importance of the physical principles underlying this theory, such as the Coulomb relation, the particle-wave duality, the notions of determinism and indeterminism, estimation of the probability of presence, and the virial theorem.

This book is composed of eight chapters. At the end of each chapter, we have added tutorials containing several exercises along with the answers.

Chapter I provides a directory of atomic constituents.

Chapter II is dedicated to the study of light, experimentally highlighting the wave-like behavior and the corpuscular character of electromagnetic vibrations in general.

In **Chapter III**, we are led to consider material particles using an identical approach and consider the behavior of both corpuscular and wave-like matter generally.

In **Chapter IV**, remaining in the microscopic domain, we discuss the various experiments that show the energy of electrons in atoms to be quantized.

Then, in **Chapter V**, we discuss the various semi-classical theories that explain the quantization of energy in the atom based on fundamental principles, as well as discussing their limitations and the need for more rigorous theory.

Chapter VI addresses the full quantum theory of the atom through the resolution of the Schrödinger equation; its resolution allows us to clarify the details of energy quantization with the model of stationary states. This model, extended to atoms with several electrons, is able to describe each atom by its electronic configuration and account for its physicochemical properties by explaining the periodic classification of the elements.

Chapter VII, being the largest chapter of this book, is the culmination of previous chapters. It is devoted to an analysis of chemical bonding both from the electronic point of view with Lewis's elementary theory, which allowed the principles defining a chemical bond between two atoms to be set down, and with the theory of molecular orbitals based on the linear combination of atomic orbitals. Part of this chapter is devoted to showing how the basic principles of physics are at work even in rudimentary models of atoms and molecules. In relation to polyatomic molecules, the notion of geometry intervenes with the shape of molecules in space. The predictive nature of a theory, such as the VSEPR method, combined with the theory of hybridization of atomic orbitals and the theory of molecular orbitals can provide the most relevant picture possible of what constitutes a molecule.

Finally, in **Chapter VIII**, which goes beyond the study of the structure of matter, we examine how this knowledge of molecules is at work in attempting to predict their reactivity. Thus, the use of the theory of molecular orbitals of polyenes is able to account for the experimental results of electrocyclic reactions.

CHAPTER I

THE CONSTITUENTS OF MATTER

I-I. The Macroscopic and Microscopic Domains

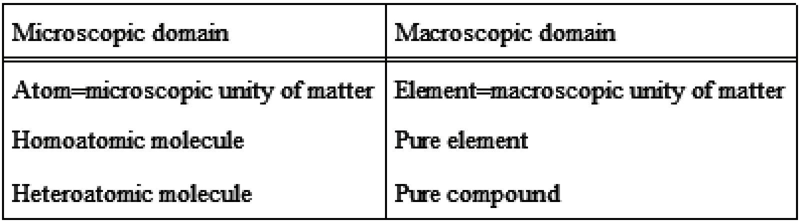
The world can be roughly divided into two domains: the macroscopic and the microscopic.

The macroscopic domain concerns that which is on the human scale or above.

The microscopic domain concerns that which is at the scale of the atom or below.

Thus, a comparison can be made between what is at the microscopic scale and what is at the macroscopic scale.

Table I-1: Microscopic and macroscopic domains



Microscopic domain	Macroscopic domain
Atom=microscopic unity of matter	Element=macroscopic unity of matter
Homoatomic molecule	Pure element
Heteroatomic molecule	Pure compound

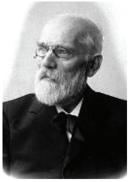
1. The macroscopic and microscopic ratio: the mole N

A. Avogadro

This ratio is given by the Avogadro[1] number, denoted by N. This overall classification must be clarified using a more quantitative measure of the microscopic character. A mole corresponds to a collection of N "individuals". In particular, we talk about the mole of atoms (N atoms), the mole of molecules (N molecules), or the mole of electrons (N electrons).

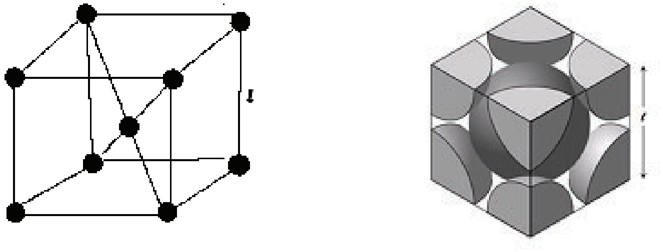
2. The value of N

As early as 1875, J. van der Waals estimated this value by interpreting the laws of real gases (based on the ideal gas law). Let us take the example of a variety of iron, α-iron, consisting of a regular assemblage of atoms, the basic pattern of which (conventional unit cell) is described as "centered cubic".



J. van der Waals[2]

In this model, the edge of the cube is l. The ball-and-stick form is shown on the left side of **Fig. I-1**. In fact, since the atoms are in contact with each other, the conventional unit cell should be represented as the *space-filling* form located on the right side of the same figure.



Ball-and-stick model. Space-filling model.

Figure I-1a: Iron α conventional unit cell.

---

[1] Amadeo Avogadro (1776-1856). Italian physicist and chemist.

[2] Johannes Diderik van der Waals (1837-1856). Dutch physicist and mathematician (1837-1923). He won the Nobel Prize in Physics in 1910.

Let us now detail the various steps leading to the calculation of the Avogadro number in the case of the α-iron crystal. Consider the space-filling form. It can be seen that there is 1/8 of an iron atom at each corner and thus each corner corresponds to a volume of $(1/8)v_{At}$, where v_{At} is the total volume of an atom. All 8 vertices correspond to a volume of approximately

$$v = 8(1/8)\, v_{At}$$

Let us add that there is a whole atom of iron in the center of the cell. If the residual gaps are neglected, this gives the cell the following total volume

$$v_{cell} \simeq \left(8\frac{1}{8} + 1\right)v_{At} = 2v_{At}$$

then

$$v_{At} \simeq \frac{v_{cell}}{2}$$

In addition, there are N atoms in a mole of atoms and thus the volume of a mole of atoms is

$$V_{At} = \mathcal{N} v_{At} = \mathcal{N}\frac{v_{cell}}{2}$$

However, the volume of the cell is, of course, that of a cube of edge l

$$v_{cell} = l^3$$

From this, we can then obtain the expression of the volume of the mole of an atom of iron

$$V_{At} = \mathcal{N} v_{At} = \mathcal{N}\frac{l^3}{2} \tag{I-1}$$

However, the density of iron is, by definition, the ratio between the mass of a mole of iron atoms M_{Fe} and its volume V_{Fe}

$$\rho_{Fe} = \frac{M_{Fe}}{V_{Fe}} \tag{I-2}$$

then

$$V_{At} = \frac{M_{Fe}}{\rho_{Fe}}$$

Let us identify the two expressions (I-1) and (I-2) for the volume of a mole of iron atoms

$$\mathcal{N}\frac{l^3}{2} = \frac{M_{Fe}}{\rho_{Fe}}$$

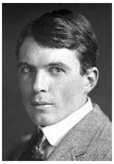
As a result, the expression of the Avogadro number can be determined experimentally by the following expression

$$\mathcal{N} = 2\frac{M_{Fe}}{\rho_{Fe} l^3} \qquad \text{(I-3)}$$

Now, we have to measure the distance l. To do this, an X-ray machine called the Debye-Scherrer chamber is used.

P. Debye[3]

P. Scherrer[4]



W. Bragg[5]

Here, the X-ray beam is focused on the iron crystal. If this beam is punctual, the crystal diffracts it. There is a symmetry of revolution around the axis of the beam. The diffracted rays form cones, the axis of which is the incident beam. On a photographic plate, we can then observe Debye-Scherrer rings, which are the traces of these cones. **Figs. I-1b** and **1c** illustrate these rings.

---

[3] Peter Debye (1884-1968). Dutch physicist known for his contributions to the study of dielectric materials. Winner of the Nobel Prize in Chemistry in 1936.

[4] Paul Hermann Scherrer (1890-1969). Swiss physicist known for his work on crystallography and, in particular, his contribution to the Debye-Scherrer method.

[5] William Bragg (1890-1971). British mathematician and crystallographic physicist. Winner of the Nobel Prize in Physics in 1915.

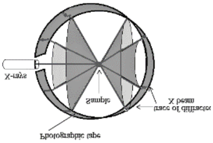


Figure I-1b: Debye-Scherrer chamber.

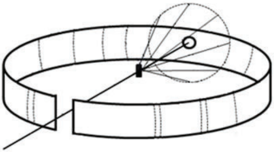


Figure I-1c: Details of diffraction rings.

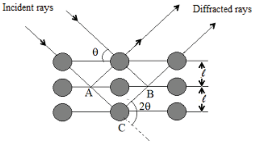


Figure I-1d: X-ray diffraction.

As schematized in **Fig. I-1d**, in a crystal there is a three-dimensional periodic repetition of elements (atoms or molecules) called nodes; these appear as dark discs on the figure representing the reticular planes passing through the centers of these elements, spaced at a distance of l. The angle θ, called the *Bragg angle*, determines the impact of a parallel X-ray beam on these reticular planes. Note that this is the complement to the usual angle of incidence in optics. The difference in the path between the two light rays depicted has a value of AC+CB = 2l sin θ. When this path difference is equal to an integer number n of wavelengths, they constructively interfere.

If λ is the wavelength of the radiation, θ is the angle of diffraction, and *l* is the inter-reticular distance of the diffracting crystal plane, then the 2θ directions of the space in which we have peaks of intensity that check Bragg's law are

$$2l\sin\theta = n\lambda$$

As such, the distance l can be deduced as

$$l = \frac{n\lambda}{2\sin\theta} \qquad \text{(I-4)}$$

where n = 1. For the iron crystal, we can find experimentally that

$$l = 2.864 \times 10^{-10} m.$$

This last result, introduced in Eq. (I-3), and using the atomic mass of iron $M_{Fe} = 55.8\ 10^{-3}$ kg and the iron density $\rho_{Fe} = 7.89\ 10^{3}$ kg.m^{-3}, allows us to propose a more precise value for the Avogadro number

$$\mathcal{N} = \frac{2 \times 55.8 \times 10^{-3}}{(2.864 \times 10^{-10})^3 \times 7.89 \times 10^3} = 6.03 \times 10^{23}$$

Note that the most accurate current value[6] of the Avogadro number is

$$\boxed{\mathcal{N} = 6.02214076 \times 10^{23}}$$

I-II. Highlighting the Complexity of Atoms

1. Experiment

The electron is an elementary or fundamental particle[7]. This can be highlighted by studying the radioactive decomposition of a piece of radium, which spontaneously emits several types of radiation:

α-radiation, which is an emission of material particles deflected in the direction of the field and which generates helium gas.

γ-radiation, which is a very high energy electromagnetic emission. This radiation is not sensitive to the action of the electric field and so the rays propagate in a straight line.

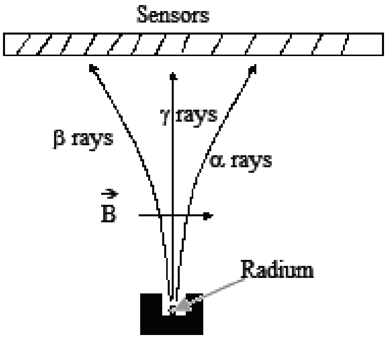


Figure I-2: Radioactive decomposition of radium.

β-radiation, which is made up of particles that are deflected in the opposite direction of the electric field and therefore carry an electrical charge inverse to that of the α-particles. Later, we will describe how this radiation is the result of the electrons. These three types of radiation are shown in **Fig. I-2**. Matter therefore appears to be made up of positive particles and negative particles.

---

[6] Peter J. Mohr, David B. Newell, & Barry N. Taylor, "CODATA Recommended Values of the Fundamental Physical Constants: 2014" [archive], July 30, 2015.

[7] An elementary or fundamental particle is a particle the composition of which is unknown or is not made up of other smaller particles.

2. Measuring the electron charge

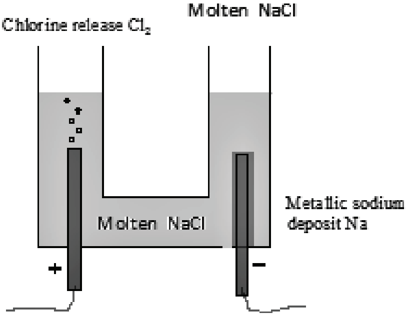


Figure I-3: Voltameter for performing electrolysis of molten sodium chloride.

A voltameter can be used to measure the charge of the electron, (See **Fig. I-3**):

Sodium chloride, under the action of the electric current, splits into Na^+ and Cl^- ions. Each ion moves to the electrode of the opposite sign. As such, metallic sodium is deposited at the anode (negative)

$$Na^+ + 1e^- \rightarrow Na$$

while at the cathode (positive) we have the reaction

$$2Cl^- \rightarrow Cl_2 + 2e^-$$

and Cl_2 molecular chlorine is released.

Let us consider the reaction at the anode. To deposit one Na atom, you have to circulate one electron

$$Na^+ + 1e^- \rightarrow Na$$

For one mole, we have

$$\mathcal{N} \times \text{ ion } Na^+ + \mathcal{N} \times e^- \rightarrow \mathcal{N} \times Na \text{ atoms}$$

The amount of electricity needed to deposit one mole of sodium atoms has been measured as Q = 96485 Coulomb[8]. This is the Faraday constant[9].

---

[8] Charles-Augustin Coulomb (1736-1806). French officer, engineer, and physicist. He clarified the laws of solid friction and formulated the law of attraction between electrified solids.

[9] Michael Faraday (1791-1867). British physicist and chemist.

C-A. Coulomb

M. Faraday

This amount must correspond to *N* times the elementary charge, i.e.

$$\mathcal{N}q = 96485 \text{ Coulombs}$$

so that

$$q = \frac{96485}{6.02214076\times10^{23}} = 1.602\times10^{-19}C$$

$$\boxed{q_e = -q = -1.602\times10^{-19}C}$$

3. Measuring the electron mass: the J. J. Thomson[10] experiment

In a famous experiment, pictured in **Fig. I-4** and called the J. J. Thomson experiment, the ratio q_e/m_e is determined.

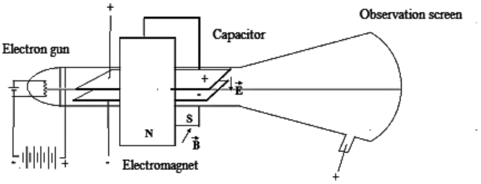


Figure I-4: Thomson experimental device.

This determination is made by studying the trajectory of an electron in an electric field perpendicular to its movement.

The electrons, emitted by the thermoionic effect (resistive heating) in an electron gun, are accelerated by the potential difference with the aid of a positive electrode before entering between the plates of a capacitor and the hole of an electromagnet. If the electric field is acting alone, the electrons of charge q_e undergo the action of an electrostatic force $\mathbf{f_{el}}$

$$\overrightarrow{f_{el}} = q_e\vec{E}$$

which is in the direction of the electric field with the modulus

---

[10] Sir J. J. Thomson (1856-1940). British physicist. Nobel Prize in Physics in 1906 for his studies on electrical conductivity in gas and discoverer of the electron.

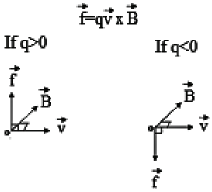
$$\left\| \vec{f}_{el} \right\| = q_e E$$

If induction **B** is acting alone, an electron of charge q_e and velocity **v** that enters a magnetic induction **B** perpendicular to the velocity vector **v** undergoes the action of a magnetic force $\mathbf{f}_{mgt}$, the direction of which is given by the right-hand rule (see the figure on the right)

$$\vec{f}_{mgt} = q_e \vec{v} \times \vec{B}$$

with the modulus

$$\left\| \vec{f}_{mgt} \right\| = q_e v B$$



If the electric field and the magnetic field act simultaneously, so that the electrostatic force is equal and opposite to the electromagnetic force, then we can write

$$\left\| \vec{f}_{el} \right\| = \left\| \vec{f}_{mgt} \right\|$$

i.e.

$$q_e E = q_e v B$$

Simplifying the expression by q_e, we get

$$E = vB$$

Hence the expression for the speed with which the electron will continue its path in a straight line without being deflected is

$$v = \frac{E}{B} \tag{I-5}$$

and, as such, we can know the speed modulus, which will be useful to us in the following.

4. Determining the electron q/m ratio

Now, let us consider an electron with mass m_e and charge q_e arriving at point O with uniform velocity v in the space between the capacitor plates. One can schematically represent the trajectory of the electron **as shown in Fig. I-5.**

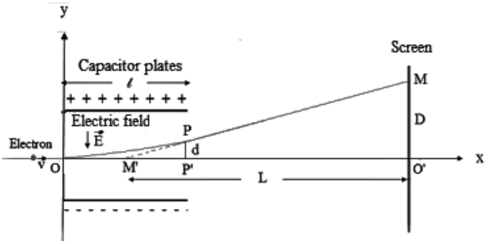


Figure I-5: Electron trajectory.

The electron is subject solely to the action of the electrostatic force. It follows from point O and, as long as it remains between the capacitor plates, describes a trajectory that will become parabolic. Once it has passed point P, marking the end of the space between the capacitor plates, its trajectory will show a straight and uniform movement and it will reach the observation screen at point M.

Consider the entry point O. The electron is subjected to an electrostatic force and its acceleration γ can be broken down in both directions of the plane, either x or y. Given the fundamental relationship of the dynamics **f** = m**γ**, for each component we can write

$$\gamma_x = 0; \quad \gamma_y = \frac{f}{m_e} = \frac{q_e E}{m_e}$$

By integrating each expression with respect to time, according to the x and y axes, respectively, we obtain

$$v_x = \gamma_x t + v_{0x}\,; \quad v_y = \gamma_y t + v_{0y}$$

where v_{0x} is the initial velocity of the electron along the x axis.

We can identify that the velocity v of the electron calculated in v_{0y} is the initial velocity along the y axis. Before the application of the electrostatic force, this is zero. The velocity v_y along the y axis is the integral in relation to the acceleration γ_y, so that

$$v_x = v \quad ; \quad v_y = \frac{qE}{m}t$$

Let us integrate these speeds with respect to time in order to get the coordinates for x and y

$$x = vt \quad ; \quad y = \frac{1}{2}\frac{q_e E}{m_e}t^2 \tag{I-6}$$

By reversing the left equation of Eq. (I-6), for time t we get

$$t = \frac{x}{v}$$

This allows us to rewrite y, as given by the right equation of Eq. (I-6), in the form of a dependence on the initial velocity v of the electron, its mass m_e, and the intensity of the electric field **E**

$$y(x) = \frac{1}{2}\frac{q_e E}{m_e}\left(\frac{x}{v}\right)^2$$

According to Eq. (I-5), this leads to

$$y(x) = \frac{1}{2}\frac{q_e E}{m_e}\left(\frac{Bx}{E}\right)^2 \tag{I-7}$$

By rearranging the following expression, which is that of a parabola (the left-hand part of Eq. (I-8), the derivative of which is given by the right-hand part of the same equation), we obtain

$$y(x) = \frac{1}{2}\frac{q_e B^2}{m_e E}x^2 \quad ; \quad y'(x) = \left[\frac{dy(x)}{dx}\right] = \frac{q_e B^2}{m_e E}x \tag{I-8}$$

The slope a at point P' of the abscissa x = l is the value of this derivative in x = l

$$a = \left[\frac{dy(x)}{dx}\right]_l = \frac{q_e B^2}{m_e E}l$$

The equation of the tangent y′(x) to the parabola y(x) is

$$y'(x) = ax + b \text{ i.e. } y'(x) = \left(\frac{q_e B^2}{m_e E} l\right) x + b$$

Let us now consider point M', the intersection between the tangent and the x-axis for which its ordinate y′(0) is obviously zero. Let us proceed, only for the tangent, to a change in the origin of the coordinate x for which the abscissa x becomes $\bar{x}$. The tangent equation thus becomes

$$y'(\bar{x}) = \left(\frac{q_e B^2}{m_e E} l\right) \bar{x} + b \tag{I-9}$$

Let us set $\bar{x}_{M'} = 0$ in M′. At this point, the ordinate of the tangent is zero so that in the new system of the abscissa $\bar{x}$ we have

$$0 = \left(\frac{q_e B^2}{m_e E} l\right) 0 + b$$

i.e. in the new coordinate system for $\bar{x}$, we have b = 0.

Eq. (I-9) can thus be simplified as

$$y'(\bar{x}) = \left(\frac{q_e B^2}{m_e E} l\right) \bar{x}$$

We now move on to consider point P'. The abscissa x_P for the parabola (I-8) is measured with respect to point O, i.e. x = l, while for the tangent in P, the abscissa x is measured with respect to the origin M', i.e. x = 0. An examination of **Fig. I-5** shows that the ordinate $y'(x = x_{P'})$ of the tangent y(x) in $x = x_{P'}$ is equal to the ordinate d of the parabola y(x = l)

$$y(x = l) = d = \frac{1}{2} \frac{q_e B^2}{m_e E} l^2 \tag{I-10}$$

and

$$y'(\bar{x} = \bar{x}_{P'}) = d = \left(\frac{q_e B^2}{m_e E} l\right) \bar{x}_{P'}$$

By equalizing the two expressions, we get

$$\left(\frac{q_e B^2}{m_e E} l\right) \bar{x}_{P'} = \frac{1}{2} \frac{q_e B^2}{m_e E} l^2$$

and by simplification we obtain

$$\bar{x}_{P'} = \frac{l}{2}$$

Let us return to **Fig. I-5**. Consider the similar triangles M'MO and M'PP'. Given the properties of similar triangles, one has

$$\frac{M'P'}{M'O'} = \frac{d}{D} \tag{I-11}$$

However, the length M'P' is none other than the coordinate $\bar{x}_{P'}$, which, as we have just seen, is equal to l/2. The tangent therefore cuts the x-axis at the mid-point of distance 1, i.e.

$$M'P' = \bar{x}_{P'} = \frac{l}{2}$$

In addition, by definition we have

$$M'O' = L$$

Using Eq. (I-11), we can write

$$\frac{l}{2L} = \frac{d}{D}$$

and the value of d is then deduced as

$$d = \frac{Dl}{2L}$$

Recall that d represents the ordinate of the parabola at point P' when the abscissa is l, given by the equation of the parabola Eq. (I-10). Then, we have

$$\frac{1}{2}\left(\frac{q_e B^2}{m_e E} l\right) l = \frac{Dl}{2L}$$

so that, after simplification and rearrangement, we have

$$\boxed{\left(\frac{q_e}{m_e}\right) = \frac{D}{L}\frac{E}{B^2 l}} \tag{I-12}$$

The geometric parameters D, L, and l are known, geometrically, from experimentation, while E and B are determined by the experimenter so that the electron crosses the space between the capacitor plates without being deflected with simultaneous application.

Various experiments have given the following result for the charge-to-mass ratio of the electron

$$\boxed{\frac{q_e}{m_e} = -1,759 \times 10^{11} C.\ Kg^{-1}}$$

Given the value of the charge q_e determined by other procedures such as electrolysis, which has been described above, or by Millikan's oil drop Experiment[11], i.e.

$$q_e = -1,602 \times\ 10^{-19} C$$

we obtain the following value for the mass of the electron

$$\boxed{m_e = 9,1 \times 10^{-31} Kg}$$

5. The nucleus

a. Description of the Rutherford[12] experiment

We have seen above that some natural radioactive elements, such as radium, emit α-radiation made up of He^{2+} cations carrying a positive charge equal

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[11] R. A. Millikan, Phys. Rev. (Series I) 32, 349 (1911).

[12] Ernest Rutherford (1871-1937). New Zealand and British physicist. He discovered that radioactivity was accompanied by the disintegration of chemical elements and won the Nobel Prize in Physics in 1908.

to twice the absolute value of the electron charge. These α-particles are emitted with a very high initial speed.

One can produce a narrow beam of these particles by placing two successive diaphragms, D_1 and D_2, in their path, as shown in **Fig. I-6**.

E. Rutherford

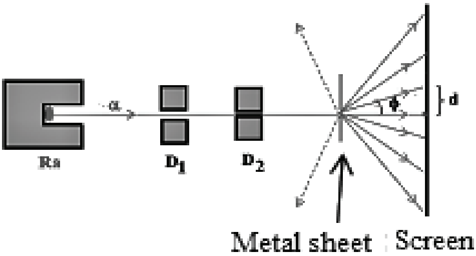


Figure I-6a: The Rutherford experiment

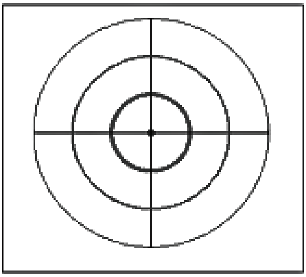


Figure I-6-b: Impact distribution.

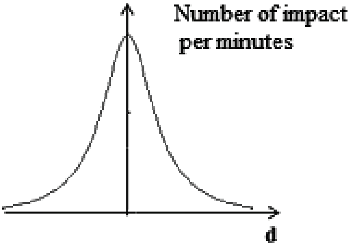


Figure I-6-c: Number of impacts per mn.

The α-particles can then be detected by the scintillation they produce in a screen of zinc sulfide. The apparatus is placed in a high vacuum environment. When a thin sheet of gold is inserted between the second diaphragm and the screen, we observe that:

(i) the gold leaf is not damaged;

(ii) the majority of the α-particles cross the gold leaf without deviating from the initial trajectory;

(iii) some particles are deflected by angle ϕ and meet the screen at distance d from the central spot;

(iv) the number of deviating particles decreases as angle ϕ increases;

(v) and the number of deviating particles increases with the atomic number Z of the metallic element that constitutes the sheet.

b. Interpretation of the Rutherford experiment

The Rutherford experiment shows that:

(i) Atoms are made up almost entirely of empty space, i.e. vacuum. In fact, if the atoms formed a compact whole, the particles would bounce off the metal sheet.

(ii) The force producing the observed deviations is the Coulomb force, which is exerted between the positively charged α-particles and centers of repulsion. These carry a positive charge.

(iii) These positive centers, which are called nuclei, constitute almost the entire mass of the atom since the mass of the negative particle, the electron, is about 2,000 times smaller than the mass of the lightest atom.

(iv) The force exerted on an α-particle, which carries the charge $q_\alpha = +2e$, is

$$f = k\frac{Qq}{r^2}$$

where Q is the charge of the positive center and k is a constant equal to $1/(4\pi\varepsilon_0)$.

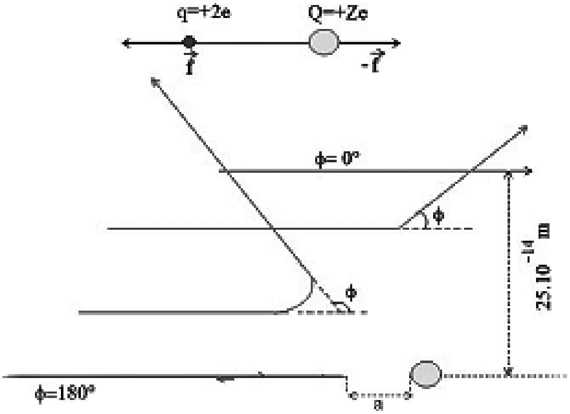


Figure I-6d: Repulsion and deviation between α particles and the positive center.

It can be seen that the (Q/e) ratio is an integer characteristic of the metal of the sheet and is the atomic number, denoted Z, of the metal. As we shall see later, it corresponds to the number of the box in which the metal is found in the periodic table.

Now, let us see what happens when an α-particle approaches the metal sheet. It will be subjected to the force of repulsion that we saw above and will describe a planar hyperbolic trajectory. The angle of deviation φ becomes all the more important as the initial direction of the particle passes closer to the nucleus. The results show that if the particle passes at a distance greater than 25×10^{-14} m from the positive center, it will not be deflected. The particles that are sent backwards (φ = 180°) are those going in the direction that passes through the positive center. Having approached the distance from the positive center, they turn back. At this stage, the initial kinetic energy is fully converted into potential electrostatic repulsion energy. The distance a of the particles decreases as their initial kinetic energy increases. It tends towards a limit, the distance a_0, which we assimilate to the radius of the positive center. We find that a_0 is about 10^{-14} m.

This positive center corresponds to the nucleus of an atom of the metal constituting the sheet. This nucleus contains particles, known as subnuclear particles, the nature of which we shall now discover.

c. The proton

The name ‘proton’ comes from the Greek and means ‘first’ or ‘in the first place’. This name was coined by Rutherford, whose experience we have just recounted highlighting positive centers in matter called the nuclei.

In 1919, Rutherford discovered that hydrogen nuclei, known to be the lightest nuclei, could be produced as a result of collisions with nitrogen atoms. He came to the conclusion that the proton could be a fundamental particle making up the nuclei.

Today, the proton is no longer considered a fundamental particle.

Figure I-7: Quarks inside a proton.

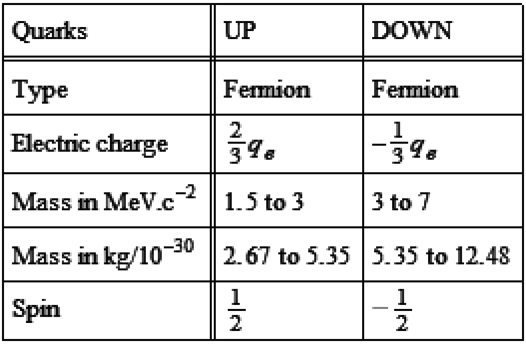
Figure 1-8: Quarks inside a neutron.

The new theory of matter, known as the standard model, considers it to be a composite particle made up of three sub-particles known as quarks[13].Quarks have a mass and an electrical charge that is fractional. These features are described in **Table I-2**.

---

[13] A quark is an elementary particle and a constituent of observable matter. Quarks combine to form hadrons, composite particles, of which protons and neutrons, among others, are known examples. The two up quarks and the proton’s down quark are linked by a strong interaction, transmitted by gluons. These gluons are exchanged between quarks and, by the binding energy they represent, constitute about 99 % of the mass of the proton. In addition to these three valence quarks (which determine the quantum numbers of the particle) and gluons, the proton, like other hadrons, consists of a ‘sea’ of pairs of virtual quarks-antiquarks that appear and disappear permanently.

Table I-2: Different types of quarks



Quarks	UP	DOWN
Type	Fermion	Fermion
Electric charge	$\frac{2}{3}q_e$	$-\frac{1}{3}q_e$
Mass in MeV.c^{-2}	1.5 to 3	3 to 7
Mass in kg/10^{-30}	2.67 to 5.35	5.35 to 12.48
Spin	$\frac{1}{2}$	$-\frac{1}{2}$

The rest of the mass of quarks contributes about 1 % of the mass of the proton. It is due to the bonding energy of the quarks, carried out by a field of gluons. This is symbolized in **Fig. I-7** by the grey springs connecting the up quarks and the down quarks.

The proton is part of a set of particles called fermions[14], in the framework of Fermi-Dirac statistics[15]. Composed of three quarks, it is part of the family of baryons[16]. The proton is made up of two UP quarks each with charge

---

[14] In the physics of particles, a fermion (named after Enrico Fermi) is a half-integer spin particle (i.e. 1/2, 3/2, 5/2...). It obeys Fermi-Dirac statistics. A fermion can be an elementary particle, such as an electron, a composite particle, such as proton, or all their antiparticles. All the elementary particles that have been observed are either fermions or bosons (hypothetical dark matter, not observed in 2018, is not currently categorized). Elemental fermions are grouped into two families the leptons (electrons, muons, tauons, and neutrinos), which are not subject to strong interaction and quarks, and are subject to the four interactions existing in nature. The other fermions are all composites. According to the Pauli exclusion principle, two identical fermions cannot be in the same place in the same quantum state. Thus, in the atom, all electrons have different quantum numbers; this is also the case in all other fermion systems.

[15] In quantum mechanics and statistical physics, the Fermi-Dirac statistic refers to the statistical distribution of indistinguishable fermions (all similar) on the energy states of a thermodynamic equilibrium system. The distribution in question is due to a particularity of fermions: the semi-whole spin particles are subject to the Pauli exclusion principle, namely that two particles cannot occupy the same quantum state simultaneously.

[16] In the physics of particles, a baryon (from the Greek βαρις, 'heavy') is a category of non-elementary particles, consisting of three quarks, whose most well-known representatives are the proton and neutron.

(2/3) q_e and spin (1/2), and one DOWN quark of charge -(1/3) q_e and spin -(1/2). Thus, its charge is

$$q_p = \frac{2}{3}q_e \times 2 - \frac{1}{3}q_e \times 1 = q_e$$

and its spin $\bar{s}$ is

$$\bar{s}_p = \frac{1}{2} \times 2 - \frac{1}{2} \times 1 = \frac{1}{2}$$

For the proton, the ratio q_p/m_p is equal to

$$\frac{q_p}{m_p} = 9.578\,844 \times 10^7 C.\ kg^{-1}$$

The electric charge of the positive proton[17], which is exactly equal to the elementary charge e, is

$$\boxed{q_p = +1,602176565 \times 10^{-19} C}$$

which gives us the mass of the proton

$$\boxed{m_p = 1.67262 \times 10^{-27} kg}$$

Thus, the mass of a proton is about 1836.15 times that of an electron.

Its radius is about 0.84 femtometer (fm), but its precise measurement remains a puzzle that is still to be solved. From a recent experiment carried out in September 2019[18], it would appear that its radius is

$$\boxed{r_p = 0.833 \pm\ 0.010\, fm}$$

---

[17] The electric charge of the proton is equal to the sum of the electrical charges of its quarks: each UP quark is 2/3 e and each DOWN quark is -1/3 e.

[18] A team from the University of York (Canada) was able to measure, using Ramsey interferometry (a technique that also appears in atomic clocks) and with unrivalled precision, the difference in energy between two excited states of the electron of an ordinary hydrogen atom. A measurement that can be traced back to the radius of the proton was established at 0.833±0.01 femtometer.

The proton is a positive particle. To determine its characteristics, one has to study its behavior in a bubble chamber. However, one can also use the device described below—the mass spectrometer.

Bubble chamber principle

The principle of a bubble chamber (a detector developed in 1953 by the American physicist Glaser[19], winner of the Nobel Prize in Physics in 1960) is as follows: a liquid (often hydrogen) is placed in a bubble chamber and compressed by a piston (phase (1), **Fig. 1-9**); its temperature is higher than its boiling temperature under atmospheric pressure, but lower than its boiling temperature under the pressure at which it is placed.

D. Glaser

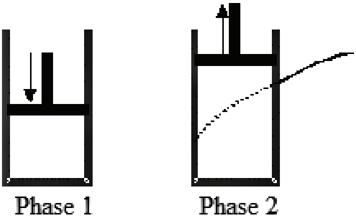


Figure I-9: Principle of the bubble chamber.

Immediately after the passage of the particle to be detected, the piston is relaxed (for about 1 ms, phase (2)) and the liquid (see **Fig. I-9**) returns to atmospheric pressure. Boiling begins around the ions created by the particle.

If you use a flash and take a photograph, the trajectory is materialized by a string of small bubbles.

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[19] Donald Glaser (1926-2013). American physicist who developed a particle detector in 1953, winning him the Nobel Prize in Physics in 1960 at the age of 34.

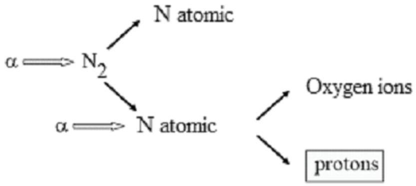


Figure I-10: Example of proton production in a bubble chamber.

N_2 liquid nitrogen molecules are bombarded with α-particles. These break the nitrogen molecule into nitrogen atoms according to the scheme shown in **Fig. I-10**. The protons are then sent towards the bubble chamber and the trajectory is materialized by the bubbles that the bubble chamber and the trajectory is materialized by the bubbles that appear with the passage of the charged particle.

b. The neutron

The neutron is a sub-atomic particle with zero electric charge and spin 1/2 that of the proton. Neutrons are present in the nucleus of atoms and linked with protons by the strong interaction. Neutrons bound in an atomic nucleus are generally stable, but free neutrons are unstable and disintegrate in just under 15 minutes. Free neutrons are produced in nuclear fission and fusion operations.

The neutron is not an elementary particle but a composite particle formed by the assembly of three components, the quarks: one UP quark and two DOWN quarks, linked by gluons as shown in **Fig. I-8**. The characteristics of these quarks are given in **Table I-2**.

Its charge q_n is

$$q_n = \frac{2}{3}q_e \times 1 - \frac{1}{3}q_e \times 2 = 0$$

with a half integer spin.

The mass of the neutron is more difficult to determine because it is a particle with zero charge. We are therefore obliged to proceed indirectly. To this end, we use a source of neutrons created by the collision of α-particles ($_2^4He^{2+}$) with beryllium atoms

$$_2^4He^{2+} + {}_4^9Be \rightarrow {}_6^{12}C + {}_0^1\mathbf{n}$$

which are sent to a bubble chamber containing, successively, hydrogen and nitrogen. These neutrons $_0{}^1n$ then collide with molecules of nitrogen (or hydrogen), breaking them up into atoms that themselves collide with neutrons and give rise to charged particles. These can be studied in the bubble chamber and make it possible to determine the mass of the neutron indirectly.

In practice, the study of trajectories in the bubble chamber makes it possible to identify the speed v_H of the hydrogen atoms (or v_N of nitrogen) after impact with a neutron. If the tank is filled with liquid hydrogen, one can then express the initial speed v_0 of the neutron-projectile of mass m_n before the impact with a hydrogen atom of mass m_H, as shown in **Fig. I-11**.

Figure I-11: collision between a neutron and a hydrogen atom.

Let us express the initial velocity v_0 of the neutron using the laws of conservation of momentum and kinetic energy.

The conservation of momentum

$$m_n\vec{v}_0 + m_H\vec{V}_{H_0} = m_n\vec{v}_n + m_H\vec{V}_H$$

where m_n is the mass of the neutron; m_H the mass of a hydrogen atom; and V_H is the speed of hydrogen atoms after impact with neutrons.

Given the orientation of the axis, we can express the previous equation in terms of algebraic values

$$m_n v_0 + m_H V_{H_0} = -m_n v_n + m_H V_H$$

Since the proton has negligible speed compared to that of the incident neutron, we have $V_{H_0} \approx 0$, i.e.

$$m_n v_0 = -m_n v_n + m_H V_H$$

or

$$m_n(v_0 + v_n) = m_H V_H \tag{I-13}$$

The conservation of kinetic energy

$$\frac{1}{2}m_n v_0^2 + \frac{1}{2}m_H V_{H_0}^2 = \frac{1}{2}m_n v_n^2 + \frac{1}{2}m_H V_H^2$$

by simplifying this expression, we get

$$m_n v_0^2 + m_H V_{H_0}^2 = m_n v_n^2 + m_H V_H^2$$

since $V_{H_0} \approx 0$, we have

$$m_n v_0^2 = m_n v_n^2 + m_H V_H^2$$

which can be rearranged to give

$$m_n(v_0^2 - v_n^2) = m_H V_H^2$$

$$m_n(v_0 + v_n)(v_0 - v_n) = m_H V_H^2 \tag{I-14}$$

Now, we introduce the result of (I-13) into this equation

$$m_H V_H(v_0 - v_n) = m_H V_H^2$$

After simplifying, we get

$$(v_0 - v_n) = V_H$$

Let us express the speed of the neutron as a function of the other parameters

$$v_n = v_0 - V_H \tag{I-15}$$

From Eq. (I-13), introducing Eq. (I-15), we get

$$m_n(v_0 + v_0 - V_H) = m_H V_H$$

i.e.

$$m_n(2v_0 - V_H) = m_H V_H$$

We can then express the initial speed v_0 of the neutron by rearranging this last expression as

$$v_0 = \frac{V_H(m_H+m_n)}{2m_n}$$

Similarly, if we replace liquid hydrogen with liquid nitrogen in the bubble chamber, we can write

$$v_0 = \frac{vV_N(m_N+m_n)}{2m_n}$$

If we use the same neutron source, we can then write

$$\frac{V_N(m_N+m_n)}{2m_n} = \frac{V_H(m_H+m_n)}{2m_n}$$

where m_N and V_N are, respectively, the mass and speed of the nitrogen. This leads to

$$V_N(m_N + m_n) = V_H(m_H + m_n)$$

and

$$V_N m_N + V_N m_n = V_H m_H + V_H m_n$$

By transposing and putting m_n into the factor, we get

$$V_N m_N - V_H m_H = (V_H - V_N) m_n$$

We deduce the expression of m_n as

$$\boxed{m_n = \frac{V_N m_N - V_H m_H}{(V_H - V_N)}}$$

The velocities V_H and V_N can be deduced from the study of the respective trajectories of the hydrogen or nitrogen ions that are visible in the bubble chamber. By replacing the letters with their respective values, we finally find the neutron mass

$$\boxed{m_n = 1.67493 \times 10^{-27} kg}$$

Having defined the basic bricks of matter, we can now see how their associations lead to chemical elements.

I-III. Chemical Elements

1. Definitions

a. The mass unit, abbreviated as u, amu, or Dalton

J. Dalton

Table I-3. Particle masses

Particle	SI (kg)	u
Proton	1.672649×10^{-27}	1.0072765
Neutron	1.674930×10^{-27}	1.0086649
electron	9.1095×10^{-31}	0.00055

By convention, since the 1960s the atomic mass unit has been defined as 1/12th the mass of the carbon isotope 12, thus

$$1u = 1.660538921 \times 10^{-27} kg$$

Some masses expressed in kilograms and atomic mass units are given in **Table I-3**. Note that

$$\frac{10^{-3}}{\mathcal{N}} = 1.66043 \times 10^{-27} kg \text{ with } \mathcal{N} = 6.02252 \times 10^{23}$$

and

$$1u = 1 Dalton \simeq \frac{10^{-3}}{\mathcal{N}} kg$$

b. Mass number A

"A" indicates:

(i) the mass of the nucleus expressed in u (or Dalton);

(ii) the number of nucleons contained in the nucleus given quasi-equality between the respective masses of the proton and the neutron.

c. Atomic number Z

"Z" indicates:

(i) the mass of the protons expressed in u (or Dalton);

(ii) the number of protons contained in the nucleus (due to the almost equal mass of the proton and the neutron).

d. Representation of a chemical element

In the nucleus there are A nucleons, Z protons, A-Z neutrons, and Z-Q electrons. If Q is a negative charge, then we have an anion. If Q is a positive charge, we have a cation.

$$ {}^{A}_{Z}X^{Q} \begin{cases} X \text{ is the symbol} \\ A \text{ is the mass number} \\ Z \text{ is the atomic number} \\ Q \text{ is the charge} \end{cases} $$

e. Mass defect

The mass defect, denoted Δm, is the difference between the sum of the masses of all the nucleons of a nucleus (mass of Z protons + mass of (A-Z) neutrons) and the mass of this same nucleus M(A,Z) i.e.

$$\Delta m = \underbrace{Z \times m_p + (A - Z) \times m_n}_{\text{Way 2}} - \underbrace{M(A,Z)}_{\text{Way 1}}.$$

The binding energy per nucleon is not the same, but varies according to the nuclide. The mass equivalent of the cohesion energy of nucleons is calculated by taking the difference between the two ways of calculating the mass of the nucleus. A good example is uranium 235 (${}_{92}{}^{235}U$). To simplify the equation, the mass defect can be calculated using two different methods of calculating the mass of an atom.

Way 1. Using the definition of the atomic mass unit. The mass of the nucleus is

$$m_1 = 235 \times 1.66054 \times 10^{-27} = 3.902269 \times 10^{-25} kg$$

Way 2. Using the nucleons.

92 protons: $92 \times 1.67262 \times 10^{-27} = 1.53881 \times 10^{-25}$ kg

235-92 = 143 neutrons: $143 \times 1.67493 \times 10^{-27} = 2.395150 \times 10^{-25}$ kg

Total

$$m_2 = 1.53881 \times 10^{-25} + 2.395150 \times 10^{-25} = 3.93396 \times 10^{-25}\ kg$$

Mass defect: method 2 - method 1:

$$\Delta m = m_2 - m_1 = 3.93396 \times 10^{-25} - 3.902269 \times 10^{-25} = \underline{3.1691 \times 10^{-27} kg}$$

The energy equivalent of this mass defect is given by Einstein's relation $E = mc^2$, where $c = 2.99792458 \times 10^8$ m.s^{-1} is the speed of light

$$\Delta E = \Delta m \times c^2 = 3.1691 \times 10^{-27} \times (2.99792458 \times 10^8)^2 = 2.848245 \times 10^{-10} J$$

For a mole of uranium 235 we would have

$$\Delta E_m = 2.848245 \times 10^{-10} \times \mathcal{N} = 2.848245 \times 10^{-10} \times 6.02252 \times 10^{23} = 1.715361 \times 10^{14} J$$

and thus 235 g of uranium[20] would release 1.715361×10^{14} J by nuclear fission.

---

[20] For the purposes of comparison, let us see what would be released by the combustion of a ton of coal knowing that the combustion of one mole of carbon releases 94 kcal/mole and that 1 calorie = 4.18 joules.
1 ton of coal would release $94000 \times 4.18 \times ((1000)/(12)) \times 1000 = 3.274333 \times 10^{10}$ J.
We deduce that the fission of a mole of ${}_{92}^{235}U$ (235g) would be equivalent to the combustion of $((1.715361 \times 10^{14})/(3.274333 \times 10^{10})) = 5239$ tons of coal, which shows that a lot of energy is contained in the nucleus of an atom.

2. Experimental determination of the mass of elements

Below, we describe the characteristics and use of the mass spectrometer with speed filter.

The mass spectrometer with speed filter can be considered as something like a balance for weighing atoms. It consists of four parts: an *ion producer*; a *speed filter*; an *ion deflection chamber*; and a *detector* (shown in **Fig. I-12**).

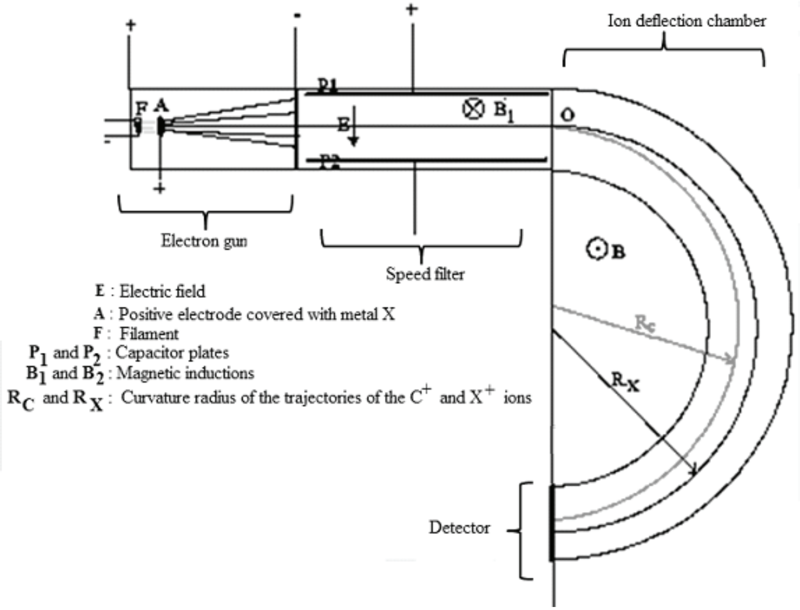


Figure I-12: The mass spectrometer with speed filter.

Ion producer

Ion production is by electrons accelerated through a positive potential difference—this is an electron gun. Electrons, emitted by the F filament, tear the X^+ ions from the X metal. These ions are accelerated by a negative potential difference and penetrate the speed filter at all speed ranges. Once there, they are subjected to the simultaneous action of an electric field **E** and a magnetic field $\mathbf{B}_1$. The electrostatic force $\mathbf{f}_{el}$ and the electromagnetic force $\mathbf{f}_{em}$ act on the ion, compensating for and allowing the straight-line path of the ion, which will then enter the deflection chamber through the O-hole (see **Fig. I-13**).

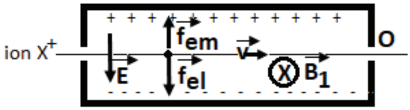


Figure I-13: Balance of forces in the speed filter.

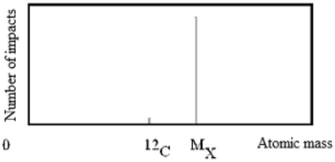


Figure I-14: Mass spectrogram.

Speed filter

One must have

$$\vec{\mathbf{f}}_{el} + \vec{\mathbf{f}}_{em} = 0$$

with

$\vec{\mathbf{f}}_{el} = q\vec{\mathbf{E}}$ for the electrostatic force directed in the sense of $\vec{\mathbf{E}}$

and

$\vec{\mathbf{f}}_{em} = q\vec{\mathbf{v}} \times \vec{\mathbf{B}}_1$ for the electromagnetic force directed in the opposite sense to $\vec{\mathbf{E}}$

The modulus of these forces are

$\left\| \vec{\mathbf{f}}_{el} \right\| = qE$ for the electrostatic force

$\left\| \vec{\mathbf{f}}_{em} \right\| = qvB_1$ for the electromagnetic force

In order for the ions to cross the filter in a straight line, we must have

$$\left\| \vec{\mathbf{f}}_{el} \right\| = \left\| \vec{\mathbf{f}}_{em} \right\|$$

i.e.

$$qE = qvB_1$$

so that

$$\boxed{v = \frac{E}{B_1}} \tag{I-16}$$

Thus, only ions with speed v equal to the ratio E/B_1 will be allowed to enter the speed filter.

Deflection chamber

In the deflection chamber, the ions are subject to the action of magnetic field **B** induction. They describe a circular trajectory and will hit the plane at the ion counters (detector). The ions enter the deflection chamber with speed **v**. They are then subjected to the action of a centripetal electromagnetic force $\mathbf{f}_{em}$, which is compensated for by a centrifugal mechanical force $\mathbf{f}_{mec}$ so that the modulus of these forces are equal

$$\left\| \vec{\mathbf{f}}_{mec} \right\| = \left\| \vec{\mathbf{f}}_{em} \right\|$$

that is

$$qvB = \frac{mv^2}{R}$$

where R is the radius of the curvature of the trajectory and the mass m of the ion. Then, the mass of the ion can be deduced as

$$m = \frac{qB}{v}R \tag{I-17}$$

although we have seen with Eq. (I-16) that

$$v = \frac{E}{B_1}$$

then Eq. (I-17) becomes

$$m = \frac{qBB_1}{E}R$$

and we find that the mass is proportional to the radius of the curvature of the ion in the deflection chamber. If we wish to discover the atomic mass of the ion, for a mole of ions we write

$$M(g) = \frac{qBB_1\mathcal{N}\times 10^5}{E}R(cm) \tag{I-18}$$

In practice, it is easier to work with a standard substance. In this case, some trace of a substance with a known atomic mass, such as carbon ^{12}C, is introduced into the X sample. Here, let R_c and R_x be the respective curvature radii of carbon C and metal X; using the previous equation, it is obvious that

$$\frac{M_X}{M_c} = \frac{R_X}{R_C} \text{ so that } M_X = \frac{M_c}{R_C}R_X$$

Since there is a proportionality between the curvature radius and the mass, and therefore between the curvature diameter and the mass, it is easy to connect the mass directly to the distance between the origin 0 and the impact of the peaks. This distance corresponds to the curvature diameter of the ion in question. This allows us to draw a graph showing the number of impacts recorded during the experiment and the atomic mass of the corresponding ion. The graph, as shown in **Fig. I-14**, is called a spectrogram. The peak corresponding to the standard substance appears, but with negligible intensity.

Now, let us look at the case of several isotopes present in a sample, for example, the case of two isotopes[21]. Let a and b be the isotopes of an element present in a sample with respective atomic masses M_a and M_b. After processing in the mass spectrometer, it can be observed that the number of impacts of a is N_a while b is N_b. The number of ion impacts indicates the quantity of the isotopes present in the sample. The resultant number needs to be reduced to a fraction or percentage.

We then proceed to normalize the intensities of the peaks. The number of impacts is proportional to the height of the peaks in the spectrogram: h_a and h_b are the respective heights of the two peaks. This normalized intensity is called *abundance*.

$$I_n = \frac{N_n}{\sum_n N_n} = \frac{h_n}{\sum_n h_n}$$

or, in the present case

---

[21] Elements are isotopes that have the same atomic number, but different mass numbers.

$$I_a = \frac{h_a}{h_a + h_b} \qquad \text{and} \quad I_b = \frac{h_b}{h_a + h_b}$$

We can is easily understand that

$$\sum_{n=a}^{b} I_n = 1$$

i.e., in the present case

$$I_a + I_b = 1$$

In addition, knowledge of the abundances can be used to calculate the natural atomic mass of the sample

$$\boxed{M = I_a \times M_a + I_b \times M_b}$$

Now that we can determine the characteristics of each element, let us look at the situation they occupy in a table of *periodic classification*.

I-IV. Periodic Classification of Elements (Descriptive)

The periodic table or Periodic Classification of Elements was invented by the Russian chemist D. Mendeleev[22] who built the first table in 1869 (it is different from the one we use today, but similar in principle). This table proposed a systematic classification of the elements known at the time in order to emphasize the periodicity of their chemical properties; to identify elements that were yet to be discovered; and to predict certain properties of chemical elements then unknown.

1. Description

The Periodic Classification of Elements used today is based on the following principles:

---

[22] Dmitri Mendeleev (1834-1907) was a Russian chemist known for his table of the classification of elements according to their physico-chemical properties.

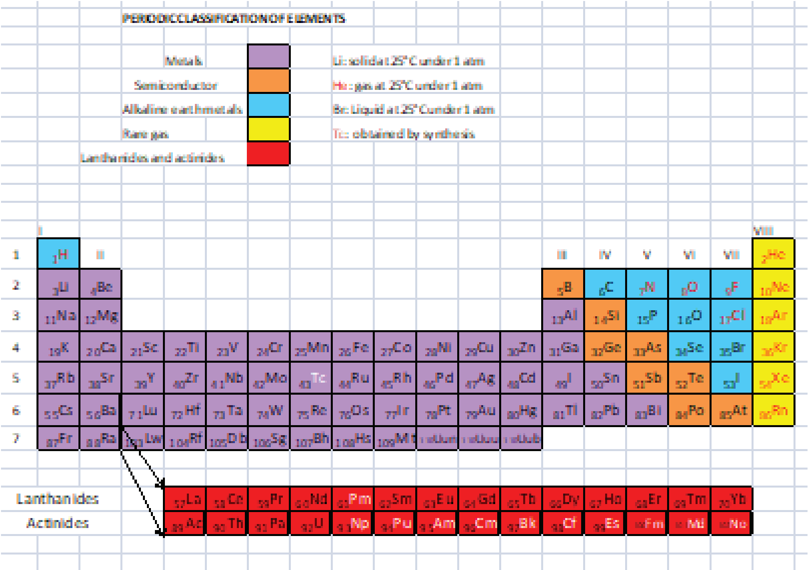
(i) Elements are ranked in order of increasing atomic number, from left to right and up and down.

(ii) Elements with the same physical-chemical properties are placed in the same column and define a *family* or a *group*.

(iii) A row of the periodic classification is called a *period*.

D. Mendeleev

Table I-4: Periodic classification of the elements



PERIODIC CLASSIFICATION OF ELEMENTS

Metals 🟪
Semiconductor 🟧
Alkaline earth metals 🟦
Rare gas 🟨
Lanthanides and actinides 🟥

Li: solid at 25°C under 1 atm
He: gas at 25°C under 1 atm
Br: Liquid at 25°C under 1 atm
Tc: obtained by synthesis

	I																	VIII
1	$_{1}$H	II											III	IV	V	VI	VII	$_{2}$He
2	$_{3}$Li	$_{4}$Be											$_{5}$B	$_{6}$C	$_{7}$N	$_{8}$O	$_{9}$F	$_{10}$Ne
3	$_{11}$Na	$_{12}$Mg											$_{13}$Al	$_{14}$Si	$_{15}$P	$_{16}$O	$_{17}$Cl	$_{18}$Ar
4	$_{19}$K	$_{20}$Ca	$_{21}$Sc	$_{22}$Ti	$_{23}$V	$_{24}$Cr	$_{25}$Mn	$_{26}$Fe	$_{27}$Co	$_{28}$Ni	$_{29}$Cu	$_{30}$Zn	$_{31}$Ga	$_{32}$Ge	$_{33}$As	$_{34}$Se	$_{35}$Br	$_{36}$Kr
5	$_{37}$Rb	$_{38}$Sr	$_{39}$Y	$_{40}$Zr	$_{41}$Nb	$_{42}$Mo	$_{43}$Tc	$_{44}$Ru	$_{45}$Rh	$_{46}$Pd	$_{47}$Ag	$_{48}$Cd	$_{49}$I	$_{50}$Sn	$_{51}$Sb	$_{52}$Te	$_{53}$I	$_{54}$Xe
6	$_{55}$Cs	$_{56}$Ba	$_{71}$Lu	$_{72}$Hf	$_{73}$Ta	$_{74}$W	$_{75}$Re	$_{76}$Os	$_{77}$Ir	$_{78}$Pt	$_{79}$Au	$_{80}$Hg	$_{81}$Tl	$_{82}$Pb	$_{83}$Bi	$_{84}$Po	$_{85}$At	$_{86}$Rn
7	$_{87}$Fr	$_{88}$Ra	$_{103}$Lw	$_{104}$Rf	$_{105}$Db	$_{106}$Sg	$_{107}$Bh	$_{108}$Hs	$_{109}$Mt	Uun	Uuu	Uub						
Lanthanides				$_{57}$La	$_{58}$Ce	$_{59}$Pr	$_{60}$Nd	$_{61}$Pm	$_{62}$Sm	$_{63}$Eu	$_{64}$Gd	$_{65}$Tb	$_{66}$Dy	$_{67}$Ho	$_{68}$Er	$_{69}$Tm	$_{70}$Yb	
Actinides				$_{89}$Ac	$_{90}$Th	$_{91}$Pa	$_{92}$U	$_{93}$Np	$_{94}$Pu	$_{95}$Am	$_{96}$Cm	$_{97}$Bk	$_{98}$Cf	$_{99}$Es	Fm	Md	No	

In this periodic table, the element characteristics and properties are symbolized by colors.

2. Period and number of electrons

Z is the number of protons in the nucleus, but also, if the element is neutral, the number of electrons around the nucleus. The classification of the elements suggests that the electrons have an organized arrangement inside the atom.

Experiment

When fast electrons are sent towards chemical elements, the electrons of these elements are torn off, with the following process

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

The energy involved in this process is called the *ionization potential* (IP) *or ionization energy* (IE). There exists an ionization potential for each extracted electron and there will be as many ionization potentials as there are electrons in the atom. As such, we may write the different processes

$$IP_1 + X \rightarrow X^+ + e^-$$

$$IP_2 + X^+ \rightarrow X^{2+} + e^-$$

$$IP_3 + X^{2+} \rightarrow X^{3+} + e^-$$

and for the last ionization potential we have

$$IP_n + X^{(n-1)+} \rightarrow X^{n+} + e^-$$

Let us consider the example of phosphorus (P) and undertake the experiment of pulling its electrons out one by one. The Ln(IP$_n$) of these ionization potentials can be plotted on a graph (**Fig. I-15**) against the number n° of the extracted electrons.

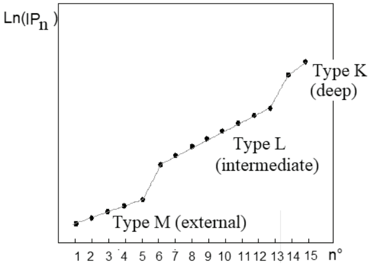


Figure I-15: “Families” of ionization potentials of phosphorus.

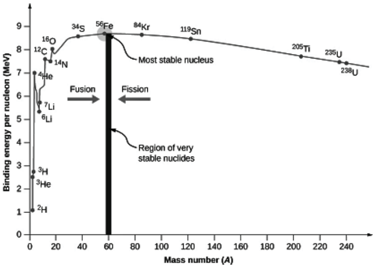


Figure I-16: Binding energy per nucleon.

In the case of $_{15}P$, the electrons may be divided into 3 categories:

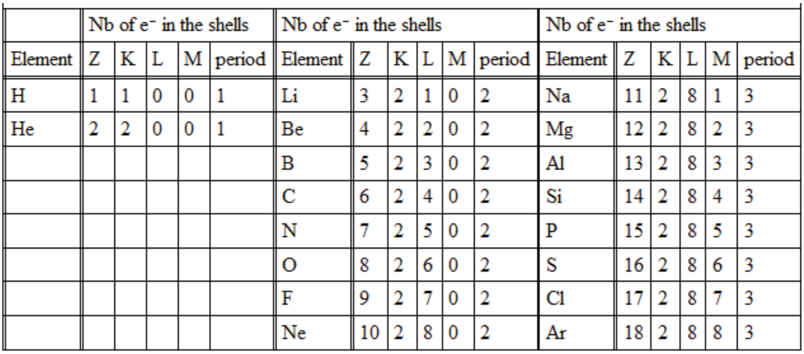
5 electrons of external-type (type M) with low ionization potential;

8 intermediate-type electrons (type L), the IPs of which align without breaking the slope;

2 deep-type electrons (type K) with high-value IP.

Ionization potentials measuring the importance of the electron's connection to the atom make it possible to distinguish between the various energy situations of the electrons. Thus, the type of ionization potential corresponds to the shells in the energy distribution of the electrons in the atom. The same experience may be repeated with other elements to obtain **Table I-5**.

Table I-5: Energetic shells in the elements



	Nb of e^- in the shells					Nb of e^- in the shells						Nb of e^- in the shells					
Element	Z	K	L	M	period	Element	Z	K	L	M	period	Element	Z	K	L	M	period
H	1	1	0	0	1	Li	3	2	1	0	2	Na	11	2	8	1	3
He	2	2	0	0	1	Be	4	2	2	0	2	Mg	12	2	8	2	3
						B	5	2	3	0	2	Al	13	2	8	3	3
						C	6	2	4	0	2	Si	14	2	8	4	3
						N	7	2	5	0	2	P	15	2	8	5	3
						O	8	2	6	0	2	S	16	2	8	6	3
						F	9	2	7	0	2	Cl	17	2	8	7	3
						Ne	10	2	8	0	2	Ar	18	2	8	8	3

There is a direct relationship between the level of shell occupancy and the period. A period of the periodic classification corresponds to the gradual saturation of the shells. We can say that the K shell is saturated with 2 electrons and the L shell with 8 electrons. If we were to continue the experiment, we would be able to show that the M shell is saturated with 18 electrons. If n is the number of the shell, it can be said that each shell can contain a maximum of $2n^2$ electrons.

3. Radioactivity

In order to complete this description of the periodic classification, we need to say something about the phenomenon of radioactivity, which concerns those elements belonging to the 6th and 7th periods of the periodic classification. This phenomenon reveals the aptitude of such elements to change into other elements, i.e. the phenomenon of transmutation.

a. Binding energy

Fig. I-16 shows the evolution of the binding energy per nucleon as a function of the number of mass A for different stable atomic nuclei.

For an atom

$$M_{Atom}(Z,A) = M_{Nucleus}(Z,A) + Zm_e - \frac{B_e}{c^2}$$

For a nucleus, we have

$$M_{Nucleus}(Z,A) = Zm_p + (A - Z)m_n - \frac{B_N}{c^2}$$

where B_N is the nuclear bond energy.

With the exception of very light nuclei, the nuclear bond energy per nucleon B_N/A varies very little (saturation of the nuclear forces) and is close to 8 MeV.

High-energy nuclei per nucleon can be obtained in two ways:

by breaking a heavy nucleus into two lighter nuclei, i.e. the fission process;
or by assembling two light nuclei into a heavier nucleus, i.e. the fusion process.

b. Nuclear forces

The core cohesion is due to the strong nuclear interaction.

Characteristics of nuclear forces:

(i) Attractive and very intense (strong binding energy of the nucleons).

(ii) Very short range ≃1 fm (different from the long range Coulomb force in $1/r^2$).

(iii) Independent of the charge (identical attraction forces neutron-neutron, proton-proton, and neutron-proton.

(iv) They are saturated.

As discussed above (see **Fig. I-2**), there are three types of particles (or radiation) emitted: α, β, and γ. These radiations are classified according to their penetrative power into a material: α radiation is the least penetrating (it can be stopped by a sheet of paper), while γ radiation is the most penetrating with several cm of lead being needed to block it. The nuclei, being unstable, spontaneously transform into other nuclei by simultaneously emitting particles; they are said to disintegrate.

c. Different disintegration processes

(i) α-emission

Radioactive entities emit α-particles. An α-particle is a helium nucleus, i.e.

$$\alpha = {}_2^4 He^{2+}$$

Consequently, when an entity emits an α-particle, its mass number diminishes by 4 units and its atomic number by 2 units, i.e.

$${}_Z^A X \rightarrow {}_{Z-2}^{A-4} Y + {}_2^4 \alpha$$

(ii) β^--emission or β^--disintegration

Here, we see the emission of an electron and an anti-neutrino (massless anti-particle). The atomic number increases by 1 unit

$${}_Z^A X \rightarrow {}_{Z+1}^{A} Y + e^- + {}_0^0 \bar{\upsilon}$$

(iii) β^+-decay

The emission of a positron[23] and a neutrino[24] (of zero mass). The atomic number decreases by 1 unit

---

[23] A positron or antielectron is the antimatter counterpart to an electron. A positron has the same mass as an electron and a spin of 1/2, but it has an electrical charge of +1.

[24] A neutrino □□is a fermion that interacts only via the weak subatomic force and gravity. The neutrino is so named because it is electrically neutral and its resting mass is so small that it was long thought to be zero.

$$ {}_{Z}^{A}X \rightarrow {}_{Z-1}^{A}\ Y + e^{+} + {}_{0}^{0}\ \upsilon $$

(iv) K-capture

As in β^+-decay, we see the emission of a neutrino, but the process is different as the nucleus captures an electron belonging to the nearest electronic shell (K). The atomic number decreases by 1 unit

$$ {}_{Z}^{A}X + e^{-} \rightarrow {}_{Z-1}^{A}\ Y + \ {}_{0}^{0}\upsilon $$

d. Radioactive series

A decay chain or radioactive decay series refer to a series of radioactive decays from an unstable parent isotope to a stable one through a sequential series of transformations.

All elements have a mass number, which can be put in the form

$$ A = 4n + r \qquad \text{(I-19)} $$

The integer r represents the radioactive series. It can only take 4 values: 0, 1, 2, and 3. The integer n characterizes the element of the series. The variation of n and r defines the radioactive series.

Three main decay chains (or families) are observed in nature, commonly called the *thorium series (A=4n)*, the *radium or uranium series (A=4n+2)*, and the *actinium series (A=4n+3).* They result in three different stable isotopes of lead. The long-lived starting isotopes of these three isotopes, respectively thorium (^{232}Th), uranium (^{238}U), and uranium (^{235}U), have existed since the formation of the earth, ignoring the artificial isotopes and their decays that have existed since the 1940s.

A fourth chain, the *neptunium series (A=4n+1)*, has the starting isotope of neptunium (^{237}Np), which has a half-life of 2.14 million years; this chain does not exist in nature. The final isotope of this chain is now known to be thallium-205.

Example

Uranium (^{238}U) is a radioactive element belonging to the r = 2 series. We can deduce the mass numbers belonging to this series.

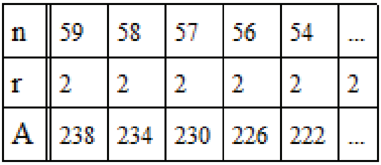
First, we have to find the value of n, characteristic of ^{238}U

$$238 = 4n + 2$$

then n = 59.

From here, we can determine the other elements by applying the formula in (I-19).

Table I-6: Radioactive series and elements



n	59	58	57	56	54	...
r	2	2	2	2	2	2
A	238	234	230	226	222	...

e. Law of radioactive decay

Let us consider the chain of uranium-lead decays in which the final step is lead. The number of uranium atoms in a sample decreases over time. The *decay rate* or *radioactive activity* is a function of the number of ^{238}U atoms present in the sample, i.e.

$$v = \lambda N_U$$

where N_U represents the number of uranium atoms and λ is the decay rate constant. This process displays first order kinetics.

We can also express the decay speed as the variation of the number of atoms per unit of time, i.e.

$$v = -\frac{dN_U}{dt}$$

we can then write

$$\frac{dN_U}{dt} = \lambda N_U$$

so that

$$\frac{dN_U}{dt} = -\lambda N_U$$

or

$$\frac{dN_U}{N_U} = -\lambda dt$$

By integration with respect to time we obtain

$$\ln\left(\frac{N_U}{N_U{}^\circ}\right) = -\lambda dt$$

where $N°_U$ is the number of uranium atoms at the initial time. This expression can be written

$$N_U(t) = N°_U\, e^{-\lambda t}$$

where $N°_U$ (t) is the number of uranium atoms at time t. This is the *radioactive decay law*.

Now, let us make a simplistic approximation by saying that all the lead present in the sample comes from the disintegration of uranium. We can then write that the number of lead atoms present in the sample at time t is

$$N_{Pb}(t) = N_U{}^\circ - N_U{}^\circ e^{-\lambda t}$$

or

$$N_{Pb}(t) = N_U{}^\circ(1 - e^{-\lambda t})$$

The ratio between the quantities of lead and uranium may then be written

$$\frac{N_{Pb}(t)}{N_U(t)} = \frac{N°_U\left(1-e^{-\lambda t}\right)}{N°_U e^{-\lambda t}} = \frac{\left(1-e^{-\lambda t}\right)}{e^{-\lambda t}}$$

If this ratio is known, then we can find the age of the sample

$$\frac{N_{Pb}(t)}{N_U(t)} = \frac{\left(1-e^{-\lambda t}\right)}{e^{-\lambda t}}$$

or

$$N_{Pb}(t)e^{-\lambda t} = N_U(t)(1 - e^{-\lambda t})$$

which may be written

$$e^{\lambda t} = \left(\frac{N_{Pb}(t)}{N_U(t)} + 1\right)$$

and finally

$$\boxed{t = \frac{1}{\lambda} Ln\left(\frac{N_{Pb}(t)}{N_U(t)} + 1\right)}$$

f. Radioactive half-life

The radioactive half-life is the time T after which the number of radioactive atoms remaining is half the initial number of atoms. In our example

$$N_u(T) = \frac{N^\circ{}_U}{2}$$

and

$$\frac{N_U{}^\circ}{2} = N^\circ{}_U e^{-\lambda T}$$

i.e.

$$\frac{1}{2} = e^{-\lambda T}$$

and

$$\boxed{T = \frac{Ln2}{\lambda}}$$

Radioactivity unit

The unit of measurement of the radioactivity of a sample is the Curie (Ci) in which 3.7×10^{10} atoms disintegrate per second.

We now have to understand why this arrangement of electrons in shells in an atom occurs. This understanding is clearly linked to the interior nature of microscopic particles and will be addressed in the next chapter. Any theoretical model that we build has to take these properties into account. In order to familiarize ourselves with the formalism used in the different models, we need to address the properties of light and, more generally, those of electromagnetic radiation.

I-V. Tutorial for Chapter I

T-I-1. The Avogadro number

1) Let us consider the crystal structure of iron where l is the length of the edge. The atomic mass of iron is 55.845 g/mol, its density is 7.86×10^3 kg/m^3, and the Avogadro number has the value $N = 6.022\times10^{23}$. Determine the length l of the edge.

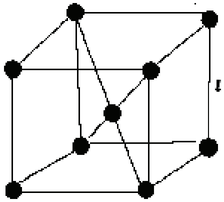


Figure T-1: α-iron cell.

ANSWER

As we can see in the figure, there is 1/8 of an iron atom at each vertex and thus each vertex corresponds to a volume $v_{At}/8$, where v_{At} is the volume of an atom.

Since there are 8 vertices, they correspond to volume $v = 8(1/8)\ v_{At}$. In addition, there is an entire atom in the center of the cell. If we neglect the residual interstices, this gives the crystal cell a total volume

$$v_{cell} = 2v_{At}$$

then

$$v_{At} = \frac{v_{cell}}{2}$$

There are N atoms in a mole of atoms, therefore the molar volume of an atom is

$$V_{At} = Nv_{At} = N\frac{v_{cell}}{2}$$

besides, the volume of the cell is

$$v_{cell} = l^3$$

then

$$V_{At} = N v_{At} = N\frac{l^3}{2} \tag{I-A1}$$

The density ρ_{Fe} of iron is

$$\rho_{Fe} = \frac{M_{Fe}}{V_{Fe}}$$

and we can deduce the molar volume of an iron atom

$$V_{Fe} = \frac{M_{Fe}}{\rho_{Fe}} \tag{I-A2}$$

Now, we identify the two expressions (I-A1) and (I-A2):

$$N\frac{l^3}{2} = \frac{M_{Fe}}{\rho_{Fe}}$$

and we obtain

$$l = \sqrt[3]{\frac{2M_{Fe}}{\mathcal{N}\rho_{Fe}}}$$

so that

$$l = \sqrt[3]{\frac{2\times 55.845\times 10^{-3}}{6.02\times 10^{23}\times 7.86\times 10^{3}}} = 2.87\times 10^{-10} m$$

2) Previously, when ^{16}O was the reference for atomic masses, the carbon isotope ^{12}C had a relative mass of 12.0038 g/mol. The new reference base is $M({}_{6}^{12}C)$=12 g/mol. How does this change the value of the Avogadro number?

ANSWER

Let m_C be the mass of a carbon atom (microscopic). If we work with the carbon reference, we have to write

$$M_C^{(C)} = \mathcal{N}^{(C)} \times m_C$$

If we work with the oxygen reference, we have

$$M_C^{(O)} = \mathcal{N}^{(O)} \times m_C$$

Now, we can make a ratio between these two expressions

$$\frac{M_C^{(C)}}{M_C^{(O)}} = \frac{\mathcal{N}^{(C)}}{\mathcal{N}^{(O)}}$$

As a result, for the Avogadro number in the carbon reference we have

$$\mathcal{N}^{(C)} = \mathcal{N}^{(O)} \frac{M_C^{(C)}}{M_C^{(O)}}$$

that is

$$\mathcal{N}^{(C)} = \mathcal{N}^{(O)} \frac{12}{12.0038} = 0.99968 \times \mathcal{N}^{(O)}$$

T-I-2. The mass spectrometer

1) Natural zinc has an atomic mass of 65.4 g/mole. Analysis with the mass spectrometer gives 3 signals corresponding to the mass numbers 64, 66, and 68 g/mole whose intensities are proportional to 5, 3, and 2 respectively. Justify the experimental atomic mass of zinc.

ANSWER

The intensities of the peaks are proportional to the abundances (fraction) of the isotopes in the sample. The intensity must be normalized so that the sum of all the intensities is equal to 1. If h_1, h_2, and h_3 represent the heights of the peaks, we have

$$I_n = \frac{h_n}{\sum_i h_i}$$

Table T-I-1: Intensities of the peaks

Peak	high	Intensity	Mass (g/mole)
1	5	$\frac{5}{5+3+2} = 0.5$	64
2	3	$\frac{3}{5+3+2} = 0.3$	66
3	2	$\frac{2}{5+3+2} = 0.2$	68

We deduce the natural atomic mass of zinc as follows

$$M = I_1 \times M_1 + I_2 \times M_2 + I_3 \times M_3$$

$$\boxed{M = 0.5 \times 64 + 0.3 \times 66 + 0.2 \times 68 = 65.4 g/mol}$$

2) Using a mass spectrometer fitted with a speed filter, two kinds of ions carrying an elementary positive charge can be separated out when analyzing a sample of natural boron. In the speed filter, the ions are subject to the action of two perpendicular fields, E and B, such that E/B = 4×10^5 S.I. ${}_6^{12}C$ atoms were incorporated into the sample of boron analyzed, giving rise to the ionic species ${}_6^{12}C^+$, which is the heaviest of the three. At the output of the speed filter, the ions enter a magnetic induction $B_1 = 0.2$ SI and perform semicircles there before reaching the detector.

a) Determine the dimensions of the E/B ratio.

ANSWER

Recall **Fig. I-9**, which presents the different parts of a mass spectrometer.

An ion X^+ produced by the collisions of the rapid electrons arrives at the speed filter. It undergoes the simultaneous influence of the electrical **E** and electromagnetic **B** fields, which generate two forces, $\mathbf{f}_{el}$ and $\mathbf{f}_{em}$ respectively.

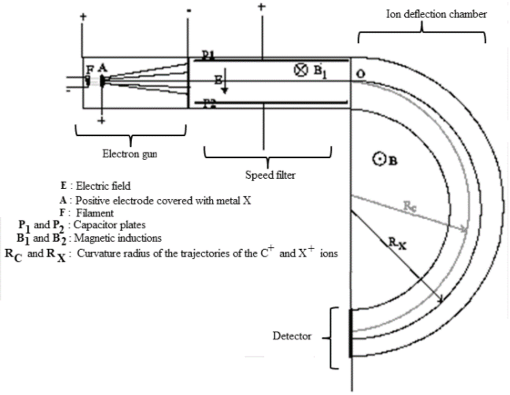


Figure T-I-2. Mass spectrometer schema.

If the ion passes through the filter without being deflected then the forces must obey the condition

$$\vec{\mathbf{f}}_{el} + \vec{\mathbf{f}}_{em} = 0$$

with

$\vec{\mathbf{f}}_{el} = q\vec{\mathbf{E}}$ for the electrostatic force having the same direction as $\vec{\mathbf{E}}$

$\vec{\mathbf{f}}_{em} = q\vec{\mathbf{v}} \wedge \vec{\mathbf{B}}_1$ for the electromagnetic force having the opposite direction as $\vec{\mathbf{B}}_1$

So, for the ions to pass through the filter in a straight line, we must have

$$\left\| \vec{\mathbf{f}}_{el} \right\| = \left\| \vec{\mathbf{f}}_{em} \right\|$$

i.e.

$$qE = qvB_1$$

then

$$v = \frac{E}{B_1}$$

The unit of this ratio is therefore at the level of meters per second.

b) The radius of the trajectory of carbon ions is $R_C = 24.92$ cm. The central impact on the detector is 4.17 cm from each of the two side signals. Determine the atomic masses of the two boron isotopes.

ANSWER

Looking at the deflection chamber, we see that the trajectories of the ions subjected to magnetic induction are semicircles tangential to the point O output of the speed filter. The difference between the peaks at the detector therefore represents the difference d between diameters. Thus, if R_1, R_2, and R_C, respectively, represent the radii of curvature of the ion trajectories 1 and 2, and of carbon ^{12}C, we can deduce the diameters of curvature of the trajectories.

The impact of carbon displays the largest diameter of curvature because it is heavy

$$D_2 = D_c - d$$

$$D_1 = D_c - 2d$$

Regarding the masses, a quick calculation shows us that, in the deflection chamber, the ions undergo the action of a magnetic induction **B**. They describe a circular trajectory and will strike the plane where there are ion counters (detector).

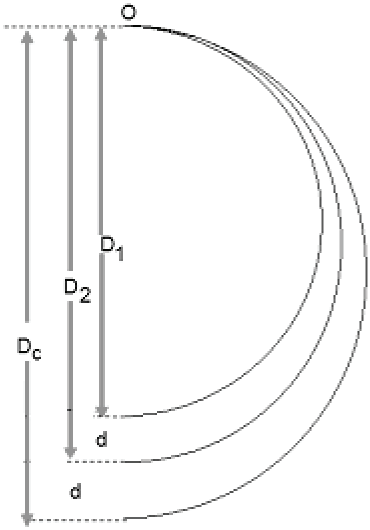


Figure I-T-3: Deviations of the isotope ions.

The ions enter the deflection chamber at speed **v**. They are then subjected to the action of an electromagnetic force $\mathbf{f}_{em}$, which serves to compensate for the effect of their speed in the form of a centrifugal mechanical force $\mathbf{f}_{mec}$, so that the moduli of these forces are equal

$$\left\| \vec{\mathbf{f}}_{mec} \right\| = \left\| \vec{\mathbf{f}}_{em} \right\|$$

so that

$$qvB = \frac{mv^2}{R}$$

where R is the radius of curvature of the trajectory and m is the mass of the ion. We then deduce the mass of the ion

$$m = \frac{qB}{v} R$$

Using

$$v = \frac{E}{B_1}$$

we obtain

$$m = \frac{qBB_1}{E} R$$

It can be seen that the mass is proportional to the curvature radius of the ion in the deflection chamber. If we wish to obtain the atomic mass of the ion, for one mole of the ion, we write

$$M(g) = \frac{qBB_1 \mathcal{N} \times 10^5}{E} R(cm)$$

In practice, it is easier to work with a standard substance and so we introduce some trace of a substance whose mass we already know into the sample, for example, ^{12}C carbon. Let R_C and R_X be the respective curvature radii of carbon and isotope 1. Using the above equation, it is obvious that

$$\frac{M_1}{M_c}=\frac{R_1}{R_C}=\frac{D_1}{D_C}$$

For isotope 2, we have

$$\frac{M_2}{M_c}=\frac{R_2}{R_C}=\frac{D_2}{D_C}$$

Considering what we said above,

$$\frac{M_1}{M_c}=\frac{D_c-2d}{D_C}$$

$$\frac{M_2}{M_c}=\frac{D_c-d}{D_C}$$

we deduce that

$$M_1= M_c\frac{(D_c-2d)}{D_C}$$

$$M_2= M_c\frac{(D_c-d)}{D_C}$$

i.e.

$$M_1= 12\frac{(2\times24.92-2\times4.17)}{2\times24.92}= 10g/mol$$

$$M_2= 12\frac{(2\times24.92-4.17)}{2\times24.92}= 11g/mol$$

c) The signal intensity of the heaviest isotope of boron is 4.3 times greater than that of the light isotope. Calculate the atomic mass of natural boron.

ANSWER

As in the previous exercise, we have to normalize the intensities. If I_1 and I_2 represent respectively the normalized intensities of isotopes 1 and 2 of boron, and if 2 is heavier than 1, then we have the system of equations

$$\begin{cases} I_1+I_2=1 \\ \frac{I_2}{I_1}=4.3 \end{cases}$$

From this, we obtain

$$I_1+4.3\times I_1=1$$

$$I_1=\frac{1}{5.3}=0.19$$

$$I_2=4.3\times I_1=4.3\times 0.19=0.817$$

and so the natural atomic mass of boron is

$$M=I_1\times M_1+I_2\times M_2$$

$$M=0.19\times 10+0.817\times 11=\underline{10.887 g/mol}$$

T-I-3. Sub-atomic particles

1) Determine the number of particles present in the following elements: $_{7}^{14}N$, $_{26}^{56}Fe$, and $_{31}^{72}Ge$.

ANSWER

The representation of a chemical element is

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

where

the number of protons = Z,

the number of neutrons = A-Z,

the number of electrons = Z-Q.

If we apply this information to these elements, we obtain the following table.

Table T-I-3

	protons	neutrons	electrons
${}^{14}_{7}N$	7	14-7=7	7
${}^{56}_{26}Fe$	26	56-26=30	26
${}^{72}_{31}Ge$	31	72-31=41	31

2) Knowing that the atomic mass unit has the value 1 u = 1.6605402×10^{-27} kg, that the respective masses of the proton and the neutron are m_{p} = 1,00727 u and m_{n} = 1,00867 u, evaluate the mass defect (in kg and in electron volts) in a lithium atom ${}_{3}{}^{7}Li$, knowing that the mass of the nucleus formed is 7,01435 u, c = 2.99792458×10^{8} m/s, e = 1.60217733×10^{-19} C.

ANSWER

Core atom mass in kg

$$m_{cor} = 7.01435 \times 1.6605402 \times 10^{-27} = \underline{1.164761 \times 10^{-26} kg}$$

The mass of the nucleons

$$m_{nuc} = 3 \times m_{protons} + (7-3) \times m_{neutrons})$$

$$m_{nuc} = 3 \times 1.00727 \times 1.6605402 \times 10^{-27} + (7-3) \times 1.00867 \times 1.6605402 \times 10^{-27}$$

$$m_{nuc} = \underline{1.171759 \times 10^{-26} kg}$$

Mass defect

$$\Delta m = m_{cor} - m_{nuc}$$

$$\Delta m = 1.164761 \times 10^{-26} - 1.171759 \times 10^{-26}$$

i.e.

$$\Delta m = \underline{-6.998 \times 10^{-29} kg}$$

In order to transform this mass defect into energy, we use Einstein's formula drawn from the theory of special relativity

$$\Delta E = \Delta m \times c^2$$

In the case of lithium, we have

$$\Delta E = -6.998 \times 10^{-29} \times \left(2.99792458 \times 10^8\right)^2$$

$$\Delta E = -6.289489 \times 10^{-12} J$$

Since 1 eV = $1.60217733 \times 10^{-19}$ J, we have

$$\Delta E(e.V) = \frac{-6.289489 \times 10^{-12}}{1.60217733 \times 10^{-19}}$$

i.e.

$$\Delta E(e.V) = \underline{-3.925589 \times 10^7 e.V}$$

T-I-4. Radioactivity

1) In the element $^A_Z X$, what do A and Z represent?

ANSWER

A is the mass number and Z is the atomic number.

2) For the radioactive element $^A_Z X$, describe the 4 types of decay.

ANSWER

1. α-decay. Radioactive nuclei emit α particles; an α-particle is a helium nucleus, i.e.

$$\alpha = {}^{4}_{X}He^{2+}$$

Consequently, when a nucleus emits an α-particle, its mass number diminishes by 4 units and its atomic number by 2 units

$${}^{A}_{Z}X \rightarrow {}^{A-4}_{Z-2}Y + {}^{4}_{X}\alpha$$

2. β^--decay. The emission of an electron and an anti-neutrino (anti-particle without mass)

$${}^{A}_{Z}X \rightarrow {}^{A}_{Z+1}Y + e^- + \bar{\upsilon}$$

3. β^+-decay. The emission of a positron and a neutrino (of zero mass)

$${}^{A}_{Z}X \rightarrow {}^{A}_{Z-1}Y + e^+ + \upsilon$$

4. K-capture. As with β^+-decay, there is the emission of a positron and a neutrino, but the process is different. It is the nucleus that captures an electron belonging to the nearest electronic shell (K)

$${}^{A}_{Z}X + e^- \rightarrow {}^{A}_{Z-1}Y + \upsilon$$

3) What is a radioactive series?

ANSWER

It is a series of elements that can be deduced from an unstable parent element through four different processes leading to the value of the mass number given by the formula

$$A = 4n + r$$

where r is the radioactive series and is an integer that defines the series. It can only take 4 values: 0, 1, 2, and 3. n is an integer characterizing the element of the series. The variation of n and r defines the radioactive series.

Three main decay chains (or families) are observed in nature: the thorium series (A = 4n); the radium or uranium series (A = 4n+2); and the actinium series (A = 4n+3). They end in three different, stable isotopes of lead. A fourth chain, the neptunium series (A = 4n+1) has neptunium (${}^{237}Np$) as its starting isotope, which has a half-life of 2.14 million years; this chain does not exist in nature. The final isotope of this chain is thallium (^{205}Tl).

4) In 1981 a new radioactive element $^{A}_{Z}X$ was discovered. By the chain of successive decays corresponding to 3 α-decays, 1 β^{+}-decay, and, finally, an α-decay, we obtain the known element $_{98}{}^{246}$Cf. Determine the mass number and the atomic number of X.

ANSWER

3 α-decays

$$
\begin{aligned}
&{}^{A}_{Z}Cf \rightarrow {}^{A-4}_{Z-2}X + {}^{4}_{X}\alpha \\
&{}^{A-4}_{Z-2}X \rightarrow {}^{A-8}_{Z-4}Y + {}^{4}_{X}\alpha \\
&{}^{A-8}_{Z-4}Y \rightarrow {}^{A-12}_{Z-6}Y + {}^{4}_{X}\alpha
\end{aligned}
$$

then, 1 β^{+}-decay

$$ {}^{A-12}_{Z-6}Y \rightarrow {}^{A-12}_{Z-7}W + e^{+} + \upsilon $$

Finally,1 α-decay

$$ {}^{A-12}_{Z-7}W \rightarrow {}^{A-16}_{Z-9}Cf + e^{+} + \upsilon $$

We must have

$$ {}^{A-16}_{Z-9}Cf = {}^{246}_{98}Cf $$

so that

$$ A - 16 = 246 $$

and

$$ Z\text{-}9 = 98. $$

Then, we have

$$ A = 246 + 16 \ \text{and}\ Z = 98 + 9 $$

i.e.

$$A = 262 \text{ and } Z = 107$$

5) Radioactive decay.
a) Define the half-life of a radioactive source.

ANSWER

The radioactive half-life is the time T after which the number of radioactive atoms remaining is half the initial number of atoms.

b) What relation links the half-life T and the radioactive constant of a sample?

ANSWER

$$T = \frac{\ln(2)}{\lambda}$$

c) The half-life of a radioactive sample is 3.8×10^5 years.
1) Calculate the value of its radioactive constant in the SI unit.

ANSWER

$$\boxed{\lambda = \frac{Ln2}{T}}$$

$$\boxed{\lambda = \frac{\ln(2)}{(3.8 \times 10^5)\times(365.25)\times(24)\times(3600)} = 5.780134 \times 10^{-14} s^{-1}}$$

d) After how much time has the initial quantity of radioactive nuclei divided by 8?

ANSWER

The radioactive decay law is

$$N(t) = N^\circ e^{-\lambda t}$$

where N(t) is the quantity of radioactive nuclei in the sample at time t and N° is the initial quantity.

The half-life of the sample is T. We can then evaluate the radioactive constant λ

$$\lambda = \frac{\ln 2}{3.8 \times 10^5} = 1.824072 \times 10^{-6} \textit{années}^{-1}$$

If Nº is the quantity of radioactive nuclei in the sample, the remaining quantity N(t) will be

$$N(t) = \frac{N°}{8}$$

so that we may write

$$\frac{N°}{8} = N° e^{-\lambda t}$$

and

$$\frac{1}{8} = e^{-\lambda t}$$

also

$$e^{\lambda t} = 8$$

Then, the time t necessary to obtain a quantity corresponding to N°/8 is

$$t = \frac{\ln(8)}{\lambda}$$

and

$$t = \frac{\ln(8)}{1.824072 \times 10^{-6}} = 1.14 \times 10^6 \text{ years}$$

e) A radioactive source of half-life T = 65 years has 1.256×10^{21} radioactive nuclei at instant t. Calculate the activity of this source at time t.

ANSWER

The activity of a radioactive sample is defined as the rate at which radioactive particles are emitted

$$A(t) = \lambda N(t)$$

or

$$A(t) = \lambda N(t) = \frac{\ln(2)}{T} N(t)$$

$$A(t) = \frac{\ln(2)}{65.0 \times (365.25) \times (24) \times (3600)} 1.256 \times 10^{21} = 4.24 \times 10^{11} Becquerels$$

since 1 Curie = 3.7×10^{10} radioactive decays per seconds

$$A(t) = \frac{4.24 \times 10^{11}}{3.7 \times 10^{10}} = 11,46 \text{ Curie}$$

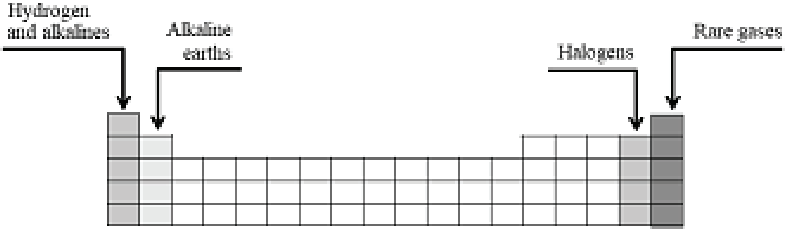
T-I-5. Periodic classification

1) Schematically, draw the periodic table and correctly place the families of elements (alkaline, alkaline earth, halogens, and rare gases).

ANSWER

First, draw a table with 18 columns and then place the families.

Table T-I-3. Periodic classification



2) The evolution of the natural logarithm of the successive ionization potentials of an element is given as a function of the order n of the extracted electron.

a) What is the element?

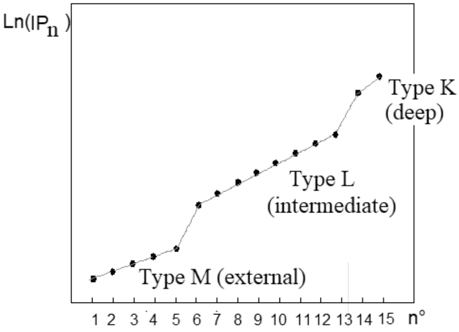


Figure T-I-4: Successive IPs of phosphorus.

ANSWER

There are 15 IPs and thus it is phosphorus.

b) Why are there changes in the slope of the curve?

ANSWER

Atoms have energy shells, but the energy situation of atoms is not homogeneous. The closer an electron is to the nucleus, the more energy it takes to pull it out. The points on the line mean that the electrons belong to the same energy shell. Where there is a break in the slope, it means that we are passing to another shell.

CHAPTER II

THE WAVE-LIKE AND CORPUSCULAR NATURE OF LIGHT

II-I. Some Reminders About the Wave-Like Nature of Light

According to Maxwell's[1] theory, light results from the simultaneous propagation of an electric field and a magnetic field, perpendicular to each other and varying periodically.

J. Maxwell

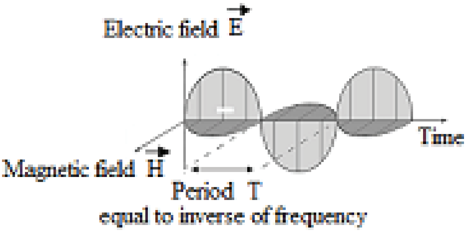


Figure II-1: Electromagnetic propagation of light.

Several concepts have to be understood to describe the phenomenon of light.

---

[1] James Maxwell (1831-1879). Scottish physicist and mathematician. He unified the equations of electricity, magnetism, and induction in a single electromagnetic model.

1. Vibration wave function[2] Ψ

We shall only consider here the vibrations of the electric field. We can represent the vibration of a light source through the following relationship

$$\Psi = \Psi^\circ \cos(\omega t + \phi)$$

where Ψ is the elongation; Ψ° is the maximum elongation or amplitude; ω is the pulsation or angular frequency; t is the time; and ϕ is the phase angle (the angle value when t = 0).

2. Period T of a vibrational movement

This is the time it takes for the movement to reproduce identically. Let Ψ(t) be the elongation at time t and Ψ(t+T) at time t+T. At time t, we have

$$\Psi(t) = \Psi^\circ \cos(\omega t + \phi)$$

and at time (t+T)

$$\Psi(t+T) = \Psi^\circ \cos(\omega(t+T) + \phi)$$

If the elongation at time t+T is identical to the elongation at time t, we must have

$$\Psi(t+T) = \Psi(t)$$

that is

$$\Psi^\circ \cos(\omega t + \phi) = \Psi^\circ \cos(\omega(t+T) + \phi)$$

Simplifying by Ψ°, we obtain

$$\cos(\omega t + \phi) = \cos(\omega(t+T) + \phi)$$

---

[2] Strictly speaking, Ψ represents here one of the Cartesian components of the electric field **E** of a monochromatic wave. Besides, □ is the spatial part of the phase of the wave (i.e. that which includes the dependence of the position).

Given the trigonometric relationships, we can write

$$\omega t + \phi + 2\pi = \omega(t + T) + \phi$$

which leads to

$$2\pi = \omega T$$

or

$$\boxed{T = \frac{2\pi}{\omega}} \qquad \text{(II-1)}$$

T is named the *period* of vibrational motion

3. Frequency ν

This is the inverse of the period T, i.e.

$$\nu = \frac{1}{T} = \frac{\omega}{2\pi}$$

4. Angular frequency ω

This is related to the frequency

$$\boxed{\omega = 2\pi\nu} \qquad \text{(II-2)}$$

5. Wavelength λ

The wavelength is the distance traveled by the wave during period T. Light moves at a velocity of $c \simeq 3\times10^8$ ms^{-1} in a vacuum (this is very important)

$$\boxed{\lambda = cT} \qquad \text{(II-3)}$$

Note: since ν = 1/T, we have T = 1/ν and

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

6. Wavenumber $\overline{\upsilon}$

The wavenumber $\overline{\upsilon}$ is the inverse of the wavelength, so that

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

This comes to

$$\nu = c\,\bar{\nu}$$

7. Light interferences

a. Experiment

Interference patterns present a manifestation of the wave behavior of light. We can highlight this property using Young's double slit experiment.

T. Young

In **Fig. II-2a**, we can see Young's device[3]. The experimental setup has two very thin slits, S_1 and S_2, cut into a sheet of cardboard, separated by a distance of about one millimeter and illuminated by a single color (monochromatic) light source. A schematic view is given in **Fig. II-2b**.

We can see alternating dark bands and bright bands on a screen; these are light interference patterns.

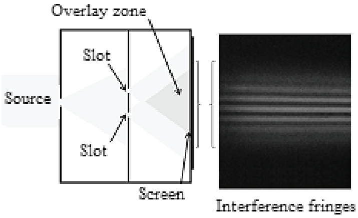


Figure II-2a: Young's device.

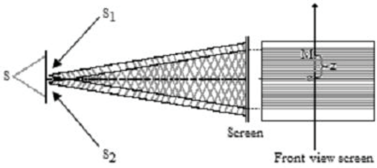


Figure II-2b: Schematic of Young's device.

---

[3] Thomas Young (1773-1829), British physicist, physician, and Egyptologist.

Let us undertake a mental experiment and visualize walking along the Oz axis at a small distance on either side of the center O and with a small photoelectric cell recording the light intensity I(z). **Fig. II-3a** displays the intensity I(z) according to position z.

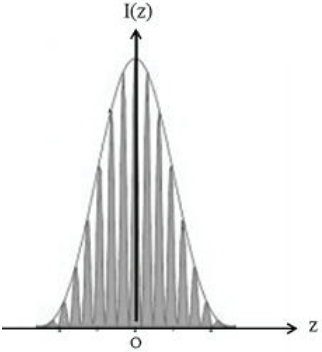


Figure II-3a: The real evolution of the light intensity I(z) in Young's double slit experiment.

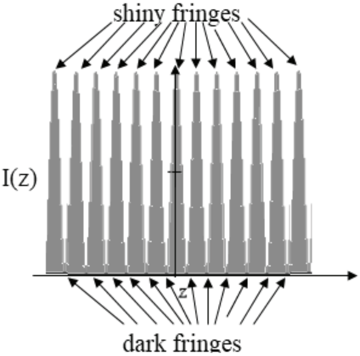


Figure II-3b: Simplified evolution of the light intensity I(z).

Strictly speaking, when looking at **Fig. II-3a** we can see that the intensity of the central band is greater than that of the lateral bands because of the phenomenon of diffraction at the slits, but we shall neglect this effect (**Fig. II-3b**) if the distance from the center O is not too large in order to simplify the theory as much as possible.

Let us define a stationary wave as a wave that does not propagate and that can take the form

$$s(x,t) = f(t) \times g(x)$$

In this sense, light interference can be considered a stationary phenomenon because, as we shall see, it generates wave functions, which have a time dependent part and another part dependent on the spatial coordinates. Indeed, the appearance of the fringes persists as long as the experience lasts and seems frozen in time. This is only a matter of appearance because, as we shall see, we have to deal with a vibrational phenomenon, the amplitude of which depends on the spatial coordinates. Each maximum of this curve corresponds to the center of a bright fringe and each minimum to that of a dark fringe. We therefore propose a theory capable of explaining this alternation of dark and bright bands.

b. Theory

This experiment can be interpreted by considering that light displays wave-like behavior. To simplify, we shall consider a wave whose elongation wave function at source S is

$$\Psi_S(t) = \Psi^\circ \cos(\omega t + \phi_S)$$

This source illuminates the plane of the slits at an equal distance from each. It is assumed that the phase in S_1 and S_2 is zero. Thus, in S_1 we have

$$\Psi_{S_1}(t) = \Psi^\circ \cos(\omega t)$$

and in S_2 we have

$$\Psi_{S_2}(t) = \Psi^\circ \cos(\omega t)$$

The S_1 and S_2 slits then behave like vibrating sources in phase.

In **Fig. II-4**, we can see a schematic presentation of the experimental assembly in order to identify the parameters used in the theory.

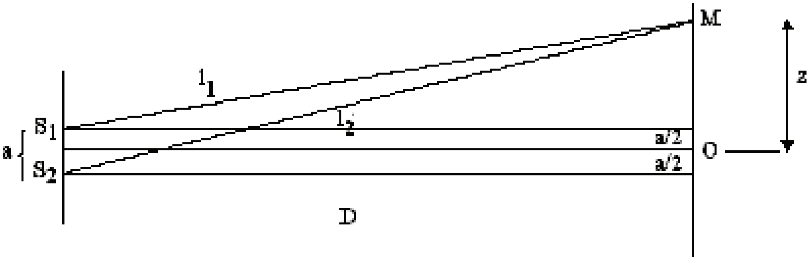


Figure II-4: The different parameters used in the interference theory.

We can plug one of the slits, for example S_2, and calculate the expression of the elongation $\Psi_{S_1}(t)$ at point M.

At S_1, the wave has as the following elongation

$$\Psi_{S_1}(t) = \Psi^\circ \cos(\omega t)$$

In M, the wave will have traveled the distance S_1M, i.e. l_1. To travel this distance, it will have taken time t_1. The speed of propagation of the wave being the velocity of light, $c \simeq 3.10^8$ m.s^{-1}, we can write

$$l_1 = c \times t_1$$

In M, the wave will have the elongation

$$\Psi_{S_1,M}(t) = \Psi^\circ \cos(\omega(t + t_1))$$

Developing the expression, we come to

$$\Psi_{S_1,M}(t) = \Psi^\circ \cos(\omega t + \omega t_1)$$

By posing

$$t_1 = \frac{l_1}{c}$$

we get

$$\omega t_1 = \omega \frac{l_1}{c}$$

or, given Eq. (II-1), we get

$$\omega = \frac{2\pi}{T}$$

so that

$$\omega t_1 = \frac{2\pi}{T}\frac{l_1}{c}$$

Remembering Eq. (II-3), we have

$$\lambda = cT$$

hence

$$\omega t_1 = \frac{2\pi}{\lambda} l_1$$

Let us call φ_1 the following expression

$$\phi_1 = \omega t_1 = \tfrac{2\pi}{\lambda} l_1 \tag{II-4}$$

we can deduce the expression of the elongation at point M of the wave coming from S_1

$$\Psi_{S_1,M}(t) = \Psi^\circ \cos(\omega t + \phi_1)_*$$

If we were to block S_1 and let S_2 work, we would get a similar expression

$$\Psi_{S_2,M}(t) = \Psi^\circ \cos(\omega t + \phi_2)$$

with

$$\phi_2 = \omega t_2 = \tfrac{2\pi}{\lambda} l_2 \tag{II-5}$$

Now, if we let the two sources work together, the elongation of the M-point can be accounted for by performing the linear combination Ψ_M of wave functions at the M-point, as follows

$$\Psi_M = \Psi_{S_1,M}(t) + \Psi_{S_2,M}(t)$$

that is

$$\Psi_M = \Psi^\circ \cos(\omega t + \phi_1) + \Psi^\circ \cos(\omega t + \phi_2)$$

and by placing Ψ° as the common factor, we get

$$\Psi_M = \Psi^\circ[\cos(\omega t + \phi_1) + \cos(\omega t + \phi_2)]$$

Let us now use the trigonometric relationship concerning the sum of two cosines

$$\cos p + \cos q = 2\cos\left(\tfrac{p+q}{2}\right)\cos\left(\tfrac{p-q}{2}\right)$$

and get

$$\Psi_M = 2\Psi^\circ \cos\left(\tfrac{\omega t+\phi_1+\omega t+\phi_2}{2}\right)\cos\left(\tfrac{\omega t+\phi_1-\omega t-\phi_2}{2}\right)$$

By simplifying

$$\Psi_M = 2\Psi^\circ \cos\left(\omega t + \tfrac{\phi_1+\phi_2}{2}\right)\cos\left(\tfrac{\phi_1-\phi_2}{2}\right)$$

applying the property

$$\cos(\alpha) = \cos(-\alpha)$$

reversing the order of φ_1 and φ_2 in the expression, we come to

$$\Psi_M = 2\Psi^\circ \cos\left(\omega t + \tfrac{\phi_1+\phi_2}{2}\right)\cos\left(\tfrac{\phi_2-\phi_1}{2}\right)$$

We get an expression with one part that depends on time and another part that is time-independent. This time-independent part can be considered in the form of an amplitude, making it possible to write the wave function as

$$\Psi_M = \underbrace{2\Psi^\circ \cos\left(\frac{\phi_2 - \phi_1}{2}\right)}_{\text{Amplitude}} \underbrace{\cos\left(\omega t + \frac{\phi_1 + \phi_2}{2}\right)}_{\text{Time-dependent part}}$$

If one poses

$$\Psi^{\circ} = 2\Psi^\circ \cos\left(\tfrac{\phi_2-\phi_1}{2}\right)$$

we define this new amplitude Ψ°. As such, the wave function can be written

$$\Psi_M = \Psi^{\circ} \cos\left(\omega t + \tfrac{\phi_1+\phi_2}{2}\right)$$

However, the most interesting part concerns the properties of this amplitude Ψ°. We shall now try to link the phase difference to the position of a point on the Oz axis. Let us express φ_2-φ_1 using eqs. (II-4) and (II-5)

$$\phi_2 - \phi_1 = \tfrac{2\pi}{\lambda}(l_2 - l_1) \qquad \text{(II-6)}$$

Consider Figure II-4. By applying the Pythagorean theorem, we can express lengths l_1 and l_2

$$l_1^2 = D^2 + (z - \tfrac{a}{2})^2$$

$$l_1^2 = D^2 + (z + \tfrac{a}{2})^2$$

Let us calculate the difference of l_2^2-l_1^2, which gives us

$$l_2^2 - l_1^2 = (z + \tfrac{a}{2})^2 - (z - \tfrac{a}{2})^2$$

or by factoring

$$(l_2 + l_1)(l_2 - l_1) = \left[(z + \tfrac{a}{2}) + (z - \tfrac{a}{2})\right]\left[(z + \tfrac{a}{2}) - (z - \tfrac{a}{2})\right]$$

By simplifying, we get

$$(l_2 + l_1)(l_2 - l_1) = \left[(z + \tfrac{a}{2} + z - \tfrac{a}{2})\right]\left[z + \tfrac{a}{2} - z + \tfrac{a}{2})\right]$$

i.e.

$$(l_2 + l_1)(l_2 - l_1) = 2za \tag{II-7}$$

Now, given that the l_2 and l_1 are in the order of magnitude of one meter and a is in the order of a millimeter, it is easy to see from **Fig. II-4** that, if one considers their sum, one can make the approximation

$$l_1 \backsimeq l_2 \backsimeq D$$

As such, Eq. (II-7) becomes

$$2D(l_2 - l_1) = 2za$$

so that the difference of l_2-l_1 is

$$l_2 - l_1 = \tfrac{za}{D} \tag{II-8}$$

We can replace l_2-l_1 in Eq. (II-7) by Eq. (II-8) above, so that

$$\phi_2 - \phi_1 = \tfrac{2\pi}{\lambda}(l_2 - l_1) = \tfrac{2\pi}{\lambda}\tfrac{za}{D}$$

The expression for $\Psi^\circ(z)$ may thus be deduced as

$$\Psi^\circ(z) = 2\Psi^\circ\cos\left(\frac{\pi}{\lambda}\frac{a}{D}z\right)$$

It can be seen that the amplitude depends on the position of point M along the z-axis. It just remains to define the link between $\Psi^\circ(z)$ and the light intensity I(z) along the interference axis.

If we plot $\Psi^\circ(z)^2$ as a function of z we obtain the following result.

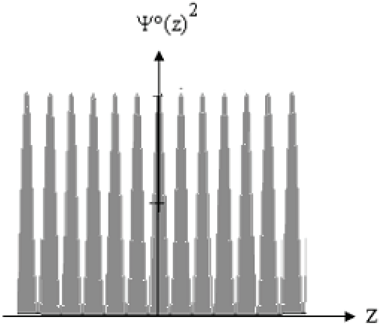


Figure II-5: Squared amplitude evolution along z axis.

This figure can be compared to **Fig. II-3b.** It is a superimposable graph with the position of the peaks and the "experimental values" of the light intensity. Consequently, the following analogy can be made[4]

$$I(z) \backsim \left(\Psi^\circ(z)\right)^2$$

A such, we can deduce that the light intensity is proportional to the square of the amplitude.

This observation then allows us to interpret and predict the position of dark or bright fringes along the z-axis.

Position of bright fringes

The minimum of the light must correspond to a square of the amplitude, which is zero

$$\min\left[\Psi^\circ(z)\right] = \min\left[2\Psi^\circ\cos\left(\frac{\pi}{\lambda}\frac{a}{D}z_{\min}\right)\right]^2 = 0$$

---

[4] In fact, illumination is actually proportional to the time average of the square of the electric field of the wave resulting from the superposition of the waves coming from the two source slits.

which happens when

$$\cos^2\left(\frac{\pi}{\lambda}\frac{a}{D}z_{\min}\right) = 0$$

or

$$\cos\left(\frac{\pi}{\lambda}\frac{a}{D}z_{\min}\right) = 0$$

This occurs when the argument of the cosine is equal to an odd number of times the value π/2

$$\frac{\pi}{\lambda}\frac{a}{D}z_{\min} = (2n+1)\frac{\pi}{2}$$

leading to

$$z_{\min}(n) = (2n+1)\frac{\lambda}{2}\frac{D}{a}$$

Inter-fringe

The distance between two successive bright fringes or two successive dark fringes is

$$i = z_{\max}(n+1) - z_{\max}(n) = (n+1)\frac{\lambda D}{a} - n\frac{\lambda D}{a} = \frac{\lambda D}{a}$$

or

$$i = z_{\min}(n+1) - z_{\min}(n) = (2(n+1)+1)\frac{\lambda}{2}\frac{D}{a} - (2n+1)\frac{\lambda}{2}\frac{D}{a} = \frac{\lambda D}{a}$$

In summary

The interference between two vibrational wave functions leads to a vibrational wave function resulting from the linear combination of these wave functions and the amplitude of which depends on the spatial coordinates.

A wave, with the amplitude of the wave function dependent on the spatial coordinates is a stationary wave and light interference patterns are thus stationary phenomena.

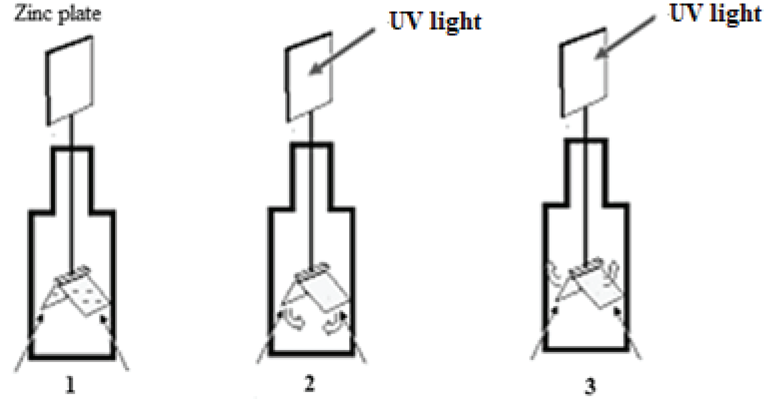
II-II. The Corpuscular Aspect of Light

In addition to its wave aspect, light has a corpuscular aspect. This aspect is illustrated by the *photoelectric effect* and the *Compton effect*.

1. Experiment

If we illuminate a zinc plate, for example, with UV radiation produced by an electric arc, we observe that electrons are torn from the metal.

To highlight this, we use a small glass bottle containing an electrometer or electroscope, which consists of a metal plate connected to a metal rod carrying very fine gold sheets, as shown in **Fig. II-6**.



Negatively charged gold leaves

The gold leaves are less and less negatively charged: they get closer

Gold leaves are becoming positively charged: They repel each other

Figure II-6: Experiment with an electrometer to prove the emission of electrons by the photoelectric effect.

(1) The gold leaves are negatively charged. They repel each other.

(2) The zinc plate is illuminated with UV light and the gold leaves therefore approach each other. Irradiation by UV light causes a fall in the negative charges, decreasing the negative charge of the gold leaves. As a result, the repulsion force becomes increasingly weak and the leaves approach each other.

(3) We maintain the illumination and the zinc plate becomes deficient in electrons, attracts the electrons of the gold leaves, and thus the gold leaves become positively charged and repel each other.

We can deduce from this experiment that the UV light tears electrons from zinc when it irradiates this metal.

If we now use red light, there is no subsequent tearing of electrons. It therefore appears that this emission of electrons by a given substance depends on the nature of the light used, that is to say on its frequency. Thus, for a given substance X, there is a frequency below which the emission of electrons no longer occurs. This is the *threshold frequency* $\nu°_X$, which is characteristic of the substance.

2. The photoelectric effect: theoretical explanation

Einstein[5] proposed an explanation of the photoelectric effect, which can be summed up in the simple formula

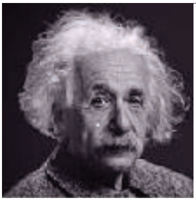
$$h\nu = W° + E_k \tag{II-9}$$

where hν is the energy of a quantum[6] of light; h is the Planck constant ($h = 6.6260755 \times 10^{-34}$ J·s); E_k is the maximum kinetic energy of ejected electrons; and W° is the work function—the energy that must be supplied to bring an electron from the inside of the substance to its periphery. **Fig. II-8** schematizes this balance.

---

[5] Albert Einstein (1879-1955) won the Nobel Prize in Physics in 1921 for his work on the photoelectric effect. He is the author of *Relativity: The Special and the General Relativity*.

[6] G. Lewis gave the quantum hν the name “photon”. Photon is derived from the Greek word for light, φως. According to A. Compton, this term was created by Gilbert N. Lewis in 1926.



A. Einstein

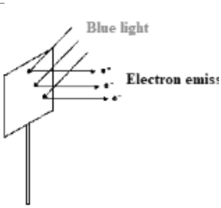


Figure II-7: The photoelectric effect.

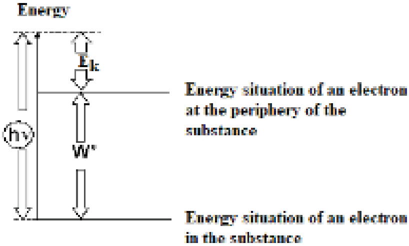


Figure II-8: Energy balance of the photoelectric effect.

3. Quantitative measurement of the photoelectric effect

To quantitatively measure the photoelectric effect, Millikan's device[7] may be used.

E. Millikan

A photon of hν energy falls onto a cathode C covered with substance X. As a result, an electron is emitted.

When V = 0, the electron crosses the grid G and strikes the plate P,

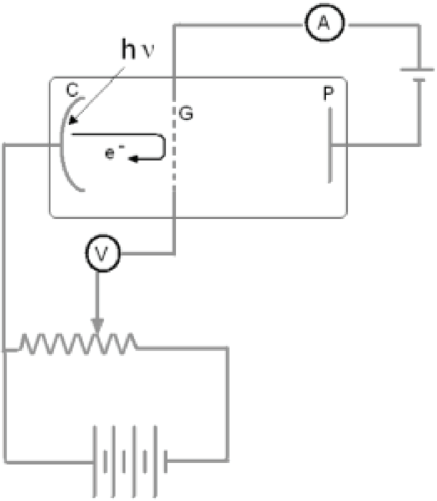


Figure II-9: Experimental device allowing measurement of the photoelectric effect.

---

[7] Edward Millikan (1868-1953) was an American physicist who won the Nobel Prize in Physics in 1923. He is known for his work on the charge of the electron and measurement of the photoelectric effect.

thus closing the circuit A-P. An electric current flows and moves the needle of the micro-ammeter A. This makes it possible to detect the arrival of an electron.As V, the potential difference between C and G, becomes more and more negative (by using the rheostat), the emitted electrons are braked by this potential difference. When V reaches the value V_R, the *stopping potential*, the electrons are stopped and no longer at plate P. As such, there is no more current across the circuit A-P. The potential energy, which must be opposed to the electrons from C, is therefore, at this time, equal to the kinetic energy of the emitted electrons

$$E_k = eV_R$$

The potential difference V_R is reported as a function of the frequency ν of the incident light. As such, we obtain the following graph. The line crosses the frequency axis at point ν_0, representing the frequency below which there is no longer a photoelectric effect. This is the threshold frequency. It is easy to interpret this graph. Let us start by finding the equation on the right. It is of the following type

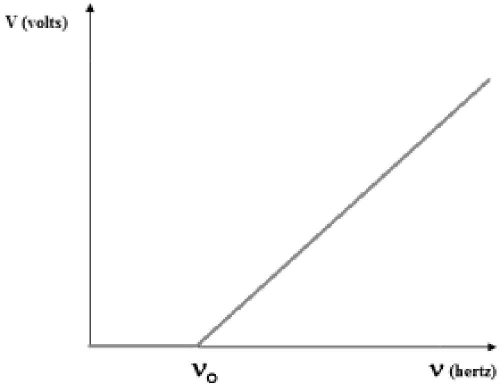


Figure II-10: The threshold potential of the Millikan experiment.

$$V_R = A\nu + B \qquad \text{(II-10)}$$

Two measurements can then be made. The first one, with light of frequency ν_1, requires the potential V_{R_1} to stop the electrons (zero plate current). The other, with a light of frequency ν_2, requires the potential V_{R2} to stop the electrons. We deduce the slope A of the curve as

$$A = \frac{V_{R_2} - V_{R_1}}{\nu_2 - \nu_1}$$

We can see that, in all cases and whatever the nature of the metal, the slope of A is

$$A = 4.12 \times 10^{-15} volt.hertz^{-1}$$

Now, we multiply the expression (II-10) by the elementary charge e

$$eV_R = eA\nu + eB$$

and evaluate the quantity eA

$$eA = 1.602 \times 10^{-19} \times 4.12 \times 10^{-15} = 6.60 \times 10^{34} joule.s$$

This is the value of Planck's constant h.

Eq. (II-10) becomes

$$eV_R = h\nu + eB \tag{II-11}$$

when $\nu = \nu_0$ then $V_R = 0$ and we see that

$$0 = h\nu_0 + eB$$

and

$$eB = -h\nu_0$$

Eq. (II-11) becomes

$$eV_R = h\nu - h\nu_0$$

By rearranging this expression, we obtain the experimental expression of Einstein's relation (II-9)

$$h\nu = W^{\circ} + eV_R$$

or

$$h\nu = W^{\circ} + E_k$$

in which it is easy to identify eV_R with the kinetic energy E_k. Furthermore, the work of extraction W° can be evaluated by irradiating the cathode C with a radiation of frequency ν°, the frequency beyond which the photoelectric effect occurs.

We then have W° = hν°. So, we can write Einstein's equation in the form

$$\boxed{h\nu = h\nu^{\circ} + eV_R}$$

which is Millikan's formula and is useful for many problems concerning the photoelectric effect.

Einstein's theory of the photoelectric effect highlights the corpuscular nature of light. The energy of light is transported in the form of a quantum of energy as photons. This conception of light seems to oppose the wave-like nature highlighted in light interference patterns.

In the conclusion of this chapter, we can see that the nature of light has a double aspect being both wave-like and corpuscular, i.e. it is both a wave and particle. As such, we speak of its wave-particle duality. This behavior is also found in the case of matter.

II-IV. Tutorial for Chapter II

T-II-1. The wave-like nature of light

1) A monochromatic source S illuminates a screen E_1 pierced by two very fine parallel slits S_1 and S_2 separated by distance a of 3 mm. The source is placed 50 cm from the two slits. It is observed that light interference occurs on a screen E_2 placed at a distance D = 3 m from plane E_1. There are 6 bright fringes on each side of the central fringe O, occupying a total length of l = 7.2 mm.

a) Calculate the wavelength of the radiation used.

ANSWER

According to the interference theory, we have the following interfringe

$$i = \frac{\lambda D}{a}$$

We have

$$i = l/12 = 7.2 \times 10^{-3}/12 = 6 \times 10^{-4} m$$

and

$$\lambda = \frac{ai}{D} = \frac{3 \times 10^{-3} \times 6 \times 10^{-4}}{3} = 6.0 \times 10^{-7} m$$

b) a and l were measured with a precision of 1/10 mm and D with a precision of 1 cm. How accurately can we know the wavelength?

ANSWER

We start from the expression for the wavelength

$$\lambda = \frac{ai}{D} = \frac{a}{D}\frac{l}{6}$$

Taking the natural logarithm of this expression, we get

$$\log\lambda = \log a + \log l - \log D - \log 6$$

Moving on to the differential gives

$$\frac{d\lambda}{\lambda} = \frac{da}{a} + \frac{dl}{l} - \frac{dD}{D}$$

Using the expression for the deviation Δ, we get

$$\frac{\Delta\lambda}{\lambda} = \frac{\Delta a}{a} + \frac{\Delta l}{l} - \frac{\Delta D}{D}$$

Moving on to the relative errors gives

$$\frac{\Delta\lambda}{\lambda} = \frac{\Delta a}{a} + \frac{\Delta l}{l} + \frac{\Delta D}{D}$$

We then obtain the expression of the relative error of the wavelength, with $\Delta a = \Delta l = 0.1$ mm; $\Delta D = 10^{-2}$ m. The expression becomes

$$\frac{\Delta\lambda}{\lambda}=\frac{0.1}{3}+\frac{0.1}{7.2}+\frac{0.01}{3}=5\times10^{-2}$$

We then deduce

$$\Delta\lambda = 6.0\times10^{-7}\times5\times10^{-2} = 3.0\times10^{-8} = 0.3\times10^{-7}m$$

Therefore, the measurement of λ lies between these two values

$$\lambda-\Delta\lambda \leqslant \lambda \leqslant \lambda+\Delta\lambda$$

i.e.

$$6.0\times10^{-7}-0.3\times10^{-7}m \leqslant \lambda \leqslant 6\times10^{-7}+0.3\times10^{-7}m$$

and

$$5.7\times10^{-7}m \leqslant \lambda \leqslant 6.3\times10^{-7}m$$

i.e. in nanometers

$$570\,nm \leqslant \lambda \leqslant 630\,nm$$

2) In an interference experiment with a light beam composed of 2 radiations of wavelength $\lambda_1 = 250$ nm and $\lambda_2 = 650$ nm, and where the distance between the sources is 1mm and that between the sources and the observation screen is 2m, we observe a grooved spectrum that presents 2 completely dark lines on either side of a bright central line.

a) Determine the distances from the bright central line where we observe the first completely dark line of the fluted spectrum, as well as the respective orders n_1 and n_2 corresponding to the dark lines of the two radiations under these conditions.

ANSWER

The relation giving the position of the dark fringes is

$$z_{min}(n) = (2n+1)\frac{\lambda D}{2a}$$

As such, for each wavelength we have

$$z_{1\,\min}(n_1) = (2n_1+1)\frac{\lambda_1}{2}\frac{D}{a} \quad \text{and} \quad z_{2\,\min}(n_2) = (2n_2+1)\frac{\lambda_2}{2}\frac{D}{a}$$

As the two systems must have a dark line for the same distance z, we have

$$z_{1\,\min}(n_1) = z_{2\,\min}(n_2)$$

$$(2n_1+1)\lambda_1 = (2n_2+1)\lambda_2$$

$$(2n_1+1)\frac{\lambda_1}{\lambda_2} = 2n_2+1$$

$$2n_1\frac{\lambda_1}{\lambda_2} + \frac{\lambda_1}{\lambda_2} = 2n_2+1$$

$$2n_1\frac{\lambda_1}{\lambda_2} + \frac{\lambda_1}{\lambda_2} - 1 = 2n_2$$

$$n_1\frac{\lambda_1}{\lambda_2} + \frac{1}{2}\frac{\lambda_1}{\lambda_2} - \frac{1}{2} = n_2$$

Replacing λ_1 and λ_1 by their numerical values, we get

$$n_2 = n_1\frac{\lambda_1}{\lambda_2} + \frac{1}{2}\frac{\lambda_1}{\lambda_2} - \frac{1}{2} = n_1\frac{250}{650} + \frac{1}{2}\frac{250}{650} - \frac{1}{2}$$

a relation between n_1 and n_2. We therefore have to vary n_1 to have n_2. This is given in **Table IV-T-1**.

Table IV-T-1: Positions of dark lines

n_1	n_2	$z(mm)$
0	-0.30769	0.25
1	0.07692	0.75
2	0.46154	1.25
3	0.84615	1.75
4	1.2308	2.25
5	1.6154	2.75
6	**2.0**	**3.25**
7	2.3846	3.75
8	2.7692	4.25
9	3.1538	4.75
10	3.5385	5.25
11	3.9231	5.75
12	4.3077	6.25
13	4.6923	6.75
14	5.0769	7.25
15	5.4615	7.75
16	5.8462	8.25
17	6.2308	8.75
18	6.6154	9.25
19	**7.0**	**9.75**

We deduce the distance at which grooved lines appear by applying the formula

$$z_{min}(n_1) = (2n_1+1)\frac{\lambda_1 D}{2a}$$
$$z_{min}(n_1) = (2n_1+1)\frac{250\times10^{-9}}{2}\times\frac{2}{1\times10^{-3}}$$

We can see that the number n_2 is an integer when n_1 takes the value 6. Thus, at a distance of 3.25 mm the two radiations undergo extinctions, one (250 nm) corresponding to $n_1 = 6$ and the other (650nm) corresponding to $n_2 = 2$.

The following scheme presents the evolution of the squared amplitudes corresponding to the two radiations.

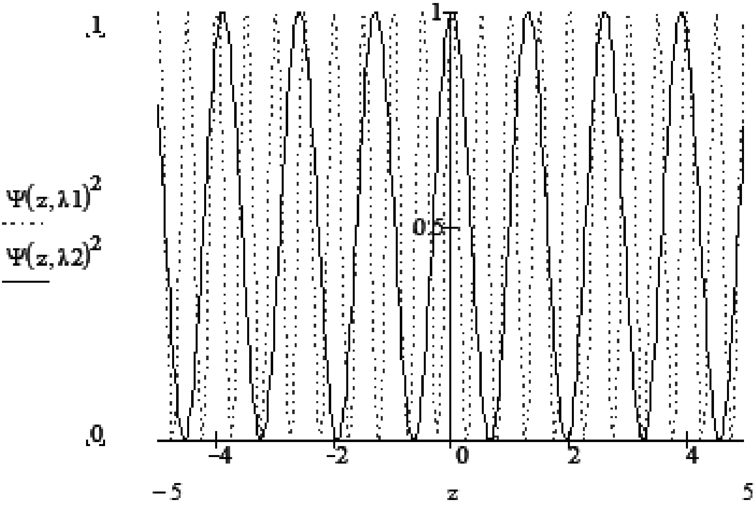


Figure II-T-1: Squared amplitudes of the two radiations.

b) How far from the central line do we see a second dark fringe?

ANSWER

Looking at the table, we can see that the next coincidence of the dark lines occurs for $n_1 = 19$ and $n_2 = 7$ and at a distance of 9.75 mm.

T-II-2. The corpuscular nature of light

The photoelectric effect.

1) Radiation with a wavelength of 250 nm is used to illuminate a metal. The photoelectrons emitted are stopped if they are opposed by a retarding potential of 0.77 V. Calculate the work of extraction of a photoelectron: $h = 6.6\times10^{-34}$ j.s; $c = 3\times10^{8}$ ms^{-1}; $e = 1.6\times10^{-19}$ C

ANSWER

According to Einstein's formula, we have

$$h\nu = W^{\circ} + E_k$$

where hν is the energy of a photon colliding with the metal; W° is the work of extraction of an electron from the metal; and E_k is the residual kinetic energy of the extracted electron. This kinetic energy can be evaluated by opposing a retarding potential V, which will brake the emitted electrons. As a result, the above formula becomes

$$h\nu = W^{\circ} + eV$$

We deduce the extraction work as follows

$$W^{\circ} = h\nu - eV \quad \text{or } W^{\circ} = \frac{hc}{\lambda} - eV$$

and

$$W^{\circ} = \frac{6.6\times10^{-34}\times3\times10^{8}}{250\times10^{-9}} - 1.6\times10^{-19}\times0.77 = 6.688\times10^{-19} joule$$

so that

$$W^{\circ} = \frac{6.688\times10^{-19}}{1.6\times10^{-19}} = 4.18 e.V$$

2) A radiation of wavelength 656 nm emitted by a hydrogen tube collides with a metal whose extraction energy is 2 eV. The photoelectrons emitted are collected by an anode. Calculate the retarding potential, which must be exactly set against them to prevent them from reaching the anode.

ANSWER

This is a variant of the previous exercise. We start with the formula

$$h\nu = W^\circ + eV$$

and deduce the following

$$V = \frac{h\nu - W^\circ}{e} \quad \text{or :} \quad V = \frac{hc}{\lambda e} - \frac{W^\circ}{e}$$

with W° expressed in joules. The quantity W°/e therefore represents the extraction work expressed in electron volts. So we have

$$V = \frac{6.6 \times 10^{-34} \times 3 \times 10^{8}}{250 \times 10^{-9} \times 1.6 \times 10^{-19}} - 2 = 2.95 Volts$$

3) The classical theory of electromagnetic waves proposes that a wave that falls on an atom, considered as a circle of radius 10^{-10} m, is absorbed and that its energy can then be used by the atom to extract its least bound electron. If the bond energy of this electron is 3 eV:

a) Calculate the time after which sufficient energy will have been absorbed by an atom irradiated by a lamp placed at a distance of 1 m emitting a power of 1 W in all directions.

ANSWER

A light of power P is irradiated by a lamp throughout the space. At distance R from the lamp, the radiated power is distributed across the surface of a sphere of radius R. The following figure presents the sphere of diffusion of the light energy.

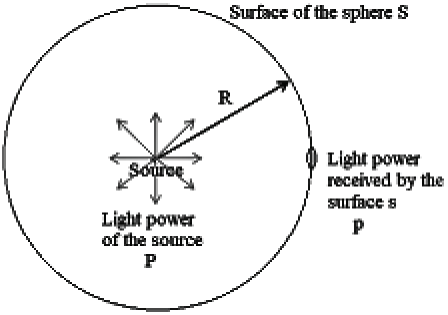


Figure II-T-2: propagation of the light power.

We can then calculate the power received by an atom considered as a disk of radius r

$$\rho = \frac{p}{s}$$

We deduce

$$\rho = \frac{p}{\pi r^2} = \frac{P}{4\pi R^2}$$

so that

$$p = \frac{P\pi r^2}{4\pi R^2} = P\frac{r^2}{4R^2}$$

Then, we have

$$p = 1\frac{(10^{-10})^2}{4(1)^2} = 2.5 \times 10^{-21} watt$$

Recall that the power is energy per unit of time

$$p = 2.5 \times 10^{-21} watt = 2.5 \times 10^{-21} J/s$$

According to classical theory, energy accumulates in the atom until it reaches a value of 3 eV. The electron is then expelled. This energy corresponds in joules to

$$E = 3 \times 1.5 \times 10^{-19} = 4.5 \times 10^{-19} J$$

We can deduce that, to reach this energy, will require time equal to

$$t = \frac{E}{p} = \frac{4.5 \times 10^{-19}}{2.5 \times 10^{-21}} = 180 s$$

However, we know that the photoelectric effect is instantaneous.

b) The wavelength, located in the UV, is 1216 Å. Calculate the number of photons that arrive at the atom in one second.

Data: h = 6.6^{-34} j.s; c = 3^8 ms^{-1}; e = 1.610^{-19} C

What conclusion can we come to?

ANSWER

According to wave theory, the energy of a photon is

$$E_{ph} = h\frac{c}{\lambda}$$

for this wavelength

$$E_{ph} = 6.6 \times 10^{-34}\frac{3 \times 10^8}{1216 \times 10^{-10}} = 1.6283 \times 10^{-18} J$$

We deduce the number of photons arriving at an atom in one second

$$N = \frac{p}{E_{ph}} = \frac{2.5 \times 10^{-21}}{1.6283 \times 10^{-18}} = 1.5353 \times 10^{-3} \text{ photons per second}$$

This result reveals, first of all, that the photoelectric effect does not concern all the atoms present. For the same atom, there is an average time between two collisions

$$\tau = 1/N = \frac{1}{1.5353 \times 10^{-3}} = 651s$$

However, it must be remembered that there are a large number of atoms in a metal and that it is always the case that one or more that will collide with the electrons. The second remark concerns the instantaneity of the photoelectric effect as the collision instantly causes the emission of an electron.

CHAPTER III

THE CORPUSCULAR AND WAVE-LIKE NATURE OF MATTER

The corpuscular aspect of matter is well known and represented through the examples of electrons, protons, neutrons, atoms, and molecule. On the other hand, the wave aspect of matter is more difficult to understand. However, multiple experiments have proven that matter displays wave-like behavior.

Louis de Broglie

Let us consider a material particle of mass m moving in space with speed v; it has a momentum

$$\vec{p} = m\vec{v}$$

According to Louis de Broglie[1], it generates what he called an "wave associated with a particle", the wavelength λ of which is given by the relation

$$\boxed{\lambda = \frac{h}{\|\vec{p}\,\|}} \qquad \text{(III-1)}$$

where h is the Planck constant and $\|\vec{p}\|$ is the modulus of momentum of the particle.

Since Louis de Broglie first presented his hypothesis, a number of experiments have proved its veracity, including: the Davisson and Germer experiment using electronic diffraction; the electronic biprism of Möllenstedt; and the Jönsson experiment using interference slits.

---

[1] Louis de Broglie (1892-1987) (pronounced "Louis de Broille") was a French mathematician and physicist. He won the Nobel Prize in Physics in 1929 for his discovery of the wave-like nature of electrons.

III-I. The Davisson and Germer Experiment

Davisson[2] and Germer[3] were experimental physicists who studied metal surfaces by irradiating them with electron beams.

They used a vacuum chamber with an electron gun that throws electrons at a piece of crystalline nickel that could pivot on itself to observe the angular dependence of the scattered electrons. Their electron sensor was mounted on a graduated circular arc so that it could be rotated to observe electrons at different diffraction angles φ (see **Fig. III-1a**).

Davisson and Germer

Surprisingly, some angles saw the scattered electron beam at maximum intensity, showing the same behavior in the case of the X-ray diffraction.

This peak can be interpreted using Bragg's law, which we met in Chapter 1, in the study of X-ray diffraction: $2l\sin\theta = n\lambda$ where θ is the Bragg angle relying the lattice spacing l in the nickel crystal to the wavelength λ of the X-rays. This supposes the attribution of wave-like behavior to electrons. As such, we may write

$$\lambda = \frac{2l\sin\theta}{n} \qquad \text{II-2)}$$

Davisson and Germer used an accelerating potential difference of 54 volts to obtain a peak at the scattering angle φ = 50°. As can be seen in **Fig. III-1b**, the scattering angle can be related to Bragg's angle by

$$2\theta = 180° - \phi$$

so that θ = 65°.

---

[2] C. J. Davisson, 1881-1958. American physicist. Winner of the Nobel Prize in Physics in 1937.

[3] L. H. Germer (1896-1971) American physicist. (https://upload.wikimedia.org/wikipedia/commons/thumb/9/99/Davisson_and_Germer.jpg/260px-Davisson_and_Germer.jpg)

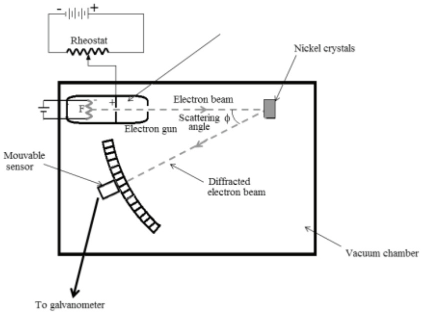


Figure III-1a: Davisson and Germer device.

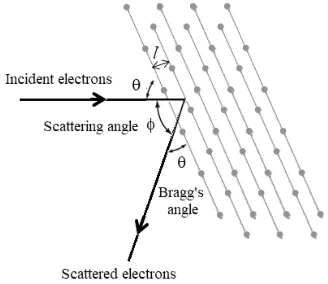


Figure III-1b: Scattering and Bragg's angles.

Using Eqs. (III-1) and and (III-2), we can evaluate the wavelength from Bragg's formula because we know the value of distance l that separates two successive reticular plans, i.e. l = 0.092nm.

In addition, if we consider the maximum of an order

$$\lambda = \frac{2\times0.092\times10^{-9}\times\sin\left(\frac{\pi}{180}\times65\right)}{1} = \underline{1.667\times10^{-10}m}$$

using de Broglie's formula, we may write

$$\lambda = \frac{h}{\|\vec{p}\|}$$

where $\|\vec{p}\|$ is the modulus of the momentum linked to the kinetic energy of the electron, so that

$$T = \frac{p^2}{2m}$$

where m is the electron mass. This gives us

$$\|\vec{p}\| = \sqrt{2mT}$$

and using the electron gun, the kinetic energy of the electron is

$$T = eV$$

where V is the accelerative potential difference. Thus, we have

$$\left\| \vec{p} \right\| = \sqrt{2meV}$$

and λ is

$$\lambda = \frac{h}{\sqrt{2meV}}$$

Using the following parameters: $h = 6.62\times10^{-34}$ J.s; $m = 9.1\times10^{-31}$ kg; $e = 1.602\times10^{-19}$ C, and the experimental potential difference of Davisson and Germer, we can find λ

$$\lambda = \frac{6.62 \times 10^{-34}}{\sqrt{2 * 9.1 \times 10^{-31} 1.602 \times 10^{-19} \times 54}} = \underline{1.668 \times 10^{-10} m}$$

As we can see, this gives the same value as the one predicted by the de Broglie relationship; this is the first verification of the de Broglie hypothesis concerning the wave-like nature of particles, such as the electron.

Now, let us look at some more recent experiments proving the veracity of the de Broglie hypothesis.

III-II. The Jönsson Experiment (1961)

In 1961, Claus Jönsson[4] carried out a real Young-type experiment for the first time with electrons scattered by slits[5].

C. Jönsson

Figure III-2:Electronic interferences.

The electrons were produced by a source that accelerated them to 50 keV, while the slits, which very narrow (~0.5 μm) and separated by about 0.1 μm, were made using copper foil. He obtained interference patterns as shown in **Fig. III-2**.

---

[4] Claus Jönsson, born in 1930. German physicist.

[5] See for example C. Jönsson, Z. Phys. 161, 454 (1961) [Am. J. Phys. 42, 4 (1974)].

III-III. The Möllenstedt Experiment (1955)

Previously, Möllenstedt[6] had realized some electronic interference figures with the aid of an electronic biprism. His results are shown in **figs. III-3a** and **III-3b**.

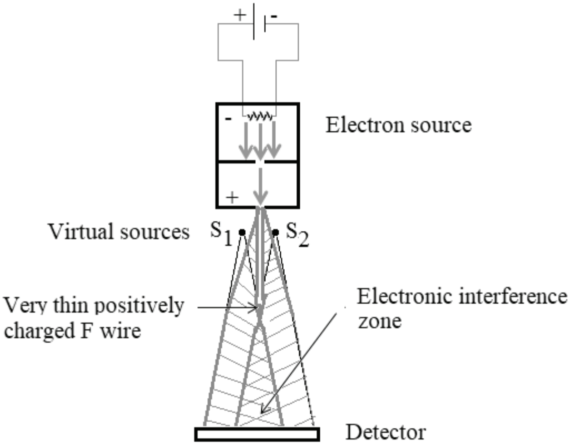


Figure III-3a. Möllenstedt device: the electronic biprism.

G. Möllenstedt

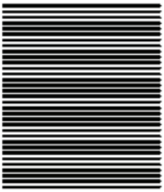


Figure III-3b. Electronic interferences

The very thin gold wire F in **Fig. III-3a** has a potential of 30,000 volts and the electron source S has a width of 500 A. One can observe an interference figure (**Fig. III-3b**, the distribution of electrons in the observation plane with maxima and minima). The system behaves like a Fresnel biprism where the secondary sources are 10.10^{-6} m apart.

In **Fig. III-4**, the evolution versus the coordinate z of the square of the amplitude is given, which reproduces the evolution of the intensity of the electronic impacts along the z-axis.

---

[6] Gottfried Möllenstedt (1912-1997). German physicist.

The theoretical explanation of the electronic interference figures is based on the same principles as those already seen in the case of light interference. The superposition of two vibrations characterized by the wave functions Ψ_1 and Ψ_2 on the interference plane leads to a stationary wave characterized by the wave function

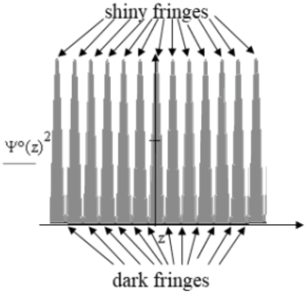


Figure III-4. Bright fringes and dark fringes.

$$\Psi(z,t) = \Psi°(z)\cos(\omega t + \Phi)$$

where

$$\Psi°(z) = 2\psi°\cos(\tfrac{\pi}{\lambda}\tfrac{a}{D}z) \tag{III-3}$$

The interfringe is i = λD/a = 0.16 10^{-6} m for D = 25cm and a=10.10^{-6} m, and the measured wavelength is

$$\lambda = 0.07 \times 10^{-10} m. \tag{III-4}$$

The electrons emitted by the S-source have the following kinetic energy

$$E_k = eV$$

where V is the accelerative difference of the potential. However, the momentum is obtained from the kinetic energy

$$E_k = \frac{p^2}{2m} \text{ i.e. } p = \sqrt{2mE_k} = \sqrt{2meV}$$

and applying the Louis de Broglie relationship we get

$$\lambda = \frac{h}{\sqrt{2meV}} \tag{III-5}$$

The identity of the result between the two ways (III-4) and (III-5) shows, once again, the veracity of Louis de Broglie's hypothesis regarding the wavelength associated with the particle.

III-IV. The Meaning of the Square of the Amplitude

In interpreting the results of the experiment on light interferences, the square of the amplitude was connected to the intensity of the light along the plane of the interference. In the case of electronic interferences, the experimental intensity along the z-axis represents the N number of electron impacts on the observation screen

$$N \propto \Psi^{\circ}(z)^2$$

As such, we can then refer to Feynman's[7] famous thought experiment.

Imagine an electron interference experiment initially involving a single electron by adjusting an electron gun and gradually increasing the rate of emission of electrons. **Fig. III-5** shows the observations for different durations of the experiment. This experiment was only recently done, although it could actually have been carried out a long time ago[8].

R. Feynman

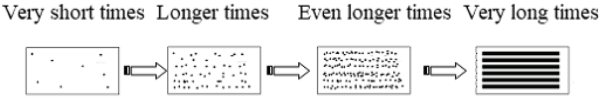


Figure III-5: Feynman's mental experience: evolution of electronic impacts over time.

As can be seen, the impacts of electrons seem to be randomly distributed over very short times, but as time passes, the lines of interference are formed by the accumulation of impacts on lines that make up the bright fringes. Thus, it may be seen that the bright fringes correspond to areas of high probability of impacts, while the dark fringes correspond to areas of zero probability of impact. $\Psi^{\circ}(z)^2$, therefore, represents the probability of impact

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[7] Richard Feynman (1918-1988). American physicist and winner of the Nobel Prize in Physics in 1965. Known for his work on quantum electrodynamics.

[8] About twenty years later, two teams, one Italian in 1976 and the other Japanese in 1989, undertook the experiment: they first replaced the slits with a filament with positive potential surrounded by plates parallel to the mass. They then attenuated the intensity of the incident electron beam from an electron microscope so that the experiment resembled Young's single photon experiment. Both teams managed to show that, after a long time, the interference figure can be reconstructed as shown in **Fig. III-5**.

at point z. The square of the amplitude of the associated wave has a probabilistic meaning.

In conclusion, we have seen that matter and light have a double aspect, both undulatory and corpuscular. This is called wave-corpuscle duality. Moreover, the wavelength of the wave associated with the particle has been assessed thanks to the Louis de Broglie relationship and the probabilistic character of the square of the wave amplitude at a point in space has been demonstrated.

III-V. Tutorial for Chapter III

T-III-1. de Broglie's wavelength

1) We consider a proton of mass m_p and of charge q_p, and an α-particle of mass m_α and charge q_α accelerated by a potential difference V of the same magnitude, but with opposite signs. Compare the wavelengths of the waves associated with these 2 particles. Data: ${}_1^1H$ and ${}_2^4\alpha$

ANSWER

Here, we use the de Broglie relation

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

The momentum of the particles is obtained by evaluating the kinetic energy of the charged particles subjected to the potential difference V

$$E_k = \frac{p^2}{2m} = q.V$$

then, we have

$$p^2 = 2m.q.V$$

and

$$p = \sqrt{2m.q.V}$$

As such, we deduce

$$\lambda = \frac{h}{\sqrt{2m.q.V}}$$

Let us consider the wavelengths λ_p and λ_α

$$\lambda_p = \frac{h}{\sqrt{2m_p.q_p.V}} \qquad \lambda_\alpha = \frac{h}{\sqrt{2m_\alpha.q_\alpha.V}}$$

The ratio of the two wavelengths shows that

$$\frac{\lambda_p}{\lambda_\alpha} = \sqrt{\frac{m_\alpha.q_\alpha}{m_p.q_p}}$$

however, we know that

$$\frac{m_\alpha}{m_p} = \frac{4m_p}{m_p} = 4 \ ; \qquad \frac{q_\alpha}{q_p} = \frac{2}{1} = 2 \ ; \qquad \frac{\lambda_p}{\lambda_\alpha} = \sqrt{8} = 2.843$$

The wavelength of the proton is longer than that of the α-particle under these conditions.

2) In an interference experiment on helium nuclei ${}_2^4He^{2+}$ (α-particle), we measured the interfringe i = 0.5 mm on a screen placed at D = 4 m from the plane of the virtual sources S_1 and S_2. S_1 and S_2 were also separated by the distance a = 1mm. Data: h = 6.6×10^{-34} j.s; the mass of a nucleon = $1.67.10^{-27}$ kg

a) Calculate the wavelength of the wave associated with the α-particles.

ANSWER

The interfringe i in an interference experiment is related to the wavelength λ

$$i = \frac{\lambda D}{a} \qquad \text{so that} \quad \lambda = \frac{ia}{D}$$

and, in our case

$$\lambda = \frac{\left(5.10^{-4}\right)(0.001)}{(4)} = 3.6954\times10^{-7}m$$

b) Deduce the speed of the α-particles.

ANSWER

Taking into account the de Broglie relation, we have

$$p = \frac{h}{\lambda} \qquad \text{with} \qquad v = \frac{p}{m} \qquad \text{so that} \qquad v = \frac{h}{m\lambda}$$

We deduce that

$$v = \frac{6.6\times10^{-34}}{\left(4\times1.67\times10^{-27}\right)\times3.6954\times10^{-7}} = 0.267 m/s$$

T-III-2. The photoelectric effect

1) When ultraviolet radiation with a wavelength of 58.4 nm emitted by a helium lamp is sent to a vapor of xenon atoms in their ground state, it can eject an electron from each of these atoms with a speed of 1.79×10^{6} m/s.

Calculate the ionization energy of xenon in eV.

Data: h = 6.6×10^{-34} J.s; c = 3×10^{8} m.s^{-1}; e = 1.610^{-19} C; m = 9.1×10^{-31} kg

ANSWER

Let us write out the relation for the photoelectric effect

$$h\nu = W^{\circ} + E_k$$

The ionization energy corresponds to the extraction work W° and we can deduce that

$$W^{\circ} = h\nu - E_k$$

The kinetic energy is

$$E_k = \frac{1}{2} m v^2$$

then

$$W^\circ = h\nu - \frac{1}{2}mv^2$$

Besides

$$h\nu = \frac{hc}{\lambda}$$

then

$$W^\circ = \frac{hc}{\lambda} - \frac{1}{2}mv^2 \text{ in Joule} \quad \text{or} \qquad W^\circ = \frac{hc}{\lambda e} - \frac{1}{2e}mv^2 \text{ in e.V.}$$

that is

$$W^\circ = \frac{6.6\times10^{-34}\times3\times10^{8}}{58.4\times10^{-9}} - \frac{1}{2}\times9.1\times10^{-31}\left(1.79\times10^{6}\right)^{2} = 1.9325\times10^{-18} \text{ Joule}$$

or, in eV

$$W^\circ = \frac{1.9325\times10^{-18}}{1.6\times10^{-19}} = 12.078 \text{ e.V.}$$

CHAPTER IV

EVIDENCE OF THE QUANTIZATION OF ENERGY IN THE HYDROGEN ATOM

What does the term *quantization* mean? It is used to describe something that is not continuous. Most life events follow the principle of continuity. Continuity in time refers to the consideration of something that undergoes transformations at different moments according to a process of continuous evolution. We consider continuity in energy in terms of objects moving in our environment, such as pedestrians, cyclists, airplanes, and automobiles, etc., and their kinetic energy can take all values. As such, we say that their kinetic energy is *continuous*.

Now we consider a world in which quantized behavior is the norm. The transformation undergone by any object will have a discrete character. The speed of a car, for example, cannot possibly take all values: it would not be allowed to be non-mobile if the driver wished to increase his speed, going from 80 to 120 miles per hour say, without any intermediate speeds. Such a situation would be very strange indeed. However, all phenomena at the microscopic scale display this behavior, especially atoms and molecules. Their energy, whatever its form, is characterized by quantization. This is the subject of this chapter—we show how the quantization of energy works.

Many experiments have been done to highlight the quantization of energy in the atom. As such, we describe here the *Franck-Hertz experiment* and the *atomic spectra* of hydrogen and hydrogenic atoms.

IV-I. The Franck-Hertz Experiment

The Franck[1]-Hertz[2] experiment was first carried out in 1914 by James Franck and Gustav Hertz.

Their aim was to prove the quantization of the energy of electrons in atoms, making it one of the fundamental experiments of quantum physics.

J. Franck

G. Hertz

1. Experimental device

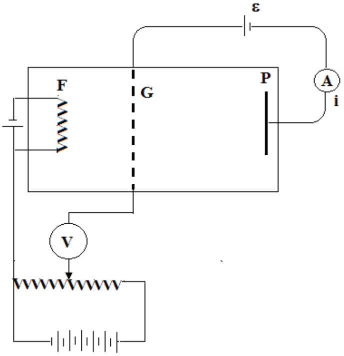

Figure IV-1: Franck-Hertz device schematic.

A is a micro-ammeter detecting the passage of a current i.

F is a heating filament that generates an electron gas by the effect thanks to a battery of accumulators.

G is a grid and between it and F one can establish a variable V potential difference (rheostat) to accelerate the electrons emitted by F.

P is a receiving plate for electrons that have passed through G.

ε is a small difference in potential to avoid low kinetic energy electrons reaching P.

---

[1] James Franck (1882-1964). German physicist known for his discovery of the laws governing the collision of an electron and an atom in collaboration with Gustav Hertz. Winner of the Nobel Prize in Physics in 1925.

[2] Gustav Ludwig Hertz. (1887-1975). German physicist known for his discovery of the laws governing the collision of an electron and an atom in collaboration with James Franck. Winner of the Nobel Prize in Physics 1925.

2. How the experimental device works in the absence of gas

First, we empty the light bulb. Electrons accelerated by the potential difference V between F and G possess kinetic energy E_k of eV value[3]

$$E_{k_G} = eV$$

These electrons pass through grid G and reach plate P. This has the effect of establishing a connection between grid G and plate P. We then observe the passage of the current i through the plate circuit. Its evolution can be plotted against the potential difference V. In **Fig. IV-2**, we present the behaviors of the current intensity in the absence of gas inside the bulb.

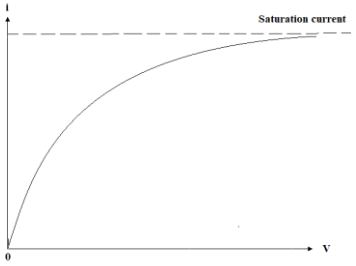

Figure IV-2: in the absence of gas.

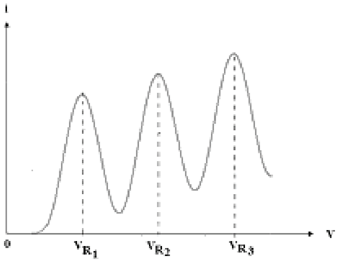

Figure IV-3: in the presence of gas.

3. How the experimental device works in the presence of gas

A monoatomic gas (e.g. helium or neon) is introduced into the bulb and the experiment is repeated. **Fig. IV-3** shows a discontinuous variation in the intensity of the current i depending on the difference in potential V. When the potential reaches a V_{R_1} value, the resonance potential, the intensity i drops and the bulb emits monochromatic frequency light.

---

[3] Indeed, at point F the total energy is $E_F = E_{KF} + E_{PF}$ and the kinetic energy in F is $E_{KF} = 0$, whereas the potential energy in F is at its maximum and equal to $E_{PF} = eV$. At point G the total energy is $E_G = E_{KG} + E_{PG}$, the kinetic energy is at its maximum, and the potential energy is $E_{PG} = 0$. Since there is conservation of the total energy, we have $E_F = E_G$ so that $E_{KF} + E_{PF} = E_{KG} + E_{PG}$ and we deduce that $E_{KG} = eV$.

If V is higher than V_{R_1}, the intensity i again grows to reach a maximum at V_{R2_1}. The gas then emits ν frequency light, but with twice the intensity, and so on.

If the potential difference is initially zero, then $V_{R2} = 2V_{R_1}$ and $V_{R_3} = 3V_{R_1}$. We also note that the energy of the emitted monochromatic light is hν with

$$h\nu = eV_{R_1} \;;\; h\nu = e(V_{R_2} - V_{R_1}) \;; h\nu = e(V_{R_3} - V_{R_2})$$

4. Interpretation of the Franck-Hertz experiment

Interpretation of the Franck-Hertz experiment is based on the notions of “elastic” and “inelastic collisions”.

a. Elastic collisions

As long as the potential difference V remains below the value V_{R_1}, the electrons emitted by the resistance F collide with the gas atoms without losing their kinetic energy. These are elastic collisions. The electrons continue their run and eventually reach the plate P and cause the current i to pass. The stronger the kinetic energy of the electrons, the greater the potential difference V, the higher the rate of passage of the electrons, and thus the higher the intensity i. The intensity of the current will therefore increase according to V.

b. Inelastic collisions

When the potential difference V reaches the value V_{R_1}, an electron hitting an atom can transmit its kinetic energy to it. It is then said that the collision is inelastic.

First inelastic collision

During this first inelastic collision, the electron transfers all of its kinetic energy. The gas then emits monochromatic ν frequency light. We therefore see the transformation of kinetic energy into light energy. After this collision, the electrons see their kinetic energy drop, and the i current plate also drops since the electrons no longer have enough energy to overcome the small stopping potential ε.

Second inelastic collision

Between V_{R_1} and V_{R_2}, the same process starts again, the remaining kinetic energy is then $e(V-V_{R_1})$ and is sufficient to allow the electron to overcome the difference in potential and increase the intensity of the current i.

If $V = V_{R_1}$, the kinetic energy available to an electron is $e(V_{R_2}-V_{R_1})$. If the latter then meets an atom, it will transmit that energy to it and the atom will return a photon of energy hν.

When $V = V_{R_3}$, the kinetic energy available to an electron is $e(V_{R_3}-V_{R_3})$ and if the latter then meets an atom, it will transmit that energy to it and the atom will restore a photon of energy hν and so on.

To schematize this, consider the case where the potential difference V is equal to 3 V_{R_1}. **Fig. IV-4** gives the example of three successive collisions with gas atoms in the space separating the filament from the grid.

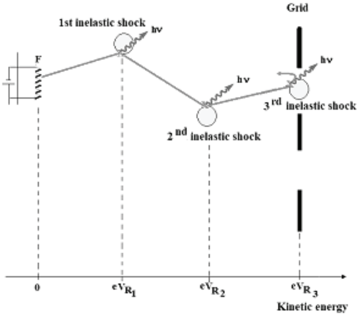

Figure IV-4: Successive inelastic shocks.

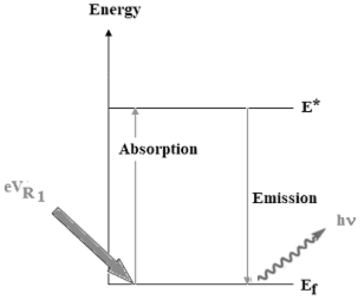

Figure IV-5: Process during an inelastic shock.

We note that, for different atoms within a gas, the amount of energy transmitted is always the same. It is therefore a characteristic of the nature of the atoms of this gas. The fact that the gas emits light during these collisions shows that it has restored the kinetic energy transmitted by the electron. As we shall see later with Bohr's theoretical model, the interpretation is that before the collision, the atom is in a fundamental state of energy E_f and after the collision it passes to a higher state of energy E*, which is called the first excited state. This process is called the *transition of absorption*. As only the fundamental state is stable, the atom immediately returns[4] from its first excited state to the fundamental state by restoring energy in the form of light energy, i.e. photons[5]. We can describe this as a *transition of emission*. These processes are illustrated in **Fig. IV-5**.

The amount of energy hν represents the difference between the energy states E_f *and* E^*. E_f *represents the fundamental state and* E^* *the first excited state. The existence of energy levels in the atom shows that energy is quantized.*

IV-II. The Emission Spectrum of Atomic Hydrogen

The Franck-Hertz experiment has shown that both a fundamental energy level and an excited energy level exist. There are also other quantized energy levels in an atom and other experiments have made it possible to better clarify this notion of quantized energy. These have been developed through the study of the emission and absorption spectra of the hydrogen atom and its analogues, described as hydrogen-like[6].

1. Obtaining an emission spectrum

A spectrum results from the dispersion of light by an experimental device (prism or network). **Fig. IV-6** shows us the dispersion of sunlight through a prism. The device is called a spectroscope.

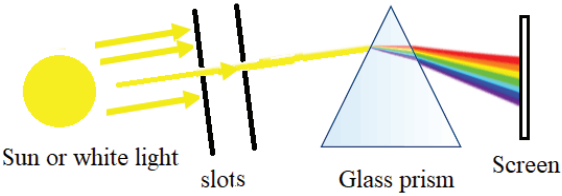

Figure IV-6: Decomposition of white light through a prism.

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[4] The lifetime of an excited state is about 10 ns.

[5] In reality, when the glow discharge regime is established, the mercury vapor appears blue. Strictly speaking, the blue light that we observe does not correspond to the return of the mercury atoms to the ground state. The photon corresponding to the transition from the 1st excited state to the ground state has an energy of 4.9 eV and therefore a wavelength of 253 nm (UV). The observed blue light, with a wavelength of 436 nm, corresponds to the transition between the 5th and the 1st excited states.

[6] Hydrogene-like: monoelectronic ions, the nuclei of which contain different numbers of protons.

The set of lights, i.e. frequencies, constituting the figure obtained on the screen is the white light spectrum.

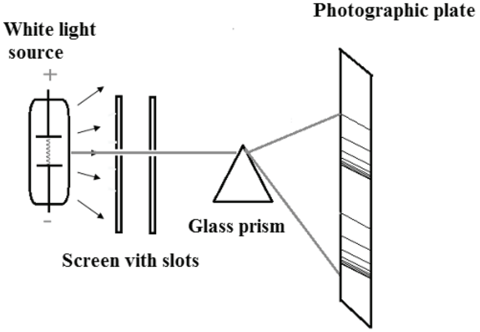


Figure IV-7. Obtaining the spectrum of atomic hydrogen.

Now, let us replace the light of the Sun with light from a hydrogen bulb, as shown in **Fig. IV-7**. Having passed through the prism, the beam is sent to a recording device (photographic plate).

In **Fig. IV-8**, we have obtained a spectrum of lines appearing in the form of several series in the different fields of light.

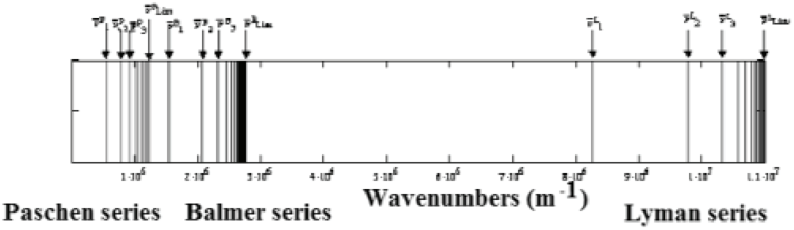


Figure IV-8: Emission spectrum of atomic hydrogen.

These lines are situated in all the domains of light and the series are identified as follows:

The ultraviolet domain, i.e. *the Lyman series.*

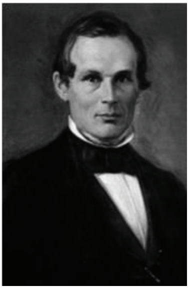
The visible domain, i.e. *the Balmer series.*

The infrared domain, i.e. *Paschen* and *Brackett* series. There are also further series, located in the infrared domain.

2. Obtaining an empirical formula

Around 1880, Balmer[7] studied the part of the spectrum located in the visible domain because, at this time, the photographic technique was limited to this domain.

J. Balmer



A. Angström

J. von Fraunhofer

Previously, the Swedish physicist Angström[8] had precisely identified the first four lines of hydrogen in the Fraunhofer[9] lines of the solar spectrum. His results are presented in **Table IV-1** and **Fig. IV-9**.

Table IV-1: Fraunhofer rays

Ray	N°	Wavelength (Å)	Wavenumber (m^{-1})
H_α	1	6532.10	1.530901×10^6
H_β	2	4860.74	2.057300×10^6
H_γ	3	4340.10	2.304094×10^6
H_δ	4	4101.20	2.438311×10^6

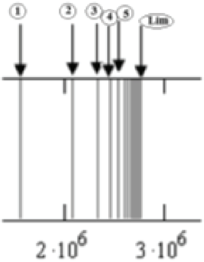


Figure IV-9: The rays of the Balmer series.

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[7] Johann Balmer (1825-1898). Swiss mathematician and physicist. Author of the famous Balmer formula.

[8] Anders Angström. (1814-1874). Swedish astronomer.

[9] Joseph von Fraunhofer (1787-1826). German optician and physicist. Inventor of the spectroscope.

To account for the position of the lines, Balmer established the following relationship from his experimental data

$$\lambda = \lambda°\left(\frac{n^2-4}{n^2}\right)$$

where λ is the wavelength of a line of the spectrum; λ° is a constant; and n is an integer equal to or greater than 3 corresponding to the line. This expression may be easily transformed into

$$\frac{1}{\lambda} = \bar{\nu} = Cst\left(\frac{1}{4} - \frac{1}{n^2}\right)$$

where Cst = 4/λ°; n is an integer equal to or greater than 3; and $\bar{\nu}$ is the wavenumber and the inverse of the wavelength λ. In **Fig. IV-9**, we can identify each line of this spectrum by number. The wavenumber of the four first rays will be

$$\bar{\nu}_1 = Cst\left(\frac{1}{4} - \frac{1}{3^2}\right);\bar{\nu}_2 = Cst\left(\frac{1}{4} - \frac{1}{4^2}\right);\bar{\nu}_3 = Cst\left(\frac{1}{4} - \frac{1}{5^2}\right);\bar{\nu}_4 = Cst\left(\frac{1}{4} - \frac{1}{6^2}\right)$$

As n_i increases, the lines get closer together, eventually creating a continuum the end of which is called the limit line and corresponds to the wavenumber ν_{Lim}

$$\bar{\nu}_{Lim} = Cst\left(\frac{1}{4} - \frac{1}{\infty^2}\right)$$

Using the wavelengths of the first lines of atomic hydrogen measured by Angström, Balmer was able to determine the Cst constant

$$\text{From ray N°1: } Cst = \frac{36}{5}\frac{1}{6532.10\times10^{-10}} = 1.1022\times10^{7}m^{-1}$$

When applied to the other rays, we find

$$\text{From ray N°2: } Cst = \frac{16}{3}\frac{1}{4860.74\times10^{-10}} = 1.0972\times10^{7}m^{-1}$$

$$\text{From ray N°3: } Cst = \frac{100}{21}\frac{1}{4340.10\times10^{-10}} = 1.0972\times10^{7}m^{-1}$$

$$\text{From ray N°4: } Cst = \frac{9}{2}\frac{1}{4101.20\times10^{-10}} = 1.0972\times10^{7}m^{-1}$$

We find practically the same value for each of the lines observed.

J. Rydberg

Even more precise measurements show that this constant is equal to 1.0973731534×10⁷ m⁻¹, which is called the Rydberg[10] constant for hydrogen, so that

$$R_H = 1,0973731534 \times 10^7 m^{-1}$$

Balmer proposed the following formula to predict the position of the lines of the visible emissions along the wavenumber scale. Here, n is an integer that can take the values 3, 4, ... up to infinity,; each value of n corresponds to a wavenumber

$$\bar{\nu}_{em}^{Balmer} = R_H\left(\frac{1}{4} - \frac{1}{n^2}\right) \text{ with } n_i > 2$$

3. Generalization to other series

T. Lyman

With progress in observation techniques, especially the photographic technique, it was quickly established that there were series of lines in the different areas of the light spectrum, such as the series in the ultraviolet domain, called the Lyman[11] series. The position of the lines[12] in this series, as with the Balmer series, can be predicted by a similar empirical law

$$\bar{\nu}_{em}^{Lyman} = R_H\left(1 - \frac{1}{n^2}\right) \text{ with } n > 1$$

---

[10] Johannes Rydberg (1854-1919) Swedish physicist known for his work in spectroscopy.

[11] Theodore Lyman (1874-1954). Known for his work on the atomic spectra of hydrogen. A series of rays bears his name.

[12] The first line of the Lyman series ultraviolet (UV) spectrum was discovered in 1906 by a Harvard physicist, Theodore Lyman, who studied the UV spectrum by electrifying hydrogen molecules. The rest of the spectrum lines were discovered by this same researcher between 1906 and 1914.

In the infrared domain, we find other series whose positions along the scale of the wavenumbers obey identical laws; these are the Paschen[13], Brackett[14], and Pfund[15] series.


F. Brackett


F. Paschen


A. Pfund

In **Table IV-2**, we summarize the formulas used to reproduce each of these series.

This is the Balmer formula in which n_f refers to the series and n_i gives the number of the ray in the series.

Table IV-2: Other series for atomic hydrogen

Series	formula
Paschen	$\bar{\nu}_{em}^{Paschen} = R_H\left(\frac{1}{9} - \frac{1}{n^2}\right)$ with $n > 3$
Brackett	$\bar{\nu}_{em}^{Brackett} = R_H\left(\frac{1}{16} - \frac{1}{n^2}\right)$ *with* $n > 4$
Pfund	$\bar{\nu}_{em}^{Pfund} = R_H\left(\frac{1}{25} - \frac{1}{n^2}\right)$ with $n > 5$

In **Table IV-3**, we have classified the different lines of the emission spectrum of atomic hydrogen corresponding to the first three series, while **Fig. IV-10** presents the corresponding theoretical lines.

---

[13] Friedrich Paschen. (1865-1947) German physicist known for his work on electric discharges in gases

[14] Frederick Brackett (1896-1988). American physicist and astronomer known for his work on the infrared radiation of the sun.

[15] August Pfund (1879-1949). American physicist known for his work in spectroscopy.

Table IV-3: Theoretical generation of atomic hydrogen spectrum rays

$$
\bar{v}_{em} = R_H\left(\frac{1}{n_f^2}-\frac{1}{n_i^2}\right)
\begin{cases}
n_f = 1 \text{ Lyman} & \begin{cases} \boxed{\begin{array}{l}
n_i = 2 \rightarrow \bar{v}_1^L = R_H\left(\frac{1}{1^2}-\frac{1}{2^2}\right) \\
n_i = 3 \rightarrow \bar{v}_2^L = R_H\left(\frac{1}{1^2}-\frac{1}{3^2}\right) \\
n_i = 4 \rightarrow \bar{v}_3^L = R_H\left(\frac{1}{1^2}-\frac{1}{4^2}\right) \\
\ldots \\
n_i = \infty \rightarrow \bar{v}_{Lim}^L = R_H\left(\frac{1}{1^2}-\frac{1}{\infty^2}\right)
\end{array}} \end{cases} \\
n_f = 2 \text{ Balmer} & \begin{cases} \boxed{\begin{array}{l}
n_i = 3 \rightarrow \bar{v}_1^L = R_H\left(\frac{1}{2^2}-\frac{1}{3^2}\right) \\
n_i = 4 \rightarrow \bar{v}_2^L = R_H\left(\frac{1}{2^2}-\frac{1}{r^2}\right) \\
n_i = 5 \rightarrow \bar{v}_3^L = R_H\left(\frac{1}{2^2}-\frac{1}{5^2}\right) \\
\ldots \\
n_i = \infty \rightarrow \bar{v}_{Lim}^L = R_H\left(\frac{1}{2^2}-\frac{1}{\infty^2}\right)
\end{array}} \end{cases} \\
n_f = 3 \text{ Paschen} & \begin{cases} \boxed{\begin{array}{l}
n_i = 4 \rightarrow \bar{v}_1^L = R_H\left(\frac{1}{3^2}-\frac{1}{4^2}\right) \\
n_i = 5 \rightarrow \bar{v}_2^L = R_H\left(\frac{1}{3^2}-\frac{1}{5^2}\right) \\
n_i = 6 \rightarrow \bar{v}_3^L = R_H\left(\frac{1}{3^2}-\frac{1}{6^2}\right) \\
\ldots \\
n_i = \infty \rightarrow \bar{v}_{Lim}^L = R_H\left(\frac{1}{3^2}-\frac{1}{\infty^2}\right)
\end{array}} \end{cases}
\end{cases}
$$

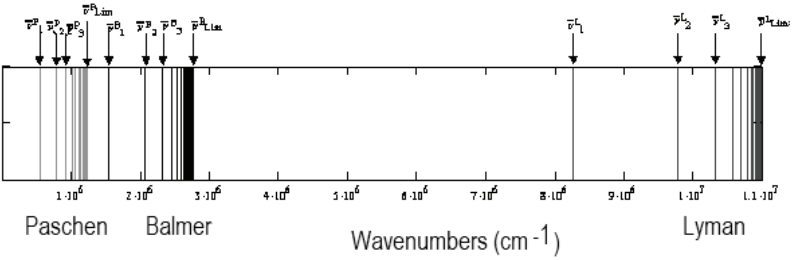

Figure IV-10: Emission spectrum of atomic hydrogen.

4. Intuitive interpretation of Balmer's formula

Consider below Balmer's formula for emission

$$\bar{\nu}_{em} = R_H\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right) \text{ with } n_i > n_f$$

where n_i and n_f are integers. We multiply on both sides by the quantity hc

$$hc\bar{\nu}_{em} = hcR_H\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right) \text{ with } n_i > n_f$$

and write the following formula as well

$$hc\bar{\nu}_{em} = \frac{hcR_H}{n_f^2} - \frac{hcR_H}{n_i^2} \text{ with } n_i > n_f$$

Given what we know about light, the quantity $hc\nu_{em}$ represents the light energy emitted by the hydrogen atom, i.e. the energy of a photon, where h is the Planck constant and c is the velocity of light in a vacuum. We can see that this energy results from a difference between two energy terms hcR_H/n_f^2 and hcR_H/n_i^2. Let the absolute values of $|E(n_f)|$ and $|E(n_i)|$ be

$$|E(n_f)| = \frac{hcR_H}{n_f^2} \text{ and } |E(n_i)| = \frac{hcR_H}{n_i^2} \tag{IV-1}$$

We can then write that the energy of the emitted photon is

$$|hc\bar{\nu}_{em}| = |E(n_f)| - |E(n_i)|$$

Now, let us use the thermodynamic convention that the energy emitted by a system has a negative sign

$$E(n_f) - E(n_i) = -hc\bar{\nu}_{em}$$

or

$$-E(n_f) + E(n_i) = hc\bar{\nu}_{em}$$

so that

$$(-E(n_f)) - (-E(n_i)) = hc\bar{\nu}_{em}$$

Given Eq. (IV-1), we thus have

$$E(n_f) = -\frac{hcR_H}{n_f^2} \quad \text{and} \quad E(n_i) = -\frac{hcR_H}{n_i^2}$$

Here, we have *quantized energy*. As we shall show with the study of models of the hydrogen atom, these quantities are none other than quantized energy levels, characterized by an integer.

In this context we see, as shown in **Fig. IV-11**, that the emission of a photon by the atom results from its journey from an energy level characterized by the integer number n_i to the energy level characterized by the integer n_f. We can thus speak of *energy transition* and can schematize the process of emission of a photon by a change in the potential energy of the atom. Here, we understand the notation i for initial and f for final. Therefore, by deduction, the general expression of an energy level in the hydrogen atom is

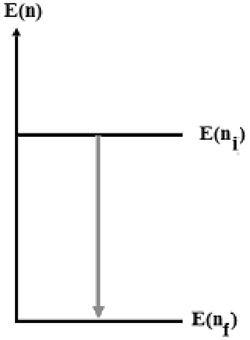

Figure IV-11: Electronic transition.

$$E(n) = E_n = -\frac{hcR_H}{n^2} \qquad \text{(IV-2)}$$

where n is the *quantum number*.

We have just seen how a simple empirical analysis allows us to realize that the energy of the electron in the hydrogen atom is quantized. The lines observed in the emission spectrum of atomic hydrogen are therefore the result of transitions from an initial level characterized by an initial quantum number n_i to a final energy level characterized by the quantum number n_f . If we evaluate the term hcR_H, we obtain

$$hcR_H = 6.626 \times 10^{-34} \times 2.998 \times 10^{8} \times 1.097 \times 10^{7} = 2.179 \times 10^{-18} J$$

or, in eV

$$\boxed{E_n = -\frac{13.606}{n^2} e.V}$$

We can draw a diagram of the energy levels of the hydrogen atom and show the transitions between those levels, which generate the rays of the atomic hydrogen emission spectrum

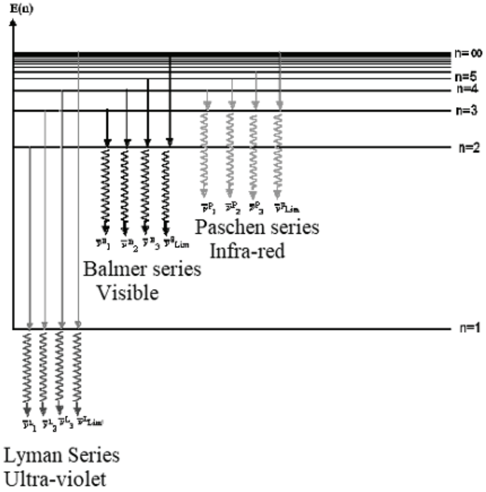

Figure IV-12: The transitions of the atomic hydrogen emission spectrum.

The emission process can also be visualized by drawing a diagram of the energy levels of the atomic and energy transitions of the first three series hydrogen emission spectrum (**Fig.IV-12**).

IV-III. The Absorption Spectrum Of Atomic Hydrogen

1. The absorption spectrum

For us to obtain an absorption spectrum, we must first pass white light through a sample. The sample will absorb some of the radiation and return a spectrum such as that shown in **Fig. IV-13**.

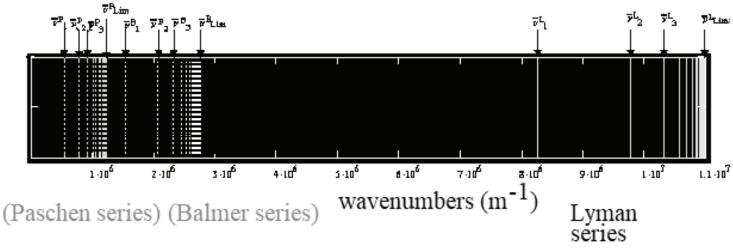

Figure IV-13: Absorption spectrum of atomic hydrogen.

The absorption spectrum represents the opposite phenomenon to the emission spectrum as transitions now take place from lower to higher levels. However, the Balmer and Paschen series do not appear at room temperature, which is why they are shown with dotted lines.

2. Particularity of the absorption spectrum

At room temperature (i.e. the lowest energy level of the electron), only the Lyman series appears, but if we raise the temperature considerably we can see the other series appear. The absorption spectrum is superimposed on the emission spectrum in terms of the position of the rays. To calculate the position of these lines we use an identical relationship, looking at where the integer numbers n_i and n_f are swapped since the transitions go from the lowest quantum number to the higher quantum numbers.

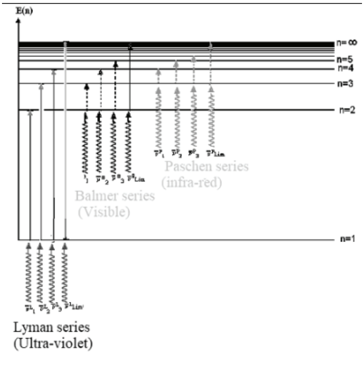

Figure IV-14: The transitions in the absorption spectra of the hydrogen atom.

$$\bar{\nu}_{abs} = R_H\left(\frac{1}{n_i^2} - \frac{1}{n_f^2}\right) \text{with } n_f > ni$$

In the case of the absorption spectrum, n_i defines the series, which is the starting point of the radiation, while n_f, being the point of arrival of the transitions, defines the ray number (**Fig. IV-14**).

One may ask why only the Lyman series appears in the spectrum at room temperature. It should be noted that in order for radiation to be observed clearly, it is necessary, among other conditions, that the number of transitioning atoms is quite high. As such, the fewer atoms at a given transition, the less visible the ray will be. There is thus a proportionality between the number of atoms where a transition occurs and the light intensity of the absorption ray.

3. The Boltzmann distribution law

In a set of hydrogen atoms, we see particular distributions between different energy levels. The most "populated" level is the fundamental state n = 1, which is that of almost all atoms. However, the higher levels may only have a small number of atoms and these numbers are reduced even further as the energy level rises. **Fig. IV-15** represents this situation.

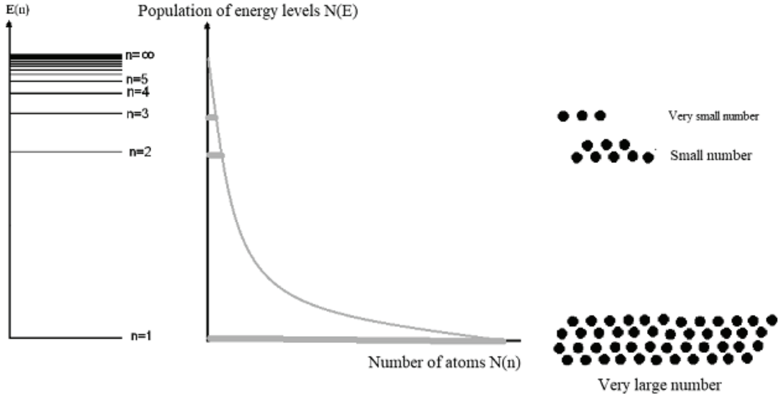

Figure IV-15: Illustration of the Boltzmann law.

L. Boltzmann

Furthermore, the ratio of the number of N_2 atoms in a given E_2 level to N_1 of an E_1 state is given by the Boltzmann[16] distribution

$$\frac{N_2}{N_1} = \exp\left(-\frac{|E_2-E_1|}{k_B T}\right)$$

where k_B is the Boltzmann constant (k_B = 1.3806568×10^{-23} J.K^{-1}) and T is the absolute temperature (in Kelvin).

Thus, since there is a proportionality between the number of atoms and the intensity of a ray having its starting point on the level considered, for cases where one compares the intensities of the lines of the Balmer series (I_B) and those of the Lyman series (I_L), we can write

$$\frac{I_B}{I_L} = \frac{N_2}{N_1} = \exp\left(-\frac{|E_2-E_1|}{k_B T}\right)$$

where N represents the number of atoms having the fundamental energy level (n = 1) and N_2 stands for the number of atoms having the energy of the 1st excited state (n = 2). Given Eq. (IV-2) and knowing that

$$E(1) = -\frac{hcR_H}{1^2} \qquad \text{and} \qquad E(2) = -\frac{hcR_H}{2^2}$$

we can write

$$\frac{I_B}{I_L} = \exp\left(-\frac{3}{4}\frac{hcR_H}{k_B T}\right)$$

We may wonder what temperature would be sufficient to observe the Balmer series in an absorption spectrum with an intensity of 1/10 of that of the Lyman series

$$\frac{1}{10} = \exp\left(-\frac{3}{4}\frac{hcR_H}{k_B T}\right)$$

---

[16] Ludwig Boltzmann (1844-1906). Austrian physicist known for his foundational works of statistical physics and as a fervent defender of the existence of atoms.

or

$$Ln(\frac{1}{10}) = -\frac{3}{4}\frac{hcR_H}{k_BT}$$

and then

$$T = \frac{3}{4}\frac{hcR_H}{k_BLn(10)}$$

which leads to

$$T = \frac{3}{4} \times \frac{6.626\times10^{-34}\times2.998\times10^{8}\times1.097\times10^{7}}{1.381\times10^{-23}\times\ln(10)} = 51427 \text{ K}$$

This temperature would be difficult to obtain on earth outside certain experimental situations (i.e. atomic and thermonuclear explosions).

IV-IV. Generalization to Hydrogenic Atoms

Hydrogenic refers to something that “looks like hydrogen”.

The Balmer formula (emission or absorption) can be extended to hydrogenic atoms. A hydrogenic atom is a single-electronic system and hydrogen itself is thus a hydrogenic atom because it has only one electron. We also have all the ions formed from the atoms that have only one electron around a nucleus, as with He^+, Li^{2+}, Be^{3+}, B^{4+}.....Na^{10+}.

All these entities behave like hydrogen and are therefore subject to the same laws. Thus, the spectra of these entities resemble the absorption and emission spectra of atomic hydrogen. The difference with hydrogen comes from the number of protons present in the nucleus. Thus, Balmer’s formula has to be changed so that we have, respectively, for emission and absorption

$$\bar{\nu}_{em} = R_HZ^2\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right) \text{with } n_i > n_f$$

$$\bar{\nu}_{abs} = R_HZ^2\left(\frac{1}{n_i^2} - \frac{1}{n_f^2}\right) \text{with } n_f > ni$$

where Z is the atomic number of the hydrogenic atom.

In conclusion, we can say that experimentation has shown that the energy of atoms can be quantized roughly, as in the Franck-Hertz experiment, or more precisely through the study of the atomic spectra of hydrogenic atoms. Discovering the facts involves understanding their underlying reasons, which is what we propose to investigate in the chapters that follow.

IV-V. Tutorial for Chapter IV

T-IV-1. The Franck-Hertz experiment

1) Briefly describe this experiment. What does it highlight?

ANSWER

In this experiment, electrons accelerated by a potential difference collide with the atoms of a gas. There are two kinds of collision: inelastic collisions with no effect on the kinetic energy of the electrons and elastic collisions in which the kinetic energy of the electrons is transmitted to the atoms of the gas. Simultaneously, the gas emits monochromatic light, the energy of which is equal to the energy difference between the ground state and the 1st excited state of the atom. This experiment therefore highlights the existence of energy levels in the atom and the quantization of energy in the atom.

2) We carry out this experiment on the vapor of a metal (monoatomic). It is observed that when the accelerating potential difference reaches the value $V_1 = 2$ volts, the gas emits light. The potential difference of $V = 6$ volts is then applied and the light is analyzed using a dispersive device. We then obtain the spectrum of this light. Represent this spectrum on a scale graduated in wavenumbers ν. Data: $e = 1.610^{-19}$ C, $h = 6.6.10^{-34}$ j.s., $c = 3.10^8$ ms^{-1}

ANSWER

According to Franck and Hertz, there is a relationship between the kinetic energy lost by an electron and the emission of light, i.e.

$$e(V_n - V_{n-1}) = hc\bar{\nu}$$

where V_n is the potential applied to the incident electron. We have successive inelastic collisions between the incident electron and an atom of the gas in the Franck-Hertz bulb, i.e.

$$e(V_1 - V_0) = hc\bar{\nu} \;\; ; \;\; e(V_2 - V_1) = hc\nu \;\; ; \;\; e(V_3 - V_2) = hc\bar{\nu}$$

With the initial potential being zero, we have

$$eV_1 = hc\bar{\nu}$$

We can deduce the wavenumber that is emitted in the first inelastic collision, i.e.

$$\bar{\nu} = \frac{hc}{eV_1}$$

or

$$\bar{\nu} = \frac{1.6 \times 10^{-19} \times 2}{6.6 \times 10^{-34} \times 3 \times 10^{8}} = 1.6161 \times 10^{6} m^{-1}$$

During the second inelastic collision, because the same quantity of kinetic energy is transmitted to another atom of the gas, we must have the following value for V_2

$$e(V_2 - V_1) = hc\bar{\nu} \;\; ; \;\; (eV_2 - eV_1) = hc\bar{\nu} \;\; ; \;\; eV_2 = hc\bar{\nu} + eV_1$$

and

$$V_2 = \frac{hc\bar{\nu} + eV_1}{e}$$

However, since

$$hc\bar{\nu} = eV_1$$

we have

$$V_2 = \frac{2eV_1}{e} = 2V_1 \quad \text{and} \quad V_2 = 2 \times 2 = 4V$$

For the third inelastic collision, we have

$$e(V_3 - V_2) = hc\bar{\nu}$$

where V_3 has the value 6 V, so that

$$e(6-4)=hc\bar{\nu} \quad \text{and} \quad 2e=hc\bar{\nu}=eV_1$$

The wavenumber of the emitted light remains the same and the spectrum of the light in this experiment will have a unique line.

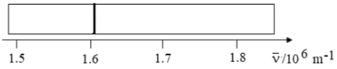

Figure T-IV-1: Unique line for the Franck-Hertz experiment.

c) Using an electron gun, electrons are sent towards a speed filter consisting of two capacitor plates parallel to each other and separated by a distance d = 2 cm.

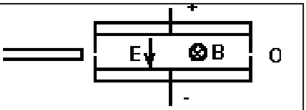

Figure T-IV-2: speed filter.

A potential difference of V = 600 volts is applied between these plates and perpendicular to the electric field thus created a magnetic induction B = 0.05 Tesla is applied. Electrons passing through the filter without being deflected pass through hole O.

Data: $e = 1.6\times10^{-19}$ C, $h = 6.6\times10^{-34}$ j.s., $c = 3.10^8$ ms^{-1}, $m = 9.1\times10^{-31}$ kg

1) What is the condition for the electrons to pass through the filter without being deflected?

ANSWER

Between the capacitor plates, an electron with velocity $\vec{v_0}$ is subject to the action of two opposite forces: an electrostatic force $\vec{f_{\text{el}}}$ created by the electrostatic field and an electromagnetic force $\vec{f_{\text{em}}}$ created by the magnetic induction $\vec{\mathbf{B}}$.

If the modulus of these forces is equal, the result of their action on the electron is zero and it crosses the speed filter without being deflected

$$\|\vec{f}_{el}\|=\|\vec{f}_{em}\| \quad \text{where } \|\vec{f}_{el}\|=qE \text{ and } \|\vec{f}_{em}\|=qvB$$

and we have

$$qE=qv_0B \text{ so that } v_0=\frac{E}{B}$$

as the required condition for the electron to cross the speed filter without being deflected.

Let us calculate this velocity. For the intensity of the electrostatic field we have

$$E = \frac{V}{d} = \frac{600}{2 \times 10^{-2}} = 3 \times 10^{4} \, volt \times m^{-1}$$

so the velocity is

$$v_0 = \frac{E}{B} = \frac{3 \times 10^{4}}{0.05} = 6.0 \times 10^{5} \, m \times s^{-1}$$

3) Those electrons that pass through the filter without being deflected emerge through hole O into a Franck-Hertz bulb filled with a monoatomic gas. When the first resonance potential V_{R_1} is reached, the gas emits monochromatic radiation of wavelength $\lambda = 4125 \times 10^{-10}$ m. Calculate the value of the first resonance potential under these conditions.

ANSWER

The energy received by the atom is equal to the gap ΔE between its ground state and the 1st excited state. This energy gap ΔE is

$$\Delta E = \frac{hc}{\lambda} \quad \text{i.e.} \quad \Delta E = \frac{6.6 \times 10^{-34} \times 3 \times 10^{8}}{4125 \times 10^{-10}} = 4.8 \times 10^{-19} j$$

In the Franck-Hertz experiment, the electron has an initial kinetic energy E°_k, but this energy is not sufficient to allow the electron to experience an inelastic collision. Such an inelastic collision may be obtained if we give additional energy to the electron by the use of a resonance potential V_{R_1}, such as

$$\Delta E = E^{\circ}_k + eV_{R_1}$$

The initial kinetic energy E°_k is

$$E^{\circ}_k = \frac{1}{2} m v_0^2 = \frac{1}{2} \times 9.1 \times 10^{-31} \times (6.0 \times 10^{5})^2 = 1.638 \times 10^{-19} J$$

thus, we have

$$V_{R_1}=\frac{\Delta E-E°_k}{e}$$

and

$$V_{R_1}=\frac{4.8\times10^{-19}-1.638\times10^{-19}}{1.6\times10^{-19}}=1.976\,volt$$

4) What would the value of the second resonance potential be?

ANSWER

As the electron undergoes a second inelastic collision, its kinetic energy again reaches the value ΔE. The second resonance potential must therefore correspond to the kinetic energy necessary to cause 2 successive inelastic collisions, i.e. $eV_{R_1}+\Delta E$

$$eV_{R_2}=eV_{R_1}+\Delta E \quad \text{so that} \quad V_{R_2}=V_{R_1}+\frac{\Delta E}{e}$$

and

$$V_{R_2}=1.976+\frac{4.8\times10^{-19}}{1.6\times10^{-19}}=4.976\,volt$$

T-IV-2. Atomic spectra

1) Using a dispersive device, we can analyze the light coming from a star; we highlight a line located in the ultraviolet domain and corresponding to a wavelength of 2225×10^{-10} m. Does this line belong to the emission spectrum of atomic hydrogen? If this is the case, say which transition it corresponds to; if not explain why. Data: $R_H = 1.1\times10^{7}$ m^{-1}

ANSWER

This is an emission spectrum. If the line belongs to atomic hydrogen, then it obeys Balmer's relation for emissions

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

If the line is in the ultraviolet domain, then it belongs to the Lyman series. If it belongs to the Lyman series, then it corresponds to one of the transitions from the upper levels to the level n = 1. As such, we have

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

then

$$\frac{\bar{\nu}}{R_H} = \frac{1}{1^2} - \frac{1}{n_i^2}$$

or, otherwise

$$\frac{1}{n_i^2} = 1 - \frac{\bar{\nu}}{R_H}$$

so that

$$\frac{1}{n_i^2} = 1 - \frac{1}{2225 \times 10^{-10} \times 1.1 \times 10^7} = 0.59142$$

which gives the result

$$n_i = \sqrt{\frac{1}{0.59142}} = 1.30$$

The quantum number corresponding to the initial level of the transition must be an integer. Consequently, we can say that the transition does not obey the Balmer relation and the line does not belong to the emission spectrum of atomic hydrogen.

2) We give the part of the emission spectrum of atomic hydrogen corresponding to the Balmer series.

<u>Exclusively</u> using the spectrum data, evaluate the Rydberg constant.

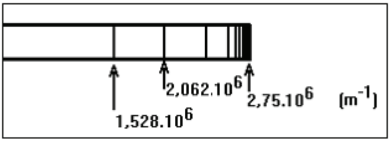

Figure T-IV-3: The Balmer series.

ANSWER

There are three ways to calculate this constant from the spectrum data.

1) Consider the line $\bar{\nu}_1$=1.528×10^6 m^{-1}. It corresponds to the first line of the Balmer series whose wavenumber is given by the Balmer relation

$$\bar{\nu}_1 = R_H\left(\frac{1}{2^2}-\frac{1}{3^2}\right) = R_H\left(\frac{9-4}{36}\right) = R_H\left(\frac{5}{36}\right)$$

so that

$$R_H = \frac{36\times 1.528}{5}\times 10^6 = 1.1002\times 10^7\,m^{-1}$$

2) Consider the line $\bar{\nu}_2$ =2.062×10^6 m^{-1}. It corresponds to the second line of the Balmer series whose wavenumber is given by the Balmer relation

$$\bar{\nu}_2 = R_H\left(\frac{1}{2^2}-\frac{1}{4^2}\right) = R_H\left(\frac{4-1}{16}\right) = R_H\left(\frac{3}{16}\right)$$

then

$$R_H = \frac{16\times 2.062\times 10^6}{3} = 1.0997\times 10^7\,m^{-1}$$

3) Consider the limit line $\bar{\nu}_{lim}$=2.750×10^6 m^{-1}. It corresponds to the limit line of the Balmer series whose wavenumber is given by the Balmer relation

$$\bar{\nu}_{\mathrm{lim}} = R_H\left(\frac{1}{2^2}-\frac{1}{\infty^2}\right) = R_H\left(\frac{1}{4}\right)$$

then

$$R_H = 4\times 2.750\times 10^6 = 1.1000\times 10^7\,m^{-1}$$

The three ways give, of course, the same result for the Rydberg constant.

3) At what temperature would atomic hydrogen have to be for the Balmer series to appear with an intensity of 1/10 that of the Lyman series in the absorption spectrum of atomic hydrogen.

Data: $h = 6.6\times10^{-34}$ j.s.; $k_B = 1.38\times10^{-23}$ j.K^{-1}; $R_H = 1.1\times10^{7}$ m^{-1}

ANSWER

There is a proportionality between the number of hydrogen atoms having energy level n and the intensity of the transitions resulting from this level. In other words

$$\frac{N_2}{N_1} = \frac{I^{Balmer}}{I^{Lyman}} \tag{T-IV-1}$$

The ratio of the numbers of atoms having energies E_2 and E_1 is given by the Boltzmann distribution law

$$\frac{N_2}{N_1} = \exp\left(-\frac{|E_2 - E_1|}{k_B T}\right)$$

where k_B is the Boltzmann constant. On the other hand, the energy of one level of the hydrogen atom is given by

$$E_n = -\frac{hcR_H}{n^2}$$

and we can deduce that

$$|E_2 - E_1| = hcR_H\left(\frac{1}{1^2} - \frac{1}{2^2}\right) = \frac{3}{4}hcR_H$$

so that

$$\frac{N_2}{N_1} = \exp\left(-\frac{3hcR_H}{4k_B T}\right)$$

We take the natural logarithm of this expression

$$Ln\left(\frac{N_2}{N_1}\right) = -\frac{3hcR_H}{4k_B T}$$

Given Eq. (T-IV-1), this expression may be written in the form

$$Ln\left(\frac{I^{Balmer}}{I^{Lyman}}\right) = -\frac{3hcR_H}{4k_BT}$$

so that

$$Ln\left(\frac{1}{10}\right) = -\frac{3hcR_H}{4k_BT} \text{ that gives } T = \frac{3hcR_H}{4k_BLn(10)}$$

and

$$T = \frac{3 \times 6.6 \times 10^{-34} \times 3 \times 10^{8} \times 1.1 \times 10^{7}}{4 \times 1.38 \times 10^{-23} \times \ln(10)} = 51407K$$

4) We give the energy levels (in eV) of the hydrogen atom. Based only on the data provided below, determine the wavelength of the radiation corresponding to the third line of the Lyman series.

Data: $e = 1.610^{-19}$ C; $h = 6.6 \times 10^{-34}$ j.s.; $c = 3 \times 10^{8}$ J.ms^{-1}

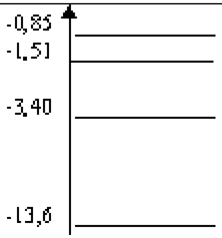

Figure T-IV-4: Energy levels.

ANSWER

This is the transition: $n_i = 4 \rightarrow n_f = 1$.

Thus, we have

$$\Delta E = |E_4 - E_1| = 13.6 - 0.85 = 12.75 \text{ e.V.}$$

since

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

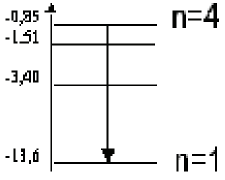

Figure T-IV-5: Emission transition

for the wavelength, we have

$$\lambda = \frac{hc}{\Delta E} = \frac{6.6 \times 10^{-34} \times 3 \times 10^{8}}{12.75 \times 1.6 \times 10^{-19}} = 97.06 \times 10^{-9} m$$

5) Here are the spectra of two hydronenoids, one of which is hydrogen. They correspond to the same series.

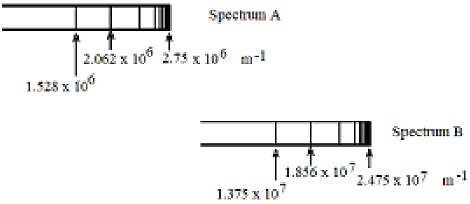

Figure T-IV-6: Two hydrogenic atom spectra.

a) Identify the spectrum concerning hydrogen.

ANSWER

The spectrum relating to hydrogen is the one presenting the weakest value of the limit line wavenumber. Indeed, the wavenumbers of a hydrogenic atom are multiples of those of hydrogen by the factor Z^2 (the squared atomic number). As such, spectrum A is the one for hydrogen.

b) Using only the data provided, determine the atomic number of the other hydrogenic atom.

ANSWER

Consider the limit lines $\bar{v}_{limA}$ and $\bar{v}_{limB}$. For each of them we can write the spectra out as if they are emission spectra

$$\bar{v}_{Lim\,A} = R_H\left(\frac{1}{n_f^2} - \frac{1}{\infty^2}\right) = R_H\frac{1}{n_f^2} \text{ and } \bar{v}_{Lim\,B} = R_H Z^2\left(\frac{1}{n_f^2} - \frac{1}{\infty^2}\right) = R_H\frac{Z^2}{n_f^2}$$

The ratio of the limit lines wavenumbers therefore gives

$$\frac{\bar{v}_{Lim\,B}}{\bar{v}_{Lim\,A}} = Z^2$$

Since n_f and R_H are the same in both cases, we can deduce

$$Z^2 = \frac{2.475 \times 10^7}{2.75 \times 10^6} = 9 \quad \text{then} \qquad Z = 3$$

This is the lithium hydrogenic atom Li^{2+}.

6) Ground state hydrogen atoms are excited by UV radiation with a wavelength of 97 nm.

a) What is the principal quantum number n_f of the state thus obtained?

ANSWER

This is an absorption spectrum. Hydrogen is in its ground state and so we use the formula

$$\bar{\nu} = R_H\left(\frac{1}{n_i^2} - \frac{1}{n_f^2}\right) \text{ i.e. } \bar{\nu} = R_H\left(\frac{1}{1^2} - \frac{1}{n_f^2}\right)$$

so that

$$\frac{1}{n_f^2} = 1 - \frac{\bar{\nu}}{R_H} \quad \text{or} \quad \frac{1}{n_f^2} = 1 - \frac{1}{R_H \lambda}$$

then

$$\frac{1}{n_f^2} = 1 - \frac{1}{1.1 \times 10^7 \times 97. \times 10^{-9}} = 6.2793 \times 10^{-2}$$

and

$$n_f = \sqrt{\frac{1}{6.2793 \times 10^{-2}}} = 3.99$$

Taking the rounding errors into account, we can deduce that the quantum number is $n_f = 4$ and that absorption takes place.

b) Calculate the wavelengths of the different radiations that these atoms can emit when they are de-excited.

ANSWER

Emission transitions are made from level $n_f = 4$ to lower levels and in turn these levels are de-energized according to the scheme.

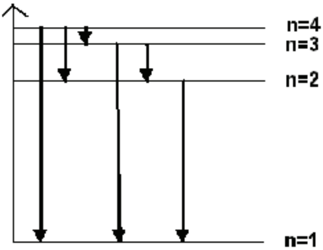

Figure T-IV-7: Emission transitions from n = 4.

We then calculate the corresponding transitions using the Balmer formula for the emission

$$\bar{v}_{41} = 1.1\times10^{7}\left(\frac{1}{1^2}-\frac{1}{4^2}\right) = 1.0313\times10^{7}\ \text{m}^{-1}\ \text{i.e.}\ \lambda_{41} = \frac{1}{1.0313\times10^{7}} = 95.9nm$$

$$\bar{v}_{42} = 1.1\times10^{7}\left(\frac{1}{2^2}-\frac{1}{4^2}\right) = 2.0625\times10^{6}\text{m}^{-1}\ \text{i.e.}\ \lambda_{42} = \frac{1}{2.0625\times10^{6}} = 48.48nm$$

$$\bar{v}_{43} = 1.1\times10^{7}\left(\frac{1}{3^2}-\frac{1}{4^2}\right) = 5.3472\times10^{5}\text{m}^{-1}\ \text{i.e.}\ \lambda_{43} = \frac{1}{5.3472\times10^{5}} = 187.nm$$

$$\bar{v}_{31} = 1.1\times10^{7}\left(\frac{1}{1^2}-\frac{1}{3^2}\right) = 9.7778\times10^{6}\text{m}^{-1}\ \text{i.e.}\ \lambda_{31} = \frac{1}{9.7778\times10^{6}} = 102.27nm$$

$$\bar{v}_{32} = 1.1\times10^{7}\left(\frac{1}{2^2}-\frac{1}{3^2}\right) = 1.5278\times10^{6}\text{m}^{-1}\ \text{i.e.}\ \lambda_{32} = \frac{1}{1.5278\times10^{6}} = 65.54nm$$

$$\bar{v}_{21} = 1.1\times10^{7}\left(\frac{1}{1^2}-\frac{1}{2^2}\right) = 8.25\times10^{6}\text{m}^{-1}\ \text{i.e.}\ \lambda_{32} = \frac{1}{8.25\times10^{6}} = 121.21nm$$

c) How much energy is needed to ionize this hydrogen atom in eV?

Data: R_{H} = 1.1×10^{7} m^{-1}; h = 6.6×10^{-34} j.s; c = 3×10^{8} m.s^{-1}; e = 1.6×10^{-19} C

ANSWER

This is the transition corresponding to the passage from level n = 1 to level n = ∞

$$\frac{hc}{\lambda_{ion}} = hcR_H\left(\frac{1}{1^2} - \frac{1}{\infty^2}\right)$$

$$\Delta E_{ion} = 6.6 \times 10^{-34} \times 3 \times 10^{8} \times 1.1 \times 10^{7} = 2.178 \times 10^{-18} J$$

$$\Delta E_{ion} = 13.6\, e.V$$

7) In the emission spectrum of atomic hydrogen, we observe a series of lines of decreasing wavelengths: 656.46 nm, 486.27 nm, 434.17 nm, and 410.29 nm.

a) Give the wavelength of the line following this series.

ANSWER

Let us transform the wavelengths into wavenumbers

$$\bar{v}_1 = \frac{1}{656.46 \times 10^{-9}} = 1.5233 \times 10^{6}$$

$$\bar{v}_2 = \frac{1}{486.27 \times 10^{-9}} = 2.0565 \times 10^{6}$$

$$\bar{v}_3 = \frac{1}{434.17 \times 10^{-9}} = 2.3032 \times 10^{6}$$

$$\bar{v}_4 = \frac{1}{410.29 \times 10^{-9}} = 2.4373 \times 10^{6}$$

subtracting $\bar{v}_1$ from $\bar{v}_2$, we get

$$\bar{v}_2 - \bar{v}_1 = 2.0565 \times 10^{6} - 1.5233 \times 10^{6} = 5.332 \times 10^{5}$$

This gap corresponds to

$$\bar{v}_2 - \bar{v}_1 = R_H\left(\frac{1}{n_f^2} - \frac{1}{n_{i_2}^2}\right) - R_H\left(\frac{1}{n_f^2} - \frac{1}{n_{i_2}^2}\right)$$

then

$$\bar{v}_2 - \bar{v}_1 = R_H\left(\frac{1}{n_{i_1}^2} - \frac{1}{n_{i_2}^2}\right)$$

Assuming that the lines of the series are successive

$$n_{i_2}^2 = n_{i_1}^2 + 1$$

so that

$$\frac{\bar{v}_2 - \bar{v}_1}{R_H} = \left(\frac{1}{n_{i_1}^2} - \frac{1}{(n_{i_1}+1)^2}\right)$$

$$\frac{5.332 \times 10^5}{1.1 \times 10^7} = \left(\frac{1}{n_{i_1}^2} - \frac{1}{(n_{i_1}+1)^2}\right) = 4.8473 \times 10^{-2}$$

which gives

$$\frac{n_{i_1}^2 + 2n_{i_1} + 1 - n_{i_1}^2}{n_{i_1}^2 (n_{i_1}+1)^2} = 4.8473 \times 10^{-2}$$

$$\frac{2n_{i_1} + 1}{n_{i_1}^2 (n_{i_1}+1)^2} = 4.8473 \times 10^{-2}$$

and the resolution of this equation gives

$$n_i = 3$$

We can then identify the 1st line

$$\bar{v}_1 = 1.1 \times 10^7 \times \left(\frac{1}{n_f^2} - \frac{1}{3^2}\right) = 1.5233 \times 10^6$$

then

$$\frac{1.5233 \times 10^6}{1.1 \times 10^7} + \frac{1}{3^2} = \frac{1}{n_f^2}$$

Thus, we deduce

$$n_f = \sqrt{\frac{1}{0.24959}} = 2$$

We are therefore in the Balmer series. The next line is

$$\bar{\nu}_2 = 1.1 \times 10^7 \times \left(\frac{1}{2^2} - \frac{1}{4^2} \right) = 2.0625 \times 10^6 m^{-1}$$

which conforms to the given statement.

As such, the next line will be

$$\bar{\nu}_3 = 1.1 \times 10^7 \times \left(\frac{1}{2^2} - \frac{1}{5^2} \right) = 2.31 \times 10^6 m^{-1}$$

which is given in the statement 2. 3032×10^6 m^{-1}.

The next line will be

$$\bar{\nu}_4 = 1.1 \times 10^7 \times \left(\frac{1}{2^2} - \frac{1}{6^2} \right) = 2.4444 \times 10^6 m^{-1}$$

which is given in the statement 2. 4373×10^6 m^{-1}.

We can therefore predict that the next line will have a wavenumber of

$$\bar{\nu}_5 = 1.1 \times 10^7 \times \left(\frac{1}{2^2} - \frac{1}{7^2} \right) = 2.5255 \times 10^6 m^{-1}$$

i.e. the wavelength

$$\lambda = \frac{1}{2.5255 \times 10^6} = 3.9596 \times 10^{-7} m$$

and

$$\lambda = 395.96 nm$$

b) What is the value of the energy and the wavelength corresponding to the limit line of this series?

Data: $R_H = 1.1\times10^7\ m^{-1}$

ANSWER

The limit line of the Balmer series is

$$\bar{\nu}_{Lim} = 1.1\times10^7\times\left(\frac{1}{2^2}\right) = 2.75\times10^6\,m^{-1}$$

$$\lambda_{Lim} = 252.55nm$$

c) Ground state hydrogen atoms are excited by UV radiation with a wavelength of 97nm.

1) What is the principal quantum number n_f of the state thus obtained?

ANSWER

If the radiation is in the UV domain, then the possible transitions will concern the Lyman series (the transitions start from $n_i = 1$). The radiations must have their wavenumber given by the Balmer relation

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

or, if $n_i = 1$

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

then

$$\frac{\bar{\nu}}{R_H} = 1-\frac{1}{n_f^2} \quad \text{and} \quad \frac{1}{n_f^2} = 1-\frac{\bar{\nu}}{R_H}$$

since

$\bar{\nu} = \frac{1}{\lambda}$ we have $\frac{1}{n_f^2} = 1 - \frac{1}{\lambda R_H}$

then

$$\frac{1}{n_f^2} = 1 - \frac{1}{97\times10^{-9}\times1.1\times10^{7}} = 6.2793\times10^{-2} \text{ and } n_f = \sqrt{\frac{1}{6.2793\times10^{-2}}} = 3.99 \text{ i.e } n_f = 4$$

The absorption transition reaches the level n = 4.

d) Calculate the wavelengths of the different radiations that these atoms can emit when they become de-excited.

ANSWER

The different emission transitions start from level n = 4. There are six: 3 belong to the Lyman series; 2 belong to the Balmer series; and 1 belongs to the Paschen series.

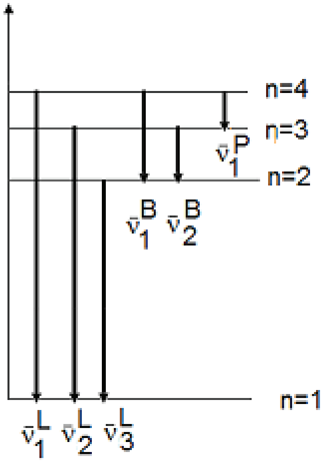

Figure T-IV-8: Emission transition from n = 4.

The wavenumbers are obtained using the Balmer relation

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

For the Lyman series, we have

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

For the Lyman series, we have

$$\bar{\nu}_1^L = 1.1\times10^7\times\left(1 - \frac{1}{2^2}\right) = 8.25\times10^6 m^{-1}$$

$$\bar{\nu}_2^L = 1.1\times10^7\times\left(1 - \frac{1}{3^2}\right) = 9.7778\times10^6 m^{-1}$$

$$\bar{v}_3^L = 1.1 \times 10^7 \times \left(1 - \frac{1}{4^2}\right) = 1.0313 \times 10^7 m^{-1}$$

For the Balmer series, we have

$$\bar{v}_1^B = 1.1 \times 10^7 \times \left(\frac{1}{4} - \frac{1}{3^2}\right) = 1.5278 \times 10^6 m^{-1}$$

$$\bar{v}_2^B = 1.1 \times 10^7 \times \left(\frac{1}{4} - \frac{1}{4^2}\right) = 2.0625 \times 10^6 m^{-1}$$

For the Paschen series, we have

$$\bar{v}_1^P = 1.1 \times 10^7 \times \left(\frac{1}{9} - \frac{1}{4^2}\right) = 5.3472 \times 10^5 m^{-1}$$

Now, let us transform these wavenumbers into wavelengths

$$\lambda_1^L = \frac{1}{\bar{v}_1^L} = \frac{1}{8.25 \times 10^6} = 1.2121 \times 10^{-7} m$$

$$\lambda_2^L = \frac{1}{\bar{v}_2^L} = \frac{1}{9.7778 \times 10^6} = 1.0227 \times 10^{-7} m$$

$$\lambda_3^L = \frac{1}{\bar{v}_3^L} = \frac{1}{1.0313 \times 10^7} = 9.6965 \times 10^{-8} m$$

$$\lambda_1^B = \frac{1}{\bar{v}_1^B} = \frac{1}{1.5278 \times 10^6} = 6.5454 \times 10^{-7} m$$

$$\lambda_2^B = \frac{1}{\bar{v}_2^B} = \frac{1}{2.0625 \times 10^6} = 4.8485 \times 10^{-7} m$$

$$\lambda_1^P = \frac{1}{\bar{v}_1^P} = \frac{1}{5.3472 \times 10^5} = 1.8701 \times 10^{-6} m$$

3) What is the energy needed to ionize this hydrogen atom in eV?

Data: $R_H = 1.1\times10^{7}\ m^{-1}$; $h = 6.6\times10^{-34}$ j.s; $c = 3\times10^{8}\ m.s^{-1}$; $e = 1.6\times10^{-19}$ C

ANSWER

It is the transition corresponding to the passage from level n = 1 to level n = ∞

$$\Delta E_{ion} = hcR_H\left(\frac{1}{1^2} - \frac{1}{\infty^2}\right)$$

$$\Delta E_{ion} = 6.6 \times 10^{-34} \times 3 \times 10^{8} \times 1.1 \times 10^{7} = 2.178 \times 10^{-18} J$$

or, in eV

$$\Delta E_{ion} = 13.6 e.V$$

CHAPTER V

THE SEMI-CLASSICAL MODEL OF THE HYDROGEN ATOM

In the preceding chapter, we studied how energy quantization has been manifested in its experimental reality.

In this chapter, we shall examine the attempts to explain the quantization of energy in the atom from theoretical considerations based on the wave-like nature of the electron. As such, we shall look at, successively, the semi-classical approach of Bohr[1] and Sommerfeld, and the entirely quantum approach of Schrödinger[2].

N. Bohr

E. Schrödinger

V-I. Bohr's Model of Hydrogenic Atoms

We have already seen in our descriptive study of the classification established by D. Mendeleev in 1869 that the elements can be grouped in rows and columns in a table according to their chemical properties.

Once the idea of atoms had been proposed, the common model of the era suggested that the atom is composed of electrons immersed in a "soup" of positive charge to balance the negative charge of the electrons (the "plum pudding" model). These are considered to be dispersed within the atom, but

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[1] Neils Bohr (1885-1962). Danish physicist known for his work in the construction of quantum mechanics. Winner of the Nobel Prize in Physics in 1922.

[2] Erwin Schrödinger (1887-1931). Austrian physicist known for his work in the construction of quantum mechanics. Winner of the Nobel Prize in Physics in 1933.

with multiple possible structures for their positioning (rotating rings of electrons for example). This model was challenged by E. Rutherford in 1909 using the results of bombardment experiments with gold leaf. These experiments showed the existence of a very small positively charged nucleus, which led to him proposing an atomic model, called the Rutherford model. This model describes the atom as being made up of negative electrons orbiting around a dense positive nucleus with circular trajectories, just like the planets of the solar system, which orbit in an almost circular manner around the Sun. In this model, the electromagnetic force replaces the gravitational force as the system's cohesive force.

However, Rutherford's planetary theory was in contradiction with the theory of accelerated electron radiation. Indeed, according to experimental observations and Maxwell's laws, an electron subjected to acceleration emits energy in the form of an electromagnetic field[3].

Brought back to the level of Rutherford's atom, the electron should describe a concentric spiral, and not a circle, which would result in it crashing into the nucleus after a few million revolutions, corresponding to a nanosecond of time. The orbits are therefore not stable.

In 1913, N. Bohr proposed a theory based on Rutherford's planetary model, which was immediately successful because it explained, in a simple way, the spectral lines of the hydrogenic atoms, while reconciling the first models of the atom and the theory of quanta. This model was generalized to the case of relativistic electrons by A. Sommerfeld in order to quantitatively write the fine structure of the spectral lines of hydrogen. However, this theory could not explain the spectrum of polyelectronic atoms (such as helium), nor the nature of chemical bonds, and was finally be replaced by quantum mechanics in 1925**.**

---

[3] This is the Larmor formula, devised by J. Larmor in 1897.

1. Principles

Bohr's model is based on several postulates:

(i) *The electron revolves around the nucleus on a circular trajectory*, as shown in **Fig. V-1**.

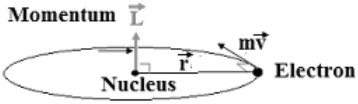


Figure V-1: Representation of classical angular momentum.

Let us consider an electron, negatively charged, revolving around a nucleus containing a positively charged proton.

(ii) Electrostatic force

The electrostatic force between two charges q_1 and q_2 separated by distance r, according to Coulomb's law, is given by the formula

$$F = \frac{1}{4\pi\varepsilon_0}\frac{q_1 q_2}{r^2}$$

where ε_0 is the permittivity of the vacuum.

2. Potential energy

We can express the force as the derivative of the potential energy V with respect to the distance r

$$F(r) = -\frac{dV(r)}{dr}$$

so that

$$dV(r) = -F(r)dr \quad \text{or} \quad dV(r) = -\frac{1}{4\pi\varepsilon_0}\frac{q_1 q_2}{r^2}dr$$

After integration, we get

$$V(r) = \frac{1}{4\pi\varepsilon_0}\frac{q_1 q_2}{r} + Cst$$

where Cst is a constant. Taking as a convention that when r→∞, V(r)→0, then Cst = 0 we have

$$V(r) = \frac{1}{4\pi\varepsilon_0}\frac{q_1 q_2}{r}$$

If $q_1 = -e$ is the electron charge and $q_2 = +e$ is that of the proton, we have

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

3. Kinetic energy

The kinetic energy of the electron moving with speed v is

$$T = \frac{1}{2}mv^2$$

where m is the electron mass. Knowing the momentum of the electron, we obtain

$$p = mv \text{ and then } T = \frac{p^2}{2m}$$

4. Orbital angular momentum

The rotational motion of the electron around the nucleus generates an angular momentum $\vec{L}$ such as

$$\vec{\mathbf{L}} = \vec{\mathbf{r}} \times m\vec{\mathbf{v}}$$

the sense and direction of which are shown in Figure V-1, where $\vec{r}$ is the position of the electron and $\vec{v}$ is its mass and velocity. If the trajectory is perfectly circular, the modulus $\|\vec{L}\|$ is

$$\left\|\vec{\mathbf{L}}\right\| = rmv = rp$$

5. Quantization of the angular momentum

According to Bohr, among the infinite number of possible circular trajectories, only a few have physical significance. These are the ones for which the orbital angular momentum modulus is a multiple of the quantity h/(2π) = $\hbar$, i.e.

$$\boxed{\left\| \vec{\mathbf{L}} \right\| = n\frac{h}{2\pi} = n\hbar}$$

where n≥1. The consequence of this postulate is that

$$n\hbar = rp \quad \text{or} \quad p = \frac{n\hbar}{r}$$

We can then express p according to r, which allows us to write the kinetic energy in the form

$$T(n,r) = \frac{p^2}{2m} = \frac{1}{2m}\left(\frac{n\hbar}{r}\right)^2 \text{ so that } T(n,r) = \frac{\hbar^2 n^2}{2m}\frac{1}{r^2}$$

4. Total energy

The total energy is the sum of the kinetic T(r) and potential V(r) energies, such as

$$E_{tot}(r) = T(n,r) + V(r) = \frac{\hbar^2 n^2}{2m}\frac{1}{r^2} - \frac{e^2}{4\pi\varepsilon_0}\frac{1}{r}$$

To simplify, one poses

$$a(n) = \frac{\hbar^2 n^2}{2m} \quad ; \quad b = \frac{e^2}{4\pi\varepsilon_0} \tag{V-1}$$

and the total energy becomes

$$E_{tot}(n,r) = a(n)\frac{1}{r^2} - b\frac{1}{r} \tag{V-2}$$

We need to find the lowest energy for the system, i.e. the value of r_e for which the derivative of the total energy in relation to r_e cancels out

$$\left[\frac{d}{dr}E_{tot}(n)\right]_{r=r_e} = 0$$

As r_e is different to zero, Eq. (V-2) can be simplified, which gives

$$2a(n)\frac{1}{r_e} + b = 0$$

so that

$$2a(n)\frac{1}{r_e} = b$$

and

$$r_e = \frac{2a(n)}{b} \tag{V-3}$$

Eq. (V-3) is introduced into the total energy equation (V-2) and we get

$$E_{tot}(n) = a(n)\frac{1}{\left(\frac{2a(n)}{b}\right)^2} - b\frac{1}{\left(\frac{2a(n)}{b}\right)}$$

after simplification, we obtain

$$E_{tot}(n) = \frac{b^2}{4a(n)} - \frac{b^2}{2a(n)}$$

and

$$E_{tot}(n) = -\frac{b^2}{4a(n)} \tag{V-4}$$

Let us now replace the terms a(n), b, and $\hbar$ with their respective expressions in Eq. (V-4)

$$E_{tot}(n) = -\frac{\frac{e^4}{(4\pi\varepsilon_0)^2}}{4\frac{\left(\frac{h}{2\pi}\right)^2 n^2}{2m}}$$

Simplifying, we get

$$\boxed{E_{tot}(n) = -\frac{me^4}{8h^2\varepsilon_0^2}\frac{1}{n^2}} \tag{V-5}$$

If we replace the constants with their values, i.e. m = 9.1093897×10⁻³¹ kg, e = 1.60217733×10⁻¹⁹ C, h = 6.6260755×10⁻³⁴ J.s, and ε_0 = 8.854187817×10⁻¹² Fm⁻¹, we get

$$\boxed{E_{tot}(n) = -2.179874 \times 10^{-18}\frac{1}{n^2}J}$$

or, in eV

$$\boxed{E_{tot}(n) = E_{tot_n} = -13.60570\frac{1}{n^2}eV} \tag{V-6}$$

5. Atomic radius

Now, let us express the radius $r_e(n)$ by introducing the definitions of a and b given in Eq. (V-1). We find

$$\boxed{r_e(n) = r_{e_n} = \frac{h^2\varepsilon_0}{\pi me^2}n^2}$$

which, using the set of known parameters, reads

$$r_e(n) = \frac{(6.6260755 \times 10^{-34})^2 \times 8.854187817 \times 10^{-12}}{\pi \times 9.1093897 \times 10^{-31}(1.60217733 \times 10^{-19})^2}n^2$$

so that

$$r_e(n) = 0.5291\,773 \times 10^{-10} n^2 \quad m \qquad \text{(V-7)}$$

given that 1Å = 10^{-10} m, we obtain

$$\boxed{r_{e_n} = 0.5291\,773\; n^2 \quad \mathring{A}}$$

6. Graphical representation

The energies and radii of the electron's preferred orbits in the hydrogen atom have been determined and these sizes are quantized since they both depend on the integer number n, introduced into the model at the level of momentum. This integer number is greater than or equal to 1, which is understandable because if n = 0 then the electron would crash into the nucleus!

Here we represent our results. In **Table V-1** we report the values of the radius corresponding to the first five trajectories. These were obtained using Eq. (V-7) giving the radius of the orbit and with 0.529 A = a_0.

Table V-1: Radius of the first orbits

n	1	2	3	4	5
re_n	a_0	$4a_0$	$9a_0$	$16a_0$	$25a_0$

Fig. V-2 gives a graph of these orbits, which are concentric circles.

7. The electronic transition hypothesis

Bohr postulated that the light energy emitted by atoms is the result of changes in the electron's orbit. In the case of emission, the transition from the upper to the lower orbits is accompanied by the emission of a photon, the energy of which is equal to the energy difference between the energy levels corresponding to the orbit

$$\Delta E_{n_2, n_1} = \left\| E_{n_2} - E_{n_1} \right\| = h\nu$$

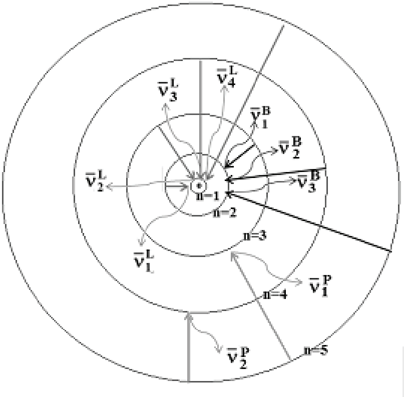


Figure V-2: Orbits and emitted radiations in Bohr's atom.

This topological vision of transitions between different orbits can be supplemented by an energetic vision using the diagram presented above in our empirical study of the hydrogen atom's spectrum. We have identified the energy levels by theoretically calculating their values and they are the same as those deduced experimentally.

As such, using Eq. (V-6) we can deduce the energy of the levels in **Table V-2**.

Table V-2: The first energy levels in Bohr's model

n	1	2	3	4	5	...	∞
$E_n(eV)$	$-13,6$	$-3,4$	$-1,51$	-0.85	-0.544	...	0

Mapping these levels on a vertical scale, we obtain the diagram in **Fig. V-3**, which is identical to the experimental emission spectrum given in **Fig. IV-12**.

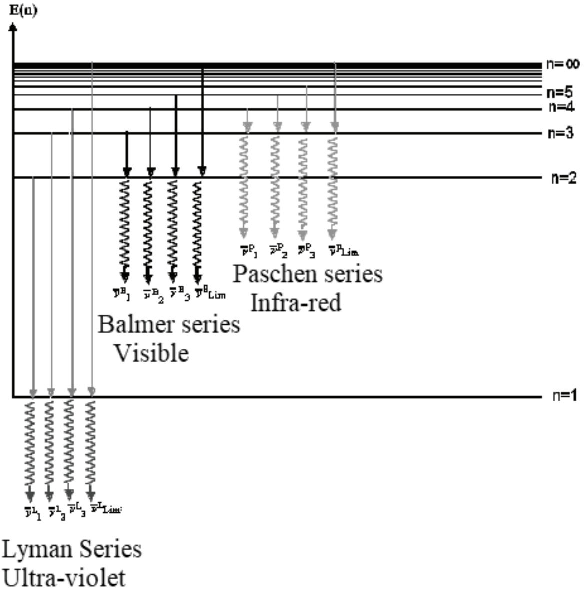


Figure V-3: Transitions corresponding to the first three series calculated by Bohr's model.

Emission transitions between these levels generate the rays of the atomic hydrogen emission spectrum presented in **Fig. V-4**, which coincide with those found experimentally.

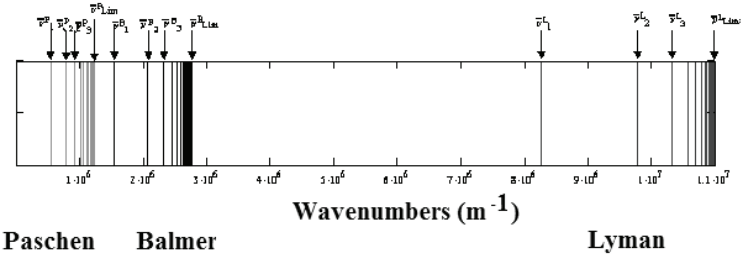


Figure V-4: Reconstruction of the emission spectrum of atomic hydrogen using Bohr's model.

To make the relevance of this model even better, we can calculate the Rydberg constant from the analytical expression of the energy levels.

For this, from Eq. (V-5)

$$E_{tot}(n) = -\frac{me^4}{8h^2\varepsilon_0^2}\frac{1}{n^2}$$

we can calculate the energy gap between two levels of the hydrogen atom, i.e.

$$\Delta E_{n_2,\,n_1} = \frac{me^4}{8h^2\varepsilon_0^2}\left(\frac{1}{n_2^2} - \frac{1}{n_1^2}\right)$$

this energy gap must be equal to the energy of the photon hc$\overline{\nu}$, i.e.

$$hc\bar{\nu} = \frac{me^4}{8h^2\varepsilon_0^2}\left(\frac{1}{n_2^2} - \frac{1}{n_1^2}\right)$$

The expression of the wavenumber of the corresponding radiation is deduced

$$\bar{\nu} = \frac{me^4}{8h^3c\varepsilon_0^2}\left(\frac{1}{n_2^2} - \frac{1}{n_1^2}\right) \text{ with } n_1 > n_2$$

We therefore compare this theoretical formula to that of the previous, experimental Balmer relationship

$$\bar{\nu}_{em} = R_H\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right) \text{ with } n_i > n_f$$

and easily infer that the Rydberg constant has the expression

$$R_H = \frac{me^4}{8h^3c\varepsilon_0^2}\ m^{-1}$$

so that

$$R_H = \frac{(9.1093897\times10^{-31})(1.60217733\times10^{-19})^4}{8(6.6260755\times10^{-34})^3(2.99792458\times10^8)(8.854187817\times10^{-12})^2}\ m^{-1}$$

$$\boxed{R_H = 1.0973731534\times10^7\ \mathrm{m}^{-1}}$$

Thus, Bohr's model allows the exact calculation of a fundamental constant, which is the basis of its success. However, this model does not take into account two factors:

- The actual orbit of the electron should be elliptical and not circular.
- The non-punctual core, which should be moving in relation to a center of gravity.

V-II. Perfecting Bohr's Model

A. Sommerfeld

Sommerfeld[4] introduced the quantization of elliptical orbits and relativity into his model of the atom.

In the Sommerfeld model, the energy takes the form

$$E_{n,l} = E_n\left(1 + \frac{\alpha^2 Z^2}{n^2}\left(\frac{n}{l+1} - \frac{3}{4}\right)\right)$$

where E_n is the energy of Bohr's model and α is the fine structure constant with a value given in the SI unit system

$$\alpha = \frac{e^2}{4\pi\varepsilon_0 \hbar c}$$

$$\alpha = \frac{\left(1.60217733\times10^{-19}\right)^2}{4\times\pi\left(8.854187817\times10^{-12}\right)\left(6.6260755\times10^{-34}/2/\pi\right)\left(2.99792458\times10^{8}\right)} = 7.297353 \times 10^{-3}$$

In addition to the quantum number n, a second quantum number appears that can take all the integer values from 0 to n-1. We move from the three energy levels described by Bohr (K, L, M) to a greater number of levels for Sommerfeld, following the introduction of quantum numbers n and l, as given in **Table V-3**.

---

[4] Arnold Sommerfeld (1868-1951). German physicist known for his contribution to the birth of quantum theory.

Table V-3: The limits of the theoretical models

Bohr	Sommerfeld	Experience (fine Structure)
K	K	1 ray
L	L_0, L_1	3 rays
M	M_0, M_1, M_2	5 rays

However, experience has also revealed the existence of:

- A thin structure of three rays instead of two for level L.
- A thin structure of five rays instead of three for level M.

To expand the theory, Sommerfeld proposed the introduction of an additional quantum number I called the internal quantum number, but was unable to provide further details. As such, his theory remained incomplete, demonstrated by the action of a magnetic field on the spectral lines emitted by atoms (the Zeeman effect).

However, all these models proved to be problematic due to their systemic instability. The electron rotating around the nucleus emits electromagnetic energy (think of synchrotron radiation in particle accelerators) and, as such, it has to lose energy, eventually falling onto the nucleus.

As such, we can see that the problem of the stability of the hydrogen atom was not solved by the semi-classical theories of Bohr and Sommerfeld and the development of a new theory was necessary.

V-III. Tutorial for Chapter V

1) Recall Louis de Broglie's relation concerning the wavelength of the wave associated with a particle of mass m and speed v

ANSWER

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

2) Express the classical angular momentum $\vec{L}$ of a particle of mass m moving in a circular orbit of radius $\vec{r}$ and animated by speed $\vec{v}$.

ANSWER

The classical angular momentum $\vec{\boldsymbol{L}}$ is the cross product of the position $\vec{\boldsymbol{r}}$ and the momentum m$\vec{\boldsymbol{v}}$

$$\vec{L} = \vec{r} \times m\vec{v}$$

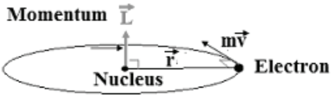


Figure T-V-1: Angular momentum.

3) We hold the assumption that the circumference of the circular trajectory of the particle can contain an integer number of times the wavelength. What can we conclude for the angular momentum modulus (1st Bohr hypothesis)?

ANSWER

The first Bohr hypothesis may be written

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

where r is the radius of the circle; λ is the wavelength; and n is an integer number. According to the Louis de Broglie relation, we have

$$\lambda = \frac{h}{p} \quad \text{then} \quad 2\pi r = n\frac{h}{p}$$

so that

$$r.p = n\frac{h}{2\pi}$$

A such, we deduce that the angular momentum rp is equal to nh/2π

$$r.p = n\frac{h}{2\pi} = n\hbar$$

4) We now consider an electron in an hydrogen atom. The potential energy is $V = -K\frac{e^2}{r}$, where K is a constant (K = 9.10^9 SI). Express the kinetic energy T of the system as a function of the square p^2 of the momentum, then express the total energy E of the system.

ANSWER

$$T = \frac{1}{2}mv^2 = \frac{p^2}{2m}$$

5) Using the relation found in c), express the total energy E as a function of r.

ANSWER

The total energy of the system can be presented in the form

$$E = T + V$$

By using the relation found in c), we deduce that

$$p = \frac{n\hbar}{r}$$

We introduce this result into the expression of T

$$T = \frac{p^2}{2m} = \frac{n^2\hbar^2}{2m}\frac{1}{r^2}$$

so that, the expression of the energy is

$$E(r) = \frac{n^2\hbar^2}{2m}\frac{1}{r^2} - \frac{Ke^2}{r}$$

6) Applying the condition for the minimization of energy with respect to the distance r, calculate the distance $r_e(n)$ for which the energy of the system passes through a minimum. Deduce the minimum energy E_n of the system. This energy represents the energy of one level of the hydrogen atom.

ANSWER

We need to get the lowest energy for the system. The energy function must therefore pass through a minimum for a distance that therefore corresponds to a zero derivative of the function E(r). To facilitate the calculations, let us write

$$A(n) = \frac{n^2\hbar^2}{2m} \text{ and } B = Ke^2$$

and the energy becomes

$$E(r) = A(n)\frac{1}{r^2} - \frac{B}{r}$$

The derivative of this expression is

$$\frac{dE(r)}{dr} = -\frac{2A(n)}{r^3} + \frac{B}{r^2}$$

for the distance r = r_e, this derivative is zero

$$\left[\frac{dE(r)}{dr}\right]_{r=r_e} = 0$$

i.e.

$$\frac{2A(n)}{r_e^3} + \frac{B}{r_e^2} = 0$$

We deduce

$$r_e = \frac{2A(n)}{B}$$

since A depends on n, we also have r_e, which depends on n. Thus we write it

$$r_e(n) = \frac{2A(n)}{B}$$

If we replace A and B by their respective expressions, we have

$$r_e(n) = \frac{2\frac{n^2\hbar^2}{2m}}{Ke^2} = \frac{\hbar^2}{mKe^2}n^2$$

i.e.

$$\boxed{r_e(n) = \frac{h^2}{4\pi^2 mKe^2}n^2}$$

Let us introduce this distance into the expression of energy. It corresponds to the distance for which the energy is at a minimum, i.e.

$$E_{Min} = \frac{A(n)}{r_e^2} - \frac{B}{r_e}$$

We see that $E_{min}(n)$ depends on n

$$E_{Min}(n) = \frac{A(n)}{\left(\frac{2A(n)}{B}\right)^2} - \frac{B}{\frac{2A(n)}{B}}$$

then

$$E_{Min}(n) = -\frac{B^2}{4A(n)}$$

By replacing A and B by their values, we obtain

$$E_{Min}(n) = -\frac{(Ke^2)^2}{4\frac{n^2\hbar^2}{2m}} = -\frac{mK^2e^4}{2\hbar^2}\frac{1}{n^2}$$

and

$$\boxed{E_{Min}(n) = -\frac{mK^2e^4}{2\left(\frac{h}{2\pi}\right)^2}\frac{1}{n^2} = -\frac{2\pi^2 mK^2e^4}{h^2}\frac{1}{n^2}}$$

This minimum energy therefore depends on an integer number and we say that it is *quantized*. We denote it by the letter E_n.

7) By applying the 2nd Bohr hypothesis concerning electronic transitions, deduce the Balmer relation and the expression of the Rydberg constant R_H.

Data: $h = 6.6\times10^{-34}$ j.s; $c = 3.10^8$ m.s^{-1}; $e = 1.6\times10^{-19}$C; $m = 9.1\times10^{-31}$ kg; $K = 9.10^9$ SI

ANSWER

This energy corresponds to an energy level of the hydrogen atom. Bohr's second hypothesis concerning electronic transitions states that when the electron of the atom changes its energy level, it emits or receives a quantum of energy hν. If we call ΔE the energy difference between two levels E_{n_i} and E_{n_f}, then we must have

$$\Delta E = |E_{n_i} - E_{n_f}| = h\nu_{n_i \to n_f}$$

Using the expression for energy, for an *energy absorption* $n_i < n_f$ we have

$$\boxed{|E_{n_i} - E_{nf}| = \frac{2\pi^2 mK^2 e^4}{h^2}\left[\frac{1}{n_i^2} - \frac{1}{n_f^2}\right]}$$

and for an *energy emission* $n_i > n_f$

$$\boxed{|E_{n_f} - E_{n_i}| = \frac{2\pi^2 mK^2 e^4}{h^2}\left[\frac{1}{n_f^2} - \frac{1}{n_i^2}\right]}$$

If we apply the Bohr condition, for an energy absorption we have

$$h\nu_{abs} = \frac{2\pi^2 mK^2 e^4}{h^2}\left[\frac{1}{n_i^2} - \frac{1}{n_f^2}\right]$$

and for an energy emission we have

$$h\nu_{emi} = \frac{2\pi^2 mK^2 e^4}{h^2}\left[\frac{1}{n_f^2} - \frac{1}{n_i^2}\right]$$

or, in frequency, for an absorption we have

$$\nu_{abs} = \frac{2\pi^2 mK^2 e^4}{h^3}\left[\frac{1}{n_i^2} - \frac{1}{n_f^2}\right]$$

and, in frequency, for an emission we have

$$\nu_{emi} = \frac{2\pi^2 mK^2 e^4}{h^3}\left[\frac{1}{n_f^2} - \frac{1}{n_i^2}\right]$$

or, in wavenumber, for an absorption we have

$$\frac{1}{\lambda_{abs}} = \bar{\nu}_{abs} = \frac{2\pi^2 mK^2 e^4}{ch^3}\left[\frac{1}{n_i^2} - \frac{1}{n_f^2}\right]$$

and, in wavenumber, for an emission we have

$$\frac{1}{\lambda_{emi}} = \bar{\nu}_{emi} = \frac{2\pi^2 mK^2 e^4}{ch^3}\left[\frac{1}{n_f^2} - \frac{1}{n_i^2}\right]$$

This is Balmer's formula for absorption and emission. We can deduce the Rydberg constant as follows

$$R_H = \frac{2\pi^2 mK^2 e^4}{ch^3}$$

the value of which is obtained by replacing the constants by their values as

$$R_H = \frac{2 \times \pi^2 \times 9.1 \times 10^{-31} \times (9 \times 10^9)^2 \times (1.6 \times 10^{-19})^4}{3 \times 10^8 \times (6.6 \times 10^{-34})^2 \times (6.6 \times 10^{-34})} = 1.1056 \times 10^7 m^{-1}$$

CHAPTER VI

THE QUANTUM MODEL OF THE HYDROGEN ATOM

In this chapter we discuss the quantum description of the hydrogen atom. Our model is that of an electron coupled to a nucleus containing a proton, forming the simplest atom in existence. First, we shall see how the double nature—corpuscular and wave-like—of particles is at work when the electron is confined to the reduced space of the atom. However, the classical laws of physics are powerless to describe what actually happens in the atom. For example, the quantized nature of energy seems a little artificial to us, especially in the assumption regarding momentum that Bohr introduces and on which his demonstration of the quantization of energy is based. In the following we shall see that this quantization is closely related to the nature of the wavelength associated with the electron when it is confined to a small space. Once the main principles are understood, we shall address the real case of the hydrogen atom by solving this problem in an exact manner.

VI-I. Theoretical Explanation of Energy Quantization: The Potential Well

1. Comparing the electron in the atom to a stationary wave

a. The amplitude wave function

In the study of electronic interference, we have shown that the amplitude wave function at coordinate z of the interference plane takes the expression

$$\Psi^\circ(z) = 2\psi^\circ \cos\left(\frac{\pi}{\lambda}\frac{a}{D}z\right)$$

where λ is the wavelength of the wave associated with the electron; a is the distance separating the interference slits; D is the distance separating the plane of the slits and the observation screen; and ψ° is the amplitude of the vibrational motion of the sources. This amplitude depends on the spatial coordinate z and is a stationary phenomenon. In addition, its other characteristic is that the square of the amplitude has physical significance, i.e. that $|\Psi°|^2$ is the probability of the electron's impact along the z′Oz axis.

We thus rely on the **assumption: electron = stationary wave.**

We shall consider the electron in the atom as a stationary wave and, as such, it has the properties associated with a stationary wave mentioned in the previous paragraph.

This means that the electron in the atom has the amplitude of its associated wave function, which depends on the spatial coordinates. The square of this amplitude will have a physical significance, which will be the probability of the presence of the electron at a point in space inside an atom.

b. A simplified model of the atom: the potential well

Consider a microscopic particle of mass m and velocity v moving in a single-dimensional space represented by an x′Ox axis. This particle generates an associated wave whose wavelength is given by the Louis de Broglie relationship

$$\lambda = \frac{h}{p} \qquad \text{(VI-1)}$$

where h is the Planck constant and p is the modulus of the momentum of the particle. We may suppose that the wave amplitude associated with this particle is a periodic function for which we shall arbitrarily choose the form[1]

$$\Psi°(x) = A\sin(\frac{2\pi}{\lambda}x)$$

where A is a constant. In order to simplify it, we can write

$$\Psi(x) \equiv \Psi°(x)$$

so that the expression of the wave function becomes

---

[1] This is the only arbitrary assumption we shall make.

$$\Psi(x) = A\sin\left(\frac{2\pi}{\lambda}x\right) \qquad \text{(VI-2)}$$

From now on, when we talk about a wave function, it will be the wave-amplitude function Ψ(x).

c. An analogy

Here, we make an analogy between an atom and a one-dimensional system.

An atom is a portion of space with a potential energy that is lower than elsewhere (indeed, the electron-nucleus attraction energy is a Coulombic energy)

$$V = -K\frac{e^2}{r}$$

where K is a constant equal to

$$K = \frac{1}{4\pi\varepsilon_0} = 8.987\,552 \times 10^9\,SI$$

and the space in which the electron moves is a sphere of radius r_e. This space can be reduced to the diameter 2 r_e. It can trivially be seen that the potential energy is greater on the outside (red) of the atom than on the inside (green).

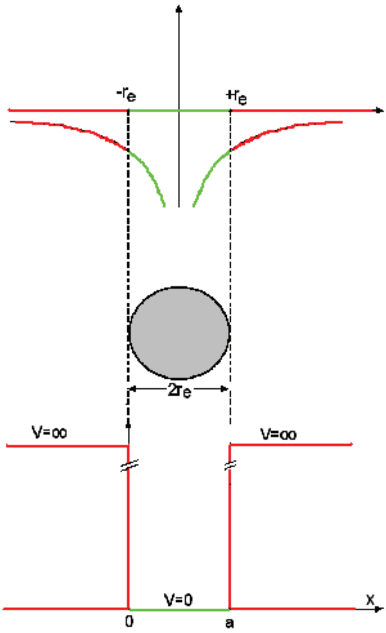
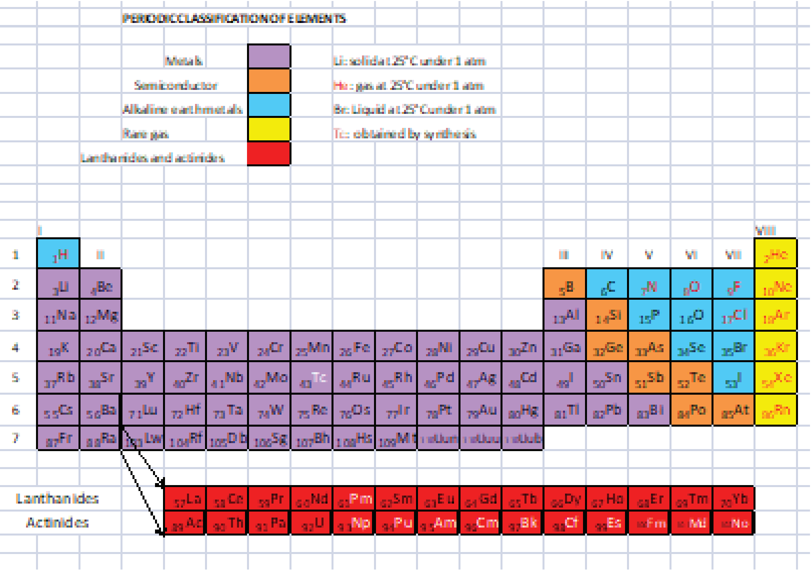


Figure VI-1: Analogy between an atom and a potential well.

We can schematize this situation using a discontinuous potential that clearly marks the outside and the inside. In this way, we can obtain a graph of an "infinite potential well", which is an atomic analogue in one dimension.

Table I-4: Periodic classification of the elements (Page 50)



PERIODIC CLASSIFICATION OF ELEMENTS

Metals	🟪	Li: solid at 25°C under 1 atm
Semiconductor	🟧	He: gas at 25°C under 1 atm
Alkaline earth metals	🟦	Br: Liquid at 25°C under 1 atm
Rare gas	🟨	Tc: obtained by synthesis
Lanthanides and actinides	🟥	

	I																	VIII
1	$_{1}$H	II											III	IV	V	VI	VII	$_{2}$He
2	$_{3}$Li	$_{4}$Be											$_{5}$B	$_{6}$C	$_{7}$N	$_{8}$O	$_{9}$F	$_{10}$Ne
3	$_{11}$Na	$_{12}$Mg											$_{13}$Al	$_{14}$Si	$_{15}$P	$_{16}$O	$_{17}$Cl	$_{18}$Ar
4	$_{19}$K	$_{20}$Ca	$_{21}$Sc	$_{22}$Ti	$_{23}$V	$_{24}$Cr	$_{25}$Mn	$_{26}$Fe	$_{27}$Co	$_{28}$Ni	$_{29}$Cu	$_{30}$Zn	$_{31}$Ga	$_{32}$Ge	$_{33}$As	$_{34}$Se	$_{35}$Br	$_{36}$Kr
5	$_{37}$Rb	$_{38}$Sr	$_{39}$Y	$_{40}$Zr	$_{41}$Nb	$_{42}$Mo	$_{43}$Tc	$_{44}$Ru	$_{45}$Rh	$_{46}$Pd	$_{47}$Ag	$_{48}$Cd	$_{49}$I	$_{50}$Sn	$_{51}$Sb	$_{52}$Te	$_{53}$I	$_{54}$Xe
6	$_{55}$Cs	$_{56}$Ba	$_{71}$Lu	$_{72}$Hf	$_{73}$Ta	$_{74}$W	$_{75}$Re	$_{76}$Os	$_{77}$Ir	$_{78}$Pt	$_{79}$Au	$_{80}$Hg	$_{81}$Tl	$_{82}$Pb	$_{83}$BI	$_{84}$Po	$_{85}$At	$_{86}$Rn
7	$_{87}$Fr	$_{88}$Ra	$_{103}$Lw	$_{104}$Rf	$_{105}$Db	$_{106}$Sg	$_{107}$Bh	$_{108}$Hs	$_{109}$Mt	$_{110}$Uun	$_{111}$Uuu	$_{112}$Uub						

Lanthanides	$_{57}$La	$_{58}$Ce	$_{59}$Pr	$_{60}$Nd	$_{61}$Pm	$_{62}$Sm	$_{63}$Eu	$_{64}$Gd	$_{65}$Tb	$_{66}$Dy	$_{67}$Ho	$_{68}$Er	$_{69}$Tm	$_{70}$Yb
Actinides	$_{89}$Ac	$_{90}$Th	$_{91}$Pa	$_{92}$U	$_{93}$Np	$_{94}$Pu	$_{95}$Am	$_{96}$Cm	$_{97}$Bk	$_{98}$Cf	$_{99}$Es	$_{100}$Fm	$_{101}$Md	$_{102}$No

In this periodic table, the element characteristics and properties are symbolized by colors.

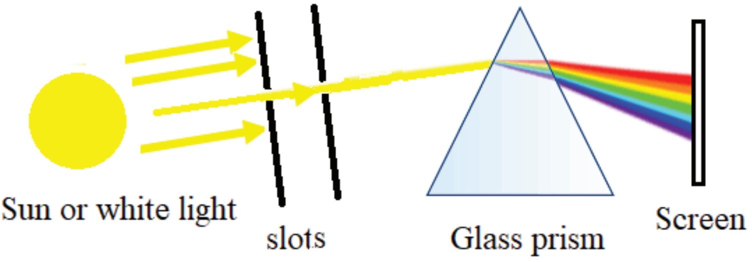


Figure IV-6: Decomposition of white light through a prism. (Page 119)

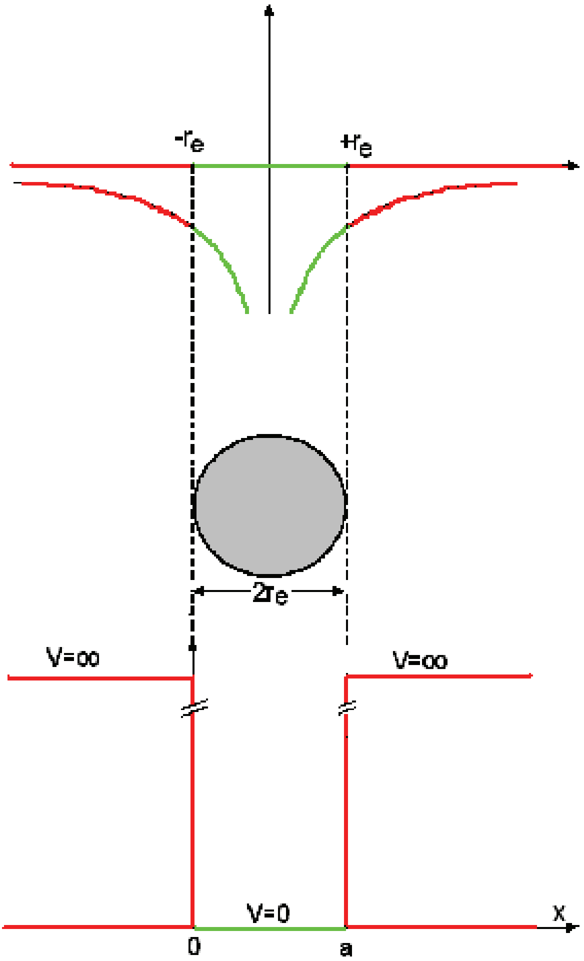


Figure VI-1: Analogy between an atom and a potential well. (Page 171)

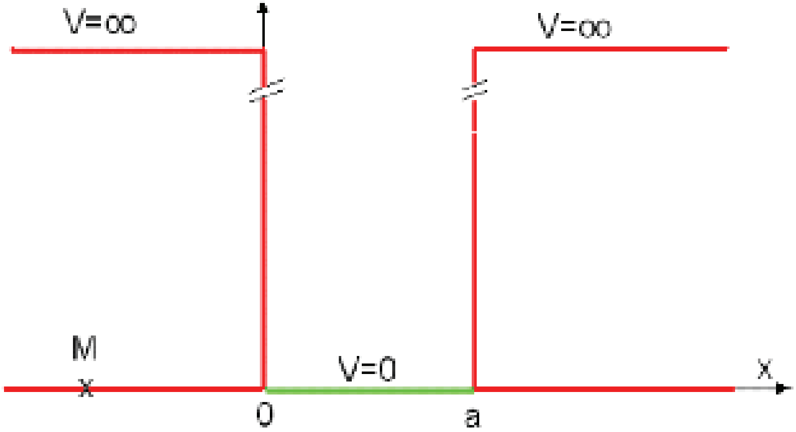


Figure VI-2: The limit conditions. (page 177)

1. A wave equation

Let us consider the wave function associated with the particle, for which we postulate the equation

$$\Psi(x) = A\sin(\frac{2\pi}{\lambda}x) \tag{VI-3}$$

It presents the characteristics of a stationary wave, namely a dependence on its spatial coordinates and the physical meaning of its square. Let us derive this expression twice

$$\frac{d\Psi(x)}{dx} = \frac{2\pi}{\lambda}A\cos(\frac{2\pi}{\lambda}x) \quad \text{and} \quad \frac{d^2\Psi(x)}{dx^2} = -\frac{4\pi^2}{\lambda^2}A\sin(\frac{2\pi}{\lambda}x)$$

We can see that, once again, we are dealing with Eq. (VI-2) and so we may write

$$\frac{d^2\Psi(x)}{dx^2} = -\frac{4\pi^2}{\lambda^2}\Psi(x)$$

Let us transpose the second member into the first, to read

$$\frac{d^2\Psi(x)}{dx^2} + \frac{4\pi^2}{\lambda^2}\Psi(x) = 0 \tag{VI-4}$$

The particle has a wavelength given by the Louis de Broglie equation (VI-1)

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

and by replacing this wavelength in Eq. (VI-4), it becomes

$$\frac{d^2\Psi(x)}{dx^2} + \frac{4\pi^2}{h^2}p^2\Psi(x) = 0$$

To simplify, let us write

$$\hbar = \frac{h}{2\pi}$$

and so we obtain the equation

$$\frac{d^2\Psi(x)}{dx^2} + \frac{p^2}{\hbar^2}\Psi(x) = 0 \tag{VI-5}$$

Let us consider p², the modulus square of the momentum of the particle, and see its relationship to the kinetic energy T of this particle

$$T = \frac{1}{2}mv^2 = \frac{1}{2}\frac{(mv)^2}{m} = \frac{p^2}{2m} \tag{VI-6}$$

we deduce that

$$p^2 = 2mT$$

Since we have

$$E_{Tot} = T + V$$

we may express the modulus square of the momentum as follows

$$p^2 = 2m(E_{Tot} - V)$$

Putting this expression into Eq. (VI-5), we get

$$\boxed{\frac{d^2\Psi(x)}{dx^2} + \frac{2m}{\hbar^2}(E_{Tot} - V)\Psi(x) = 0} \tag{VI-7}$$

This is the expression of the one dimensional time-independent Schrödinger equation, which governs the behavior of the particle in the potential well. It is a relationship as fundamental as those of classical mechanics. Normally, this equation is not demonstrable; however, the reasoning above presents the properties of the amplitude wave function and shows that the Schrödinger equation is closely related to these properties.

When we solve this equation in conditions similar to those that occur in the atom, we get, as one would expect, two types of solution:

- The energies that the particle can take under these conditions.

- The expression of the corresponding amplitude wave functions.

2. A compact form of the Schrödinger equation

Let us take the expression of the equation of the one dimensional time-independent Schrödinger equation (VI-7)

$$\frac{d^2\Psi(x)}{dx^2} + \frac{2m}{\hbar^2}(E_{Tot} - V)\Psi(x) = 0$$

Developing it, we get

$$\frac{d^2\Psi(x)}{dx^2} + \underbrace{\frac{2m}{\hbar^2}E_{Tot}\Psi(x)} - \frac{2m}{\hbar^2}V\Psi(x) = 0$$

We transpose the underlined text by a brace in the right-hand member

$$\frac{d^2\Psi(x)}{dx^2} - \frac{2m}{\hbar^2}V\Psi(x) = -\frac{2m}{\hbar^2}E_{Tot}\Psi(x)$$

and divide the whole equation by -2m/ħ², which gives

$$-\frac{\hbar^2}{2m}\frac{d^2\Psi(x)}{dx^2} + V\Psi(x) = E_{Tot}\Psi(x) \qquad \text{(VI-8)}$$

Now, we write the equation in the form

$$\underbrace{\left\{-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \hat{\mathbf{V}}\right\}}_{\hat{\mathbf{H}}}\Psi(x) = E_{Tot}\Psi(x)$$

This operator[2] is named the *Hamiltonian operator* or *energy operator* after the Irish physicist and mathematician William Rowan Hamilton[3] and is denoted $\hat{\mathbf{H}}$. Its expression is

$$\hat{\mathbf{H}} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \hat{\mathbf{V}}$$

Sir W. Hamilton

Given the new meaning of the term, entity V is the potential energy operator. Its mode of action is multiplication by the scalar function V, i.e. $\hat{V}$ = Vx. Similarly, we have the entity

$$\frac{\hbar^2}{2m}\frac{d^2}{dx^2}$$

represents the kinetic energy operator $\hat{T}$

$$\hat{\mathbf{T}} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2}$$

For the Schrödinger equation, we write

$$\hat{\mathbf{H}}\Psi(x) = E_{Tot}\Psi(x) \qquad \text{(VI-9)}$$

with

$$\hat{\mathbf{H}} = \hat{\mathbf{T}} + \hat{\mathbf{V}}$$

---

[2] An operator is a series of operations performed on a number or function. For example, the operator "square root" **(√( ))** applied to the number 2 gives: √2 = 1.414; the operator "square" **( )²** applied to the same number gives $(2)^2 = 4$; or the **derivative operator d/dx** applied to the x^2 function gives the result:

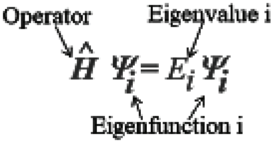
$$\frac{d}{dx}(x^2) = 2x$$

[3] Sir William Hamilton (1805-1865). Irish mathematician, physicist, and astronomer. Known for his discovery of quaternions; his research was important in the development of quantum mechanics.

Eq. (VI-9) means that when one applies the **H** operator to the wave function, the solution of the Schrödinger equation, one gets a scalar, the energy, multiplied by the wave function.

We therefore use the terms of the *eigenvalue equation* for the Schrödinger equation; the *eigenfunctions* of the Hamiltonian **H** for its wave function solutions; and the *eigenvalues* for the corresponding energies E_i

Table VI-1: Operator, eigenvalue, and eigenfunction



Generally speaking, the action of an **O** operator on one of its eigenfunctions f(x) generates a scalar, which is the operator's eigenvalue multiplied by this eigenfunction

$$\hat{\mathbf{O}} f(x) = scalar \times f(x)$$

3. Solving the Schrödinger equation for a particle in a potential well

a. Trapped Particles: Limit Conditions

Here we have a particle of mass m located on a segment of width defining an infinite potential well. Inside the well, the potential energy is zero and the Schrödinger equation governing the particle is therefore

$$\frac{d^2\Psi(x)}{dx^2} + \frac{2m}{\hbar^2}E_{Tot}\Psi(x) = 0$$

This equation is a second order differential equation without a second member. It generally admits functions such as

$$\Psi(x) = A\sin(kx) + B\cos(kx)$$

where A and B are constants and where we have

$$k^2 = \frac{2m}{\hbar^2}E_{Tot} \tag{VI-10}$$

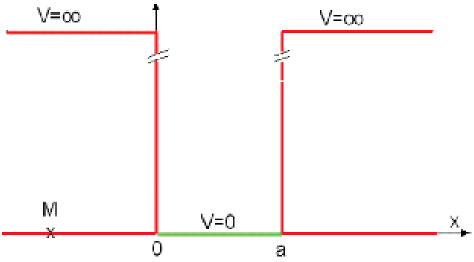


Figure VI-2: The limit conditions.

In **Fig. VI-2**, consider the potential well and a point M placed in the "red" zone (outside the well):

First limit condition

Now let us consider the possibility that the particle may be in M. For this to be the case, it would be necessary for the kinetic energy of the particle to be infinite so as to break down the potential barrier, which is infinitely high. As a result, there is no chance of finding the particle in M. This means that the probability of finding the particle at point M is negligible or zero. This is true for all points in the "red area" of **Fig. VI-2**, especially point 0. As such, we must have

$$\Psi(0)^2 = 0 \quad \text{then} \quad \Psi(0) = 0$$

This is the *first limit condition*. The consequence is that

$$\Psi(0) = A\sin(k0) + B\cos(k0) = 0$$

implying that B = 0 and that the wave function takes the form

$$\Psi(x) = A\sin(kx)$$

Let us now see what the application of the second limit condition gives.

Second limit condition

What was said for the first limit condition is valid for the second: the probability of the presence of the particle in the zone x∈]a,+∞[is null. It is inferred that

$$\Psi(a)^2 = 0 \quad \text{so that} \quad \Psi(a) = 0$$

with the consequence that

$$\Psi(a) = A\sin(ka) = 0$$

Since A is a constant that cannot be zero, it is inferred that

$$\sin(ka) = 0$$

Allowed solutions for energy

Given the properties of the circular functions, one must have ka = nπ, where n is an integer number that can take all the integer values from 0 to infinity. We shall see later that the value n = 0 has no physical significance even though it is part of the mathematical solution.

Squaring the expression, we come to

$$k^2 = \frac{n^2\pi^2}{a^2} \tag{VI-11}$$

Let us equalize this equation with Eq. (VI-10)

$$\frac{2m}{\hbar^2}E_{Tot} = \frac{n^2\pi^2}{a^2}$$

simplifying the change in notation E_{Tot} = E(n), we get

$$E(n) = \frac{\pi^2\hbar^2}{2ma^2}n^2$$

and replacing constant ħ by h, we obtain

$$\boxed{E(n) = \frac{h^2}{8ma^2}n^2} \tag{VI-12}$$

This is the expression of the energy of a particle in an infinite potential well where n is an integer number; it is inferred that the energy can only take certain values and we can say that the energy is quantized. Now, let us see if the value n = 0 is allowed. If n = 0, then the constant k is zero according to Eq. (VI-11). The consequence is that the wave function Ψ(x) is zero whatever the value of x. This means that the probability of the presence of the particle is zero whatever the position on the Oa segment. It also means that the particle is not in the well, a conclusion that is opposed to the initial hypothesis, which envisaged the presence of a particle in the potential well. Therefore, the solution n = 0 has no physical significance and must be ruled out.

Finally, the solutions of the Schrödinger equation are

$$E(n) = \frac{h^2}{8ma^2} n^2 \quad \text{with} \quad n = 1, 2, 3 \ldots \infty$$

We can now adapt our notation concerning the eigensolutions of the Schrödinger equation. Since the energy is discrete, we must denote it as E_n rather than E(n). Similarly, the wave functions must be denoted Ψ_n (x) instead of Ψ(n,x), so that

$$E_n = \frac{h^2}{8ma^2} n^2 \quad \text{with} \quad n = 1, 2, 3 \ldots \infty$$

The corresponding wave functions

From Eq. (VI-10), we deduce

$$k = \frac{n\pi}{a}$$

Hence, the expression for the wave function solutions of the Schrödinger equation are

$$\Psi_n(x) = A \sin\left(\frac{n\pi}{a} x\right) \quad \text{with} \quad n = 1, 2, 3 \ldots \infty$$

b. Representation of the stationary states of the particle in a potential well

We have just seen how the resolution of the Schrödinger equation leads to two types of solutions: quantized energies corresponding to the Hamiltonian H eigenvalues of the system and the corresponding wave functions corresponding to the Hamiltonian $\widehat{\mathbf{H}}$ eigenfunctions. Both solutions can be represented graphically.

Energy level diagram

Here, we consider the energy. Using the energy unit system

$$1u = \frac{h^2}{8ma^2} \text{ we have: } E_n = n^2\,u \quad \text{with} \quad n = 1,2,3\ldots$$

giving the first four levels in **Table VI-3**.

Table VI-3: First eigenvalues

n	1	2	3	4
E_n	1	4	9	16

By deferring the values on an energy scale, we get the energy level diagram shown in **Fig. VI-3**. The energy levels are shown on the left. Energy is expressed in unity h²/(8 ma²).

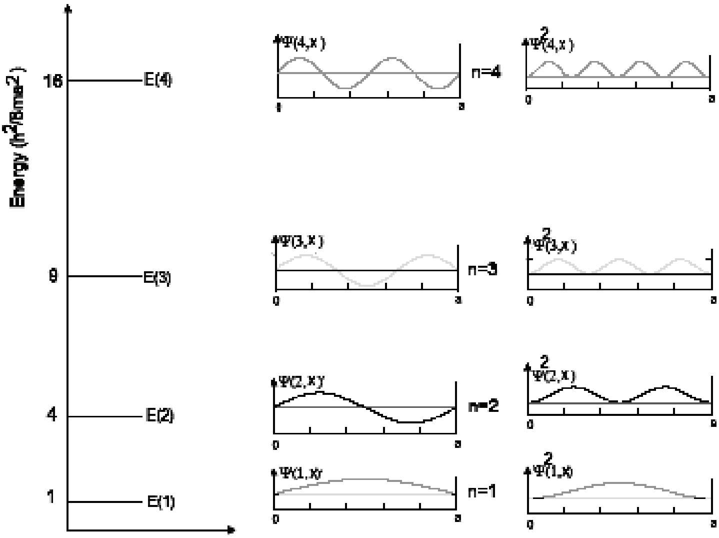


Figure VI-3: Energy levels, wave functions, and probabilities of presence of the four first stationary states of a particle in an infinite potential well.

The wave functions

The wave functions (center of **Figure VI-3**) display ripples along the sides of the well. A simple calculation allows us to calculate the relationship between the wavelength associated with the particle and the width of the well. Indeed, if we consider that the particle energy is purely kinetic (V = 0), we can write

$$E_n(n) = T_n = \frac{h^2}{8ma^2}n^2$$

However, according to Eq. (VI-6), we have

$$T_n = \frac{p_n^2}{2m}$$

By equalizing the last two relationships we get

$$\frac{p_n^2}{2m} = \frac{h^2}{8ma^2}n^2$$

where p is the quantized momentum. It may be deduced that

$$|p_n| = \frac{h}{2a}n$$

However, the wavelength of the quantized wave associated with the particle is expressed by

$$\lambda_n = \frac{h}{|p_n|}$$

and it may be deduced that

$$\lambda_n = \frac{2a}{n}$$

We can see that the wavelength λ_n is about the size of the width of the well. This behavior of a system of quantized energy is characteristic of microscopic systems and the wavelength associated with the particle is about the size of the space in which it moves. Thus, an electron in the hydrogen atom must have an associated wavelength of the order of magnitude of an atomic diameter, i.e. of the order of the angstrom. This behavior also explains that as energy increases, the number of points where the probability of presence (right graph) cancels out increases. These zero probability points are described as knots within the space where the particle is located.

c. Wave function normalization

The normalization of a wave function allows us to examine the physics of the studied system. To understand this normalization, we have to consider the evolution of the probability of the particle's presence in one of its stationary states, for example, the fundamental state $\Psi_1(x)$.

Fig. VI-4 gives, in ordinate fashion, the evolution of the probability of presence $\Psi_1(x)^2$ as a function of position x in the potential well.

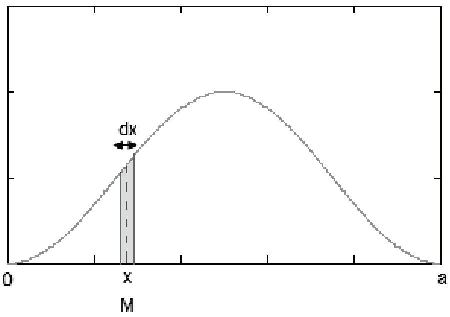


Figure VI-4: Probability density evolution $\Psi(1,x)^2$ for the potential well.

Let there be a point M of abscissa x and the probability of a particle being present at point M is $\Psi(0,x)^2$. Now, we consider an element of length dx around the x coordinate.

It may be considered that the elementary probability of presence of the particle dP in the infinitesimal segment dx will be the surface of the grayed-out trapezoid. As dx is infinitely small. one can equate this area with that of the rectangle formed by the height $\Psi_1(x)^2$ and by the dx segment, so that

$$dP \simeq \Psi_1(x)^2 dx \tag{VI-13}$$

We may deduce that

$$\Psi_1(x)^2 = \frac{dP}{dx}$$

The probability $\Psi_1(x)^2$ appears as a probability per unit of length. We can speak then, in a lazy fashion, of the "probability density". Of course, this can be generalized to the set of probability densities $\Psi_n(x)^2$. Now, let us describe the normalization process of a wave function.

The physical data of the potential well model is premised on the fact that a particle may be found somewhere between O and a. We can mathematically translate this by saying that the response to finding a particle between O and a is a certainty, i.e. it is equal to unity. This certainty therefore corresponds to the sum of all the elementary probabilities dp that the segment Oa can carry. In other words, we can write

$$\int_0^a dP = 1$$

Replacing dP with the expression in (VI-13), we obtain

$$\int_0^a \Psi(n,x)^2 dx = 1$$

This operation is the "normalization of the wave function". For the model to have physical meaning, its wave functions must be *normalized* or *normed.* The consequence of this operation is the assignment of a value to the parameter A in front of the sine function. As such, we can replace the wave function with its analytical expression

$$\int_0^a (A\sin(\frac{n\pi}{a}x))^2 dx = 1$$

or

$$A^2 \int_0^a \sin^2(\frac{n\pi}{a}x)dx = 1$$

where A is the *normalization constant* of the function. To evaluate this constant, we need to evaluate the integral. Thus, we write

$$I = \int_0^a \sin^2(\frac{n\pi}{a}x)dx$$

and hence

$$A^2 I = 1$$

To resolve this integral, the degree of the sine function must be diminished. We use the sinusoidal circular function for this purpose

$$\sin^2 ax = \tfrac{1}{2}(1 - \cos(2ax)) \tag{VI-14}$$

which gives

$$I = \tfrac{1}{2}\int_0^a 1 - \cos(2\frac{n\pi}{a}x))dx$$

This expression may be decomposed into two integrals

$$I = \tfrac{1}{2}(I_1 - I_2) \quad \text{with } I_1 = \int_0^a dx \quad \text{and} \quad I_2 = \int_0^a \cos(2\tfrac{n\pi}{a}x)dx$$

The first integral is obvious

$$I_1 = a$$

while for the second one we have

$$I_2 = \tfrac{a}{2n\pi}\Big[\sin(\tfrac{2n\pi}{a}x)\Big]_0^a = \frac{a}{2n\pi}[\sin(2n\pi) - 0] = 0$$

which leads us to

$$I = \tfrac{1}{2}a \quad \text{and we deduce } A^2\tfrac{1}{2}a = 1$$

i.e.

$$A^2 = \frac{2}{a} \quad \text{and} \quad A = \sqrt{\frac{2}{a}}$$

The normalized function is thus

$$\boxed{\Psi_n(x) = \sqrt{\frac{2}{a}}\,\sin(\frac{n\pi}{a}x)} \tag{VI-15}$$

4. Heisenberg's uncertainty principle

The model of the particle in an infinite potential well allows us to discover a fundamental principle in quantum mechanics, as stated by Heisenberg[4] in the general relation

$$\Delta r . \Delta p \geq \hbar$$

where Δr and Δp are, respectively, the absolute uncertainties of the position and the momentum of a particle in an atom, and $\hbar$ is the Planck constant divided by 2π. Recall that in classical mechanics, momentum is the product of the mass times the speed of the particle

W. Heisenberg

$$\vec{p} = m\vec{v}$$

Consider a particle in a potential well with quantized energy that is equal to

$$E_n = \frac{h^2 n^2}{8ma^2} \quad \text{with} \quad n = 1, 2, 3 \ldots \infty$$

Inside the well, the potential energy of the particle is given by the null hypothesis, we deduce that its energy is purely kinetic, which leads to the relation demonstrated above

$$p_n^2 = \left(\frac{h}{2a} n\right)^2$$

We can deduce that the algebraic value of the momentum is

$$p_n = \pm \|\vec{p}_n\| = \pm \frac{h}{2a} n$$

---

[4] Werner Heisenberg (1901-1976). German physicist known for being one of the founders of quantum mechanics. He was awarded the Nobel Prize in Physics in 1932 "for the creation of quantum mechanics, the application of which led, among other things, to the discovery of allotropic varieties of hydrogen".

In other words, the largest value of p is +|p| while the lowest value is -|p|. The uncertainty of the measurement of p is therefore

$$\Delta p = +\|\vec{p}_n\| - (-\|\vec{p}_n\|) = 2\|\vec{p}_n\|$$

On the other hand, the uncertainty of the measurement of the position of the particle is of the order of magnitude of the width of the well, i.e.

$$\Delta x = a$$

Let us derive the product of the uncertainties

$$\Delta x.\Delta p_n = a.2\|\vec{p}_n\| = a.2\frac{h}{2a}n = n\,h$$

Since n is greater than or equal to 1, we deduce

$$\boxed{\Delta x.\Delta p_n \geq h}$$

We thus find an approximate expression of the general Heisenberg relation. This relationship is extremely important because it defines the framework for using a physical representation of phenomena on the quantum scale. According to this principle, it is impossible to know the position of a particle in an atom as soon as we know its momentum and hence its energy.

This prohibits the representation of the situation of an electron in an atom like that given by Bohr in his semi-classical theory of the hydrogen atom, which was based on the notion of the trajectory of an electron orbiting around the nucleus, a bit like a planet revolving around the sun. The examples below help explain this.

Table VI-2: Comparison between macroscopic and microscopic scales

Macroscopic scale	Microscopic scale
Particle: ball moving on a 1 m length rail	Particle: electron in an atom of 10^{-10} meter radius
Mass: m about $10^{-3}kg$	Mass: m around $10^{-30}kg$
Speed: v around $1ms^{-1}$	Speed v around $10^{6}ms^{-1}$
Error on speed $\Delta v = 10^{-3}ms^{-1}$	Error on speed $\Delta v = 10^{3}ms^{-1}$
Error on the momentum $\Delta p = m \times \Delta v = 10^{-3} \times 10^{-3} = 10^{-6}$	Error on the momentum $\Delta p = m \times \Delta v = 10^{-30} \times 10^{3} = 10^{-27}$
Calculated error on position $\Delta r = \frac{h}{\Delta p} = \frac{10^{-33}}{10^{-6}} = 10^{-27}m$	Calculated error on position $\Delta r = \frac{h}{\Delta p} = \frac{10^{-33}}{10^{-27}} = 10^{-6}m$
Perfect precision Compatible with the notion of trajectory The particle is well located	Lack of precision. The error represents 10000 times the size of the atom Unable to locate the particle

5. Eigenvalues and mean values of an operator

Consider the Schrödinger equation written in compact form

$$\hat{\mathbf{H}}\Psi_n(x) = E_n\Psi_n(x)$$

We recall that, written in this form, the equation shows its solutions as the eigenvalues E_n and the eigenfunctions $\Psi_n(x)$. To realize the meaning of this equation, let us apply the Hamiltonian operator **H** to the wave functions $\Psi_n(x)$

$$\hat{\mathbf{H}}\Psi_n(x) = \left\{-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\right\}\left\{\sqrt{\frac{2}{a}}\ \sin(\frac{n\pi}{a}x)\right\}$$

or

$$\hat{\mathbf{H}}\Psi_n(x) = -\frac{\hbar^2}{2m}\sqrt{\frac{2}{a}}\ \frac{d^2}{dx^2}\left\{\sin(\frac{n\pi}{a}x)\right\}$$

Deriving once, we get

$$\hat{\mathbf{H}}\Psi_n(x) = -\frac{\hbar^2}{2m}\sqrt{\frac{2}{a}}\,\frac{n\pi}{a}\,\frac{d}{dx}\left\{\cos\left(\frac{n\pi}{a}x\right)\right\}$$

and for a second time, we get

$$\hat{\mathbf{H}}\Psi_n(x) = \frac{\hbar^2}{2m}\frac{n^2\pi^2}{a^2}\left\{\sqrt{\frac{2}{a}}\,\sin\left(\frac{n\pi}{a}x\right)\right\}$$

which can be written by returning to the expression $\Psi_n(x)$

$$\hat{\mathbf{H}}\Psi_n(x) = \left[\frac{\hbar^2}{2m}\frac{n^2\pi^2}{a^2}\right]\Psi_n(x)$$

and replacing $\hbar$

$$\hat{\mathbf{H}}\Psi_n(x) = \left[\frac{h^2}{8ma^2}n^2\right]\Psi_n(x)$$

The quantity in the square brackets on the right side of the equation corresponds to the energy E_n. As such, we can see the meaning of the expression

$$\hat{\mathbf{H}}\Psi_n(x) = E_n\Psi_n(x) :$$

The action of the energy operator on a wave function gives a scalar—the energy E_n multiplied by the wave function $\Psi_n(x)$.

From a general point of view, if we consider an operator $\hat{\boldsymbol{O}}$ corresponding to a physical quantity O and **F** a function that is an eigenfunction of **O**, then we can have the following equation, which can be verified under certain conditions

$$\hat{\mathbf{O}}\mathbf{F} = O\mathbf{F}$$

In this case, the physical quantity O is the eigenvalue of the operator $\hat{\boldsymbol{O}}$ with the associated eigenfunction **F**. However, the eigenfunction of one operator is not necessarily the eigenfunction of another.

This is the case for example of the position operator $\hat{\boldsymbol{x}}$, which does not accept the same eigenfunctions as $\hat{\boldsymbol{H}}$.

The operator position $\hat{x}$ acts on a function, multiplying it by the variable x. The function is an eigenfunction of $\hat{H}$ and so we have

$$\hat{\mathbf{x}} \times \Psi_n(x) = x \times \Psi_n(x) \tag{VI-16}$$

We see that x is not an eigenvalue because in this case it would be a scalar. Consequently, knowledge of the physical quantity corresponding to the operator x is impossible with the wave function $\Psi_n(x)$. It is thus necessary to proceed differently to get an idea of the position of the particle when it is in a stationary state $\Psi_n(x)$ and the energy of which is known. We shall calculate a mean value of the Hamiltonian operator on the wave function $\Psi_n(x)$.

By definition, the mean value of the operator $\hat{x}$ calculated on the wave function $\Psi_n(x)$ noted $<\mathbf{x}>_\psi$ is

$$\langle \hat{\mathbf{x}} \rangle_\psi = \frac{\int_0^a \Psi_n(x) \hat{\mathbf{x}} \Psi_n(x) dx}{\int_0^a \Psi_n(x)^2 dx}$$

or, taking into account the mode of action of the operator $\hat{x}$ given by Eq. (VI-16), we find

$$\langle \hat{\mathbf{x}} \rangle_\psi = \frac{\int_0^a \Psi_n(x)^2 x dx}{\int_0^a \Psi_n(x)^2 dx} \tag{VI-17}$$

This relation appears as the sum of the probabilities to have the x coordinate.

Let us replace $\Psi_n(x)$ by its expression (VI-15) in Eq. (VI-17)

$$\langle \hat{\mathbf{x}} \rangle_\psi = \frac{\int_0^a \left\{ \sqrt{\frac{2}{a}} \sin(\frac{n\pi}{a} x) \right\}^2 x dx}{\int_0^a \left\{ \sqrt{\frac{2}{a}} \sin(\frac{n\pi}{a} x) \right\}^2 dx}$$

We know that the eigenfunction $\Psi(n,x)$ is normalized and the denominator of the previous equation is equal to 1. The expression is thus written as

$$\langle \hat{\mathbf{x}} \rangle_\psi = \int_0^a \left\{ \sqrt{\frac{2}{a}} \sin(\frac{n\pi}{a}x) \right\}^2 x dx$$

or

$$\langle \hat{\mathbf{x}} \rangle_\psi = \tfrac{2}{a} \int_0^a \sin^2(\frac{n\pi}{a}x) x dx$$

Let us calculate the integral. The expression under the integral must be transformed so as to drop its degree. To do this, we make use of the circular function (VI-14) and obtain

$$\langle \hat{\mathbf{x}} \rangle_\psi = \frac{2}{a} \int_0^a \frac{1 - \cos(2\frac{n\pi}{a}x)}{2} x dx$$

or, by separating the terms under the integral

$$\langle \hat{\mathbf{x}} \rangle_\psi = \frac{1}{a} \left(\int_0^a x dx - \int_0^a \cos(2\frac{n\pi}{a}x) x dx \right)$$

Let us write

$$\langle \hat{\mathbf{x}} \rangle_\psi = \frac{1}{a} (I_1 - I_2)$$

with

$$I_1 = \int_0^a x dx \quad \text{and} \quad I_2 = \int_0^a \cos(2\frac{n\pi}{a}x) x dx$$

Calculation of I_1.

$$I_1 = \left[\frac{x^2}{2} \right]_0^a = \frac{a^2}{2}$$

Calculation of I_2.

$$I_2 = \int_0^a \cos(2\frac{n\pi}{a}x) x dx$$

We need to integrate by parts

$$u = x; \quad du = dx$$
$$dv = \cos(\frac{2n\pi}{a}x)dx; \qquad v = \frac{a}{2n\pi}\sin(\frac{2n\pi}{a}x)$$

and
$$\int udv = uv - \int vdu$$

$$I_2 = \tfrac{a}{2n\pi}\Big[x\sin(\frac{2n\pi}{a}x)\Big]_0^a - \frac{a}{2n\pi}\int_0^a \sin(\frac{2n\pi}{a}x)dx$$

or

$$I_2 = \frac{a}{2n\pi}\Big[a\sin(\frac{2n\pi}{a}a) - x\sin(\frac{2n\pi}{a}a)\Big] - \Big(\frac{a}{2n\pi}\Big)^2\Big[\cos(\frac{2n\pi}{a}x)\Big]_0^a$$

$$I_2 = \frac{a}{2n\pi}\underbrace{\Big[a\sin(\frac{2n\pi}{a}a) - x\sin(\frac{2n\pi}{a}a)\Big]} - \Big(\frac{a}{2n\pi}\Big)^2\underbrace{\Big[\cos(\frac{2n\pi}{a}a) - \cos(\frac{2n\pi}{a}0)\Big]}$$

The expressions underlined by braces are null

$$\langle\hat{\mathbf{x}}\rangle_\psi = \frac{1}{a}\left(\frac{a^2}{2} - 0\right) = \frac{a}{2}$$

This is the mean value of the operator of position $\hat{\boldsymbol{x}}$ of the particle in the potential well, also called the first moment of the operator $\hat{\boldsymbol{x}}$.

6. Fluctuation of mean values

A mean value implies uncertainty about its measurement. This information is given by the calculation of the fluctuation or absolute error on the measurement of the quantity. Let us take, once again, the case of the particle's position.

By definition, the fluctuation of the mean value of the position operator calculated on the wave function $\Psi_n(x)$ will be

$$\Delta x_\Psi = \sqrt{\langle\hat{\mathbf{x}}^2\rangle_\Psi - \langle\hat{\mathbf{x}}\rangle_\Psi^2} \tag{VI-18}$$

where $\langle \hat{x}^2 \rangle$ is the mean value of the square of the operator position $\hat{x}$, also called the *second moment* of the operator. A such, we have to calculate this quantity

$$\langle \hat{\mathbf{x}}^2 \rangle_\Psi = \frac{\int_0^a \left\{ \sqrt{\frac{2}{a}} \sin(\frac{n\pi}{a}x) \right\}^2 x^2 dx}{\int_0^a \left\{ \sqrt{\frac{2}{a}} \sin(\frac{n\pi}{a}x) \right\}^2 dx}$$

Since $\Psi_n(x)$ is normalized, we may write

$$\langle \hat{\mathbf{x}}^2 \rangle_\Psi = \int_0^a \left\{ \sqrt{\frac{2}{a}} \sin(\frac{n\pi}{a}x) \right\}^2 x^2 dx$$

or

$$\langle \hat{\mathbf{x}}^2 \rangle_\Psi = \frac{2}{a} \int_0^a \left\{ \sin(\frac{n\pi}{a}x) \right\}^2 x^2 dx$$

Now, let us write

$$J = \int_0^a \left\{ \sin(\frac{n\pi}{a}x) \right\}^2 x^2 dx$$

then we have

$$\langle \hat{\mathbf{x}}^2 \rangle_\Psi = \frac{2}{a} J$$

The expression under the integral must be transformed so as to drop its exponent. To do this, we use the circular function (VI-14), which comes out as

$$J = \int_0^a \frac{1 - \cos(2\frac{n\pi}{a}x)}{2} x^2 dx$$

or

$$J = \frac{1}{2} \left(\underbrace{\int_0^a x^2 dx}_{J_1} + \underbrace{\int_0^a \cos(2\frac{n\pi}{a}x) x^2 dx}_{J_2} \right)$$

Let us solve the integrals J_1 and J_2

$$J = \frac{1}{2}\left(J_1 + J_2 \right)$$

Calculation of J_1.

$$J_1 = \int_0^a x^2 dx = \frac{1}{3}[x^3]_0^a = \frac{1}{3}a^3$$

Calculation of J_2.

$$J_2 = \int_0^a \cos(2\frac{n\pi}{a}x)x^2 dx$$

Now, using integration by parts

$$\int udv = uv - \int vdu$$

Let

$$u = x^2 \qquad du = 2xdx$$
$$dv = \cos(2\frac{n\pi}{a}x)dx \qquad v = \frac{a}{2n\pi}\sin(2\frac{n\pi}{a}x)$$

Then we obtain

$$J_2 = \underbrace{\left[\frac{a}{2n\pi}\sin(2\frac{n\pi}{a}x)x^2 \right]_0^a}_{J_{21}} - \underbrace{\frac{a}{2n\pi}2\int_0^a \sin(2\frac{n\pi}{a}x)xdx}_{J_{22}}$$

$$J_2 = J_{21} - J_{22}$$

We can see that the first term J_{21} is null

$$J_{21} = 0$$

and the second term J_{22} may be developed as follows

$$J_{22} = \frac{a}{n\pi}\int_0^a \sin(2\frac{n\pi}{a}x)x dx \qquad J_{22} = \frac{a}{n\pi}J_{221}$$

$$J_{221} = \int_0^a \sin(2\frac{n\pi}{a}x)x dx$$

where a new integration by parts may be performed

$$u = x \qquad du = dx$$
$$dv = \int_0^a \sin(2\frac{n\pi}{a}x)x dx \qquad v = -\frac{a}{2n\pi}\cos(2\frac{n\pi}{a}x)$$
$$\int udv = uv - \int vdu$$
$$J_{221} = -\left[x\frac{a}{2n\pi}\cos(2\frac{n\pi}{a}x)\right]_0^a + \frac{a}{2n\pi}\int_0^a \cos(2\frac{n\pi}{a}x)dx$$
$$J_{221} = -\frac{a^2}{2n\pi}\cos(2n\pi) + \left(\frac{a}{2n\pi}\right)^2\left[\sin(2\frac{n\pi}{a}x)\right]_0^a$$
$$J_{221} = \frac{a^2}{2n\pi} \text{ and } J_{22} = \frac{a}{n\pi}J_{221} \text{ that is } J_{22} = \frac{a}{n\pi}\frac{a^2}{2n\pi}$$
$$J_2 = -J_{22} \text{ i.e. } J_2 = -\frac{a^3}{2n^2\pi^2}$$

and finally

$$J = \frac{1}{2}\left(\frac{1}{3}a^3 - \frac{a^3}{2n^2\pi^2}\right)$$

$$\langle \mathbf{x}^2\rangle_\Psi = \frac{2}{a}\frac{1}{2}\left(\frac{1}{3}a^3 - \frac{a^3}{2n^2\pi^2}\right) \text{ i.e. } \langle \hat{\mathbf{x}}^2\rangle_\Psi = a^2\left(\frac{1}{3} - \frac{1}{2n^2\pi^2}\right)$$

The fluctuation of the mean value of the position operator is

$$\Delta x_\Psi = \sqrt{\langle \mathbf{x}^2\rangle_\Psi - \langle \mathbf{x}\rangle_\Psi^2}$$

$$\Delta x_\Psi = \sqrt{\frac{a^2}{3} - \frac{a^2}{2n^2\pi^2} - \frac{a^2}{4}} \text{ that is } \Delta x_\Psi = \sqrt{\frac{a^2}{12} - \frac{a^2}{2n^2\pi^2}}$$

so that we obtain the expression for Δx_Ψ

$$\boxed{\Delta x_{\Psi} = a\sqrt{\frac{1}{12} - \frac{1}{2n^2\pi^2}}} \qquad \text{(VI-19)}$$

VI-II. Schrödinger's Model of the Hydrogen Atom

We have just solved the Schrödinger equation for a one-dimensional system. We now extend these principles to the resolution of a three-dimensional system—the hydrogen atom.

1. Comparison between the 1-D and 3-D problem

Table VI-3 draws some parallels between the resolution of a one-dimensional system and a three-dimensional system such as the hydrogen atom. While the resolution of the one-dimensional system does not pose a difficult theoretical problem, in the case of the hydrogen atom, the resolution of the Schrödinger equation is more complex and has to be undertaken in several stages.

Table VI-3: Comparison between 1-D and 3-D systems

1-D system	**3-D system**
Particle in a potential well	electron in the hydrogen atom
1 dimensional Schrödinger equation	3 dimensional Schrödinger equation
$\frac{d^2\Psi(x)}{dx^2}+\frac{2m}{\hbar^2}(E - V)\Psi(x)$	$\frac{\partial^2\Psi(x,y,z)}{\partial x^2}+\frac{\partial^2\Psi(x,y,z)}{\partial y^2}+\frac{\partial^2\Psi(x,y,z)}{\partial y^2}+\frac{2m}{\hbar^2}(E - V)\Psi(x,y,z)$
Resolution $\Downarrow$	Resolution $\Downarrow$
-Energies	-Energies
-1 dimensional eigenfunctions	-3 dimensional eigenfunctions
-1 quantum number	-3 quantum numbers

2. The 3-D Schrödinger equation

Consider a nucleus carrying a positive charge around which an electron moves. The theoretical model uses the fact that this electron is a wave that is considered stationary. We have previously studied a stationary phenomenon in the form of interference. In a stationary phenomenon, the amplitude of the wave associated with the particle depends on the spatial coordinates and the square of this amplitude has a probabilistic meaning.

Let Ψ be the amplitude wave function of the wave associated with the electron in the hydrogen atom. This function is related to the energy of the particle by the Schrödinger equation presented above. It leads to two types of solutions—for wave functions and for energy levels. The wave function-energy level pair defines what is termed a *stationary state*.

The amplitude wave function (which we shall call the wave function), being that of a stationary wave, depends on the spatial coordinates. In the case of the hydrogen atom, which is a three-dimensional entity, the wave function will, itself, be three-dimensional, i.e. expressed as x, y, and z. However, solving the Schrödinger equation is only possible by working in the spherical polar coordinate system in which the wave functions are expressed. It takes the form

$$\frac{\partial^2\Psi(x,y,z)}{\partial x^2}+\frac{\partial^2\Psi(x,y,z)}{\partial y^2}+\frac{\partial^2\Psi(x,y,z)}{\partial y^2}+\frac{2m}{\hbar^2}(E-V)\Psi(x,y,z) \qquad \text{(VI-20)}$$

3. Spherical polar coordinates

Fig. VI-5 gives the relationships between the Cartesian coordinates x, y, and z, and the spherical polar coordinates r, θ, and φ.

$$y = r\sin\theta\sin\phi$$
$$z = r\cos\theta$$
$$x = r\sin\theta\cos\phi$$

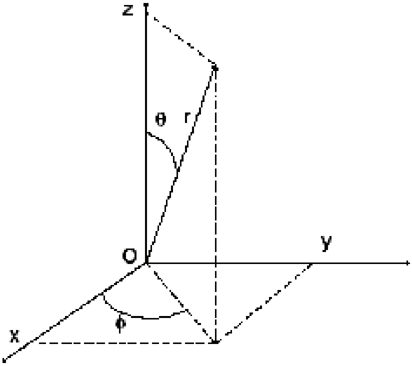


Figure VI-5: Spherical polar coordinates.

and the infinitesimal volume element is

$$dv = r^2\sin\theta dr d\theta d\phi \qquad \text{(VI 21)}$$

We shall not give all the details of the resolution of the Schrödinger equation here, but only draw out its main lines concerning the separation of the variables and the individual resolution of the differential equations relating to each variable.

4. Schrödinger's equation in spherical polar coordinates

1st step: The Laplacian ∇^2 in spherical polar coordinates

Schrödinger's equation (VI-20) may be written in the form

$$\nabla^2\Psi(x,y,z) + \frac{2m}{\hbar^2}(E - V)\Psi(x,y,z) = 0$$

where

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

∇^2 is the Laplacian of the system that we have to express in spherical polar coordinates. After some mathematical developments, which exceed the level of this course, we obtain

$$\nabla^2 = \frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r} + \frac{1}{r^2}\frac{\partial^2}{\partial \theta^2} + \frac{1}{r^2}\frac{\cos\theta}{\sin\theta}\frac{\partial}{\partial\theta} + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}$$

2nd step: Schrödinger's equation in spherical coordinates

Starting from the expression in Cartesian coordinates of the Schrödinger equation, we must obtain

$$\nabla^2\Psi(r,\theta,\varphi) + \frac{2m}{\hbar^2}(E - V)\Psi(r,\theta,\varphi) = 0 \qquad \text{(VI-22)}$$

where $\Psi(r, \theta, \phi)$ is the wave function in spherical coordinates, which we shall assume to be in the form

$$\Psi(r,\theta,\varphi) = \mathbf{R}(r).\mathbf{\Theta}(\theta).\mathbf{\Phi}(\varphi) \qquad \text{(VI-23)}$$

where $R(r)$, $\Theta(\theta)$, and $\Phi(\phi)$ are sub-functions referring to the space variables r, θ, and ϕ; E is the energy; and V is the electron nucleus attraction potential, which is of the type

$$V(r) = K\frac{e^2}{r} \text{ with } K = 9.\,10^9 SI$$

3$^{\text{rd}}$ step: Separation of variables

Let us introduce the wave function (VI-23) into the Schrödinger equation. We can then write

$$\nabla^2\Psi(r,\theta,\varphi) = \frac{\partial^2 \mathbf{R}(r).\,\mathbf{\Theta}(\theta).\,\mathbf{\Phi}(\varphi)}{\partial r^2} + \frac{2}{r}\frac{\partial \mathbf{R}(r).\,\mathbf{\Theta}(\theta).\,\mathbf{\Phi}(\varphi)}{\partial r}$$

$$+\frac{1}{r^2}\frac{\partial^2 \mathbf{R}(r).\,\mathbf{\Theta}(\theta).\,\mathbf{\Phi}(\varphi)}{\partial \theta^2} + \frac{1}{r^2}\frac{\cos\theta}{\sin\theta}\frac{\partial \mathbf{R}(r).\,\mathbf{\Theta}(\theta).\,\mathbf{\Phi}(\varphi)}{\partial \theta}$$

$$+\frac{1}{r^2\sin^2\theta}\frac{\partial^2 \mathbf{R}(r).\,\mathbf{\Theta}(\theta).\,\mathbf{\Phi}(\varphi)}{\partial \varphi^2}$$

which reduces to

$$\nabla^2\Psi(r,\theta,\varphi) = \mathbf{\Theta}(\theta)\mathbf{\Phi}(\varphi)\frac{\partial^2 \mathbf{R}(r)}{\partial r^2} + \frac{2}{r}\mathbf{\Theta}(\theta).\,\mathbf{\Phi}(\varphi)\frac{\partial \mathbf{R}(r)}{\partial r} + \frac{1}{r^2}\mathbf{R}(r)\mathbf{\Phi}(\varphi)\frac{\partial^2 \mathbf{\Theta}(\theta)}{\partial \theta^2}$$

$$+\frac{1}{r^2}\frac{\cos\theta}{\sin\theta}\mathbf{R}(r).\,\mathbf{\Phi}(\varphi)\frac{\partial \mathbf{\Theta}(\theta)}{\partial \theta} + \frac{1}{r^2\sin^2\theta}\mathbf{R}(r).\,\mathbf{\Theta}(\theta)\frac{\partial^2 \mathbf{\Phi}(\varphi)}{\partial \varphi^2}$$

Now, we divide the expression by R(r)Θ(θ)Φ(ϕ) and it becomes

$$\nabla^2\Psi(r,\theta,\varphi) = \frac{1}{\mathbf{R}(r)}\frac{\partial^2 \mathbf{R}(r)}{\partial r^2} + \frac{2}{r}\frac{1}{\mathbf{R}(r)}\frac{\partial \mathbf{R}(r)}{\partial r} + \frac{1}{r^2}\frac{1}{\mathbf{\Theta}(\theta)}\frac{\partial^2 \mathbf{\Theta}(\theta)}{\partial \theta^2}$$

$$+\frac{1}{r^2}\frac{\cos\theta}{\sin\theta}\frac{1}{\mathbf{\Theta}(\theta)}\frac{\partial \mathbf{\Theta}(\theta)}{\partial \theta} + \frac{1}{r^2\sin^2\theta}\frac{1}{\mathbf{\Phi}(\varphi)}\frac{\partial^2 \mathbf{\Phi}(\varphi)}{\partial \varphi^2}$$

This gives the following expression of Schrödinger's equation in spherical polar coordinates

$$+\frac{1}{r^2}\underbrace{\left(\frac{1}{\mathbf{\Theta}(\theta)}\frac{\partial^2 \mathbf{\Theta}(\theta)}{\partial \theta^2} + \frac{\cos\theta}{\sin\theta}\frac{1}{\mathbf{\Theta}(\theta)}\frac{\partial \mathbf{\Theta}(\theta)}{\partial \theta} + \frac{1}{\sin^2\theta}\frac{1}{\mathbf{\Phi}(\varphi)}\frac{\partial^2 \mathbf{\Phi}(\varphi)}{\partial \varphi^2}\right)}_{\text{Angular part}} = 0$$

$$\mathbf{H}\Psi(r,\theta,\varphi) = \underbrace{\frac{1}{\mathbf{R}(r)}\frac{\partial^2\mathbf{R}(r)}{\partial r^2} + \frac{2}{r}\frac{1}{\mathbf{R}(r)}\frac{\partial\mathbf{R}(r)}{\partial r} + \frac{2m}{\hbar^2}(E-V)}_{\text{Radial part}}$$

This equation may be broken down into two sub-equations: the radial part, which only depends on the coordinate r; and the angular part, which only depends on the coordinates θ and ϕ. This partition is possible because the potential V depends only on r, allowing the separation of the variables. Besides, the angular part must be periodical with respect to the variable φ with a 2π angular period and it is for that reason that the magnetic quantum number m is an integer, as used below.

4th step: Individual resolution of each part

Angular part: resolution of the part in φ

Let us write

$$\frac{1}{\mathbf{\Phi}(\varphi)}\frac{\partial^2\mathbf{\Phi}(\varphi)}{\partial\varphi^2} = -m^2$$

where m is an integer number. Thus, we have

$$\frac{\partial^2\mathbf{\Phi}(\varphi)}{\partial\varphi^2} + m^2\mathbf{\Phi}(\varphi) = 0 \tag{VI-24}$$

Eq. (VI-24) admits, as a general solution

$$\mathbf{\Phi}(m,\varphi) = \frac{1}{\sqrt{2\pi}}.e^{im\varphi}$$

We can then express the part in θ such that

$$\frac{1}{\mathbf{\Theta}(l,m,\theta)}\frac{\partial^2\mathbf{\Theta}(l,m,\theta)}{\partial\theta^2} + \frac{\cos\theta}{\sin\theta}\frac{1}{\mathbf{\Theta}(l,m,\theta)}\frac{\partial\mathbf{\Theta}(l,m,\theta)}{\partial\theta} - \frac{m^2}{\sin^2\theta} = -l(l+1)$$

where l is an integer, which gives the equation

$$\frac{\partial^2 \boldsymbol{\Theta}(l,m,\theta)}{\partial \theta^2} + \frac{\cos\theta}{\sin\theta}\frac{\partial \boldsymbol{\Theta}(l,m,\theta)}{\partial \theta} - \frac{m^2 \boldsymbol{\Theta}(l,m,\theta)}{\sin^2\theta} = -l(l+1)\boldsymbol{\Theta}(l,m,\theta)$$

or, by rearranging

$$\frac{\partial^2 \boldsymbol{\Theta}(l,m,\theta)}{\partial \theta^2} + \frac{\cos\theta}{\sin\theta}\frac{\partial \boldsymbol{\Theta}(l,m,\theta)}{\partial \theta} - \left(\frac{m^2}{\sin^2\theta} - l(l+1)\right)\boldsymbol{\Theta}(l,m,\theta) = 0$$

This differential equation admits more complicated solutions than previously. They are of the form

$$\boldsymbol{\Theta}(l,m,\theta) = \frac{2l+1}{2}\left(\frac{(l-|m|)!}{(l+|m|)!}\right)^{\frac{1}{2}} \mathbb{P}_l^{|m|}(\cos\theta)$$

The $P_l^{|m|}(cos\theta)$ terms are named *associated Legendre functions*. They are associated with *Legendre polynomials* by the function

$$\mathbb{P}_l^{|m|}(x) = (1-x^2)^{\frac{|m|}{2}} \frac{d^{|m|}}{dx^{|m|}} P_l(x)$$

A-M. Legendre[5]

Radial part

$$\frac{1}{\mathbf{R}(r)}\frac{\partial^2 \mathbf{R}(r)}{\partial r^2} + \frac{2}{r}\frac{1}{\mathbf{R}(r)}\frac{\partial \mathbf{R}(r)}{\partial r} + \frac{2m}{\hbar^2}(E-V) - \frac{l(l+1)}{r^2} = 0 \quad \text{(VI-25)}$$

Now, we multiply Eq. (VI-25) by **R**(r)

$$\frac{\partial^2 \mathbf{R}(r)}{\partial r^2} + \frac{2}{r}\frac{\partial \mathbf{R}(r)}{\partial r} + \frac{2m}{\hbar^2}(E-V) - \frac{l(l+1)\mathbf{R}(r)}{r^2} = 0$$

The resolution of this equation is complex and leads to the expression

---

[5] Adrien-Marie Legendre (1752-1833). French mathematician who made numerous contributions to mathematics.

$$\mathbf{R}_{n,l}(r) = -\left(4\frac{Z^3}{n^4 a_0^3}\frac{(n-l-1)!}{(n+l)!}\right)^{\frac{1}{2}}\left(\frac{2Zr}{na_0}\right)^{l}\mathbf{e}^{-\dfrac{Zr}{na_0}}\mathbb{L}_{n+1}^{2l+1}\left(\tfrac{2Zr}{na_0}\right)$$

where the $L_q^s(z)$ are the associated Laguerre polynomials

$$\mathbb{L}_q^s(z) = \frac{d^s}{dz^s}L_q(z)$$

and where the $L_q(z)$

$$L_q(z) = \mathbf{e}^{z}\frac{d^q}{dz^q}(\mathbf{e}^{-z}z^q)$$

are the Laguerre polynomials.

E. N. Laguerre[6]

The resolution of the radial part also leads to the expression of the quantized energy E_n. We find that

$$\boxed{E_n = -\frac{1}{2}\left(\frac{1}{4\pi\varepsilon_0}\right)^2\frac{4\pi Z^2 me^4}{h^2}\frac{1}{n^2}} \qquad \text{(VI-26)}$$

where Z is the atomic number of the nucleus; m is the mass of the electron; h is Planck’s constant; e is the elementary charge; and ε_0 is the vacuum permittivity.

5. Wave functions: solutions of the Schrödinger equation

Solving the Schrödinger equation reveals 3 quantum numbers:

(i) n is the principal quantum number, which varies from 1 to ∞ by integer values. It defines the energy of the stationary state. The energy may be written as

$$E(n) = -\frac{K^2 me^4 Z^2}{2\hbar^2}\frac{1}{n^2}$$

---

[6] E. N. Laguerre (1834-1886). French mathematician and member of the Académie Française.

where K is the proportionality constant given above and $\hbar$ is Planck's constant divided by 2π. We may express the result in eV

$$\boxed{E(n) = -\frac{13,6\, Z^2}{n^2} e.V}$$

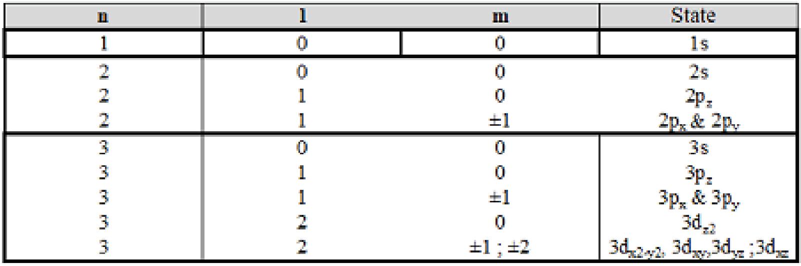
which is the expression of the energy obtained from the experimental spectra.

(ii) l is the secondary or azimuthal quantum number, which varies from 0 to n-1 by integer values.

(iii) m is the magnetic quantum number, which varies from -l to + l including 0 by integer values.

The variation of quantum numbers generates stationary states as shown in the table below.

Table VI-4: Names of the stationary states of the hydrogenic atom



n	l	m	State
1	0	0	1s
2	0	0	2s
2	1	0	$2p_z$
2	1	±1	$2p_x$ & $2p_y$
3	0	0	3s
3	1	0	$3p_z$
3	1	±1	$3p_x$ & $3p_y$
3	2	0	$3d_{z2}$
3	2	±1 ; ±2	$3d_{x2-y2}$, $3d_{xy}$, $3d_{yz}$; $3d_{xz}$

The wave functions depend on these 3 quantum numbers and the spherical polar coordinates.

Recall that the wave function solutions of the Schrödinger equation for a hydrogenic atom are of the general form

$$\Psi(r,\theta,\varphi) = \mathbf{R}(r).\mathbf{\Theta}(\theta).\mathbf{\Phi}(\varphi)$$

There are two notations for designating stationary states. For example, we can write

$$\Psi_{n,l,m}(r,\theta,\varphi)$$

or use letters to distinguish them, as shown in **Table VI-5**. These letters depend on the value of the secondary quantum number.

Table VI-5: Names of the states

letter	*s*	*p*	*d*	*f*	*g*	*h*	*i*	*k*
l	0	1	2	3	4	5	6	7

For example, the wave function of the state characterized by the set of quantum numbers n = 1, l = 0, and m = 0 is written

$$\Psi_{1,0,0} \text{ or } \Psi_{1s}$$

Note that when we are dealing with complex wave functions, the two notations are not completely equivalent. As an example, let us take the states characterized by n = 2, l = 1, and m = ±1. For these states we have the expression

$$\Psi_{2,1,\pm1} = \frac{1}{4\sqrt{2\pi}} Z^{3/2} r \mathbf{e}^{-Zr/2} \sin\theta \mathbf{e}^{\pm i\varphi}$$

We can rewrite the expression in the form

$$\Psi_{2,1,\pm1} = F(r,\theta)\mathbf{e}^{\pm i\varphi} \text{ with } F(r,\theta) = \frac{1}{4\sqrt{2\pi}} Z^{3/2} r \mathbf{e}^{-Zr/2} \sin\theta$$

and so we have two complex functions

$$\Psi_{2,1,+1} = F(r,\theta)\mathbf{e}^{+i\varphi} \text{ and } \Psi_{2,1,-1} = F(r,\theta)\mathbf{e}^{-i\varphi}$$

Now, let us make linear combinations of these wave functions

$$\Psi_{2,1,+1} + \Psi_{2,1,-1} = F(r,\theta)(\mathbf{e}^{+i\varphi} + \mathbf{e}^{-i\varphi}) \text{ and } \Psi_{2,1,+1} - \Psi_{2,1,-1} = F(r,\theta)(\mathbf{e}^{+i\varphi} - \mathbf{e}^{-i\varphi})$$

Using Euler's formula gives

$$\cos\varphi = \frac{\mathbf{e}^{+i\varphi} + \mathbf{e}^{-i\varphi}}{2} \text{ and } \sin\varphi = \frac{\mathbf{e}^{+i\varphi} - \mathbf{e}^{-i\varphi}}{2i}$$

and we can write

$$\Psi_{2,1,+1} + \Psi_{2,1,-1} = 2F(r,\theta)\cos\varphi \text{ and } \Psi_{2,1,+1} + \Psi_{2,1,-1} = 2iF(r,\theta)\sin\varphi$$

from which

$$\frac{\Psi_{2,1,+1}+\Psi_{2,1,-1}}{2}=F(r,\theta)\cos\varphi \text{ and } \frac{\Psi_{2,1,+1}+\Psi_{2,1,-1}}{2}=2iF(r,\theta)\sin\varphi$$

By reconstructing the expressions, we get

$$\frac{\Psi_{2,1,+1}+\Psi_{2,1,-1}}{2}=\frac{1}{4\sqrt{2\pi}}Z^{3/2}\mathbf{e}^{-Zr/2}\underbrace{r\sin\theta\cos\varphi}$$

$$\frac{\Psi_{2,1,+1}+\Psi_{2,1,-1}}{2i}=\frac{1}{4\sqrt{2\pi}}Z^{3/2}\mathbf{e}^{-Zr/2}\underbrace{r\sin\theta\sin\varphi}$$

Note in the formulas that the parts underlined by a brace represent the Cartesian coordinates x and y. We then use the notation

$$\Psi_{2p_x}=\frac{\Psi_{2,1,+1}+\Psi_{2,1,-1}}{2}=\frac{1}{4\sqrt{2\pi}}Z^{3/2}\mathbf{e}^{-Zr/2}r\sin\theta\cos\varphi$$

$$\Psi_{2p_y}=\frac{\Psi_{2,1,+1}+\Psi_{2,1,-1}}{2i}=\frac{1}{4\sqrt{2\pi}}Z^{3/2}\mathbf{e}^{-Zr/2}r\sin\theta\sin\varphi$$

Table VI-6 presents these wave functions, which represent the stationary states of the atom.

Table VI-6: Hydrogenic atom wave functions

n=1	$\Psi_{1s}(r) = \frac{1}{\sqrt{\pi}}(\frac{Z}{a_0})^{\frac{3}{2}} e^{-Z\frac{r}{a_0}}$
n=2	$\Psi_{2s}(r) = \frac{1}{4\sqrt{2\pi}}(\frac{Z}{a_0})^{\frac{3}{2}}(2 - \frac{Zr}{a_0})e^{-Z\frac{r}{2a_0}}$
	$\Psi_{2p_z}(r,\theta) = \frac{1}{4\sqrt{2\pi}}(\frac{Z}{a_0})^{\frac{5}{2}} re^{-Z\frac{r}{2a_0}} \cos\theta$
	$\Psi_{2p_x}(r,\theta,\phi) = \frac{1}{4\sqrt{2\pi}}(\frac{Z}{a_0})^{\frac{5}{2}} re^{-Z\frac{r}{2a_0}} \sin\theta\cos\phi$
	$\Psi_{2p_y}(r,\theta,\phi) = \frac{1}{4\sqrt{2\pi}}(\frac{Z}{a_0})^{\frac{5}{2}} re^{-Z\frac{r}{2a_0}} \sin\theta\sin\phi$
n=3	$\Psi_{3s}(r) = \frac{1}{81\sqrt{3\pi}}(\frac{Z}{a_0})^{\frac{3}{2}}\left(27 - 18\frac{Zr}{a_0} + 2\frac{Z^2r^2}{a_0^2}\right)e^{-Z\frac{r}{3a_0}}$
	$\Psi_{3p_z}(r,\theta) = \frac{\sqrt{2}}{81\sqrt{\pi}}(\frac{Z}{a_0})^{\frac{5}{2}}(6 - \frac{Zr}{a_0})re^{-Z\frac{r}{3a_0}} \cos\theta$
	$\Psi_{3p_x}(r,\theta,\phi) = \frac{\sqrt{2}}{81\sqrt{\pi}}(\frac{Z}{a_0})^{\frac{5}{2}}(6 - \frac{Zr}{a_0})re^{-Z\frac{r}{3a_0}} \sin\theta\cos\phi$
	$\Psi_{3p_y}(r,\theta,\phi) = \frac{\sqrt{2}}{81\sqrt{\pi}}(\frac{Z}{a_0})^{\frac{5}{2}}(6 - \frac{Zr}{a_0})re^{-Z\frac{r}{3a_0}} \sin\theta\sin\phi$
	$\Psi_{3d_{z^2}}(r,\theta) = \frac{1}{81\sqrt{6\pi}}(\frac{Z}{a_0})^{\frac{7}{2}} r^2e^{-Z\frac{r}{3a_0}}(3\cos^2\theta - 1)$
	$\Psi_{3d_{xz}}(r,\theta,\phi) = \frac{\sqrt{2}}{81\sqrt{\pi}}(\frac{Z}{a_0})^{\frac{7}{2}} r^2e^{-Z\frac{r}{3a_0}} \sin\theta\cos\theta\cos\phi$
	$\Psi_{3d_{yz}}(r,\theta,\phi) = \frac{\sqrt{2}}{81\sqrt{\pi}}(\frac{Z}{a_0})^{\frac{7}{2}} r^2e^{-Z\frac{r}{3a_0}} \sin\theta\cos\theta\sin\phi$
	$\Psi_{3d_{xy}}(r,\theta,\phi) = \frac{1}{81\sqrt{2\pi}}(\frac{Z}{a_0})^{\frac{7}{2}} r^2e^{-Z\frac{r}{3a_0}} \sin^2\theta\sin 2\phi$
	$\Psi_{3d_{x^2-y^2}}(r,\theta,\phi) = \frac{1}{81\sqrt{2\pi}}(\frac{Z}{a_0})^{\frac{7}{2}} r^2e^{-Z\frac{r}{3a_0}} \sin^2\theta\cos 2\phi$

6. Operator and wave function notation

Exact solution

The Schrödinger equation may be written in a compact form using the operators and wave functions. Recall the expression in Eq. (VI-22)

$$\nabla^2\Psi_{n,l,m}(r,\theta,\varphi) + \frac{2m}{\hbar^2}(E - V(r))\Psi_{n,l,m}(r,\theta,\varphi) = 0 \qquad \text{(VI-27)}$$

where

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

Developing expression (VI-27) as

$$\nabla^2 \Psi_{n,l,m}(r,\theta,\varphi) + \frac{2m}{\hbar^2} E\Psi_{n,l,m}(r,\theta,\varphi) - \frac{2m}{\hbar^2} V(r)\Psi_{n,l,m}(r,\theta,\varphi) = 0$$

and rearranging it, we get

$$\nabla^2 \Psi_{n,l,m}(r,\theta,\varphi) - \frac{2m}{\hbar^2} V(r)\Psi_{n,l,m}(r,\theta,\varphi) = -\frac{2m}{\hbar^2} En\Psi_{n,l,m}(r,\theta,\varphi)$$

Dividing all the expression by -2m/ħ², we get

$$\frac{\hbar^2}{2m}\nabla^2 \Psi_{n,l,m}(r,\theta,\varphi) + V(r)\Psi_{n,l,m}(r,\theta,\varphi) = E\Psi_{n,l,m}(r,\theta,\varphi)$$

Now, we may use the same procedure as for Eq. (VI-8) in the one-dimensional case. We then obtain

$$\underbrace{\left(-\frac{\hbar^2}{2m}\nabla^2 + V(r)\right)}\Psi_{n,l,m}(r,\theta,\varphi) = E\Psi_{n,l,m}(r,\theta,\varphi)$$

As with the one-dimensional case, the quantity underlined by a brace is the Hamiltonian operator and is denoted **H**. Thus, the Schrödinger equation may be written in the form

$$\hat{\mathbf{H}}\Psi_{n,l,m}(r,\theta,\varphi) = E_n \Psi_{n,l,m}(r,\theta,\varphi) \tag{VI-28}$$

with

$$\hat{\mathbf{H}} = -\frac{\hbar^2}{2m}\nabla^2 + V(r)$$

where -(ħ²/2m)**∇**² is the kinetic energy operator and **V**(r) is a function of the position is the potential energy **V** operator

$$\hat{\mathbf{H}} = \hat{\mathbf{T}} + \hat{\mathbf{V}}$$

7. The mean value of an operator

When the wave function is an eigenfunction of the Hamiltonian operator **H**, but not of another operator, **r** for example, we can calculate the mean value<**r**>$_{\psi}$ of this operator for this wave function using the following expression

$$\langle \hat{\mathbf{r}} \rangle_{\psi} = \frac{\iiint \Psi_{n,l,m}(r,\theta,\varphi)\hat{\mathbf{r}}\Psi_{n,l,m}(r,\theta,\varphi)dx}{\iiint \Psi^{*}_{n,l,m}(r,\theta,\varphi)\Psi_{n,l,m}(r,\theta,\varphi)dx} \tag{VI-29}$$

where $\Psi^{*}_{n,l,m}(\mathrm{r},\theta,\phi)$ is the complex conjugate of the function $\Psi_{n,l,m}(\mathrm{r},\theta,\phi)$.

a. Dirac notation

The stationary state solutions of the time-independent Schrödinger equation can be assimilated to vectors in Hilbert space. These kinds of vectors, called “ket” and “bra”, were imagined by Dirac so as to simplify the writing of mathematical formulas. Thus, the Schrödinger equation that we wrote above (VI-28) is written in this new formalism as

$$\hat{\mathbf{H}}|\Psi_{n,l,m}\rangle = E_n|\Psi_{n,l,m}\rangle$$

| $\Psi_{n,l,m}$> is the vector named *ket* belonging to the set of state vectors of Hilbert space. The projection of this vector into the space of positions **r**, represented by the vector bra <**r**|, gives the wave function

$$\langle \vec{\mathbf{r}}|\Psi_{n,l,m}\rangle = \Psi_{n,l,m}(r,\theta,\varphi)$$

b. Mean value of an operator

Consider for example the position operator **r**, the action of which is multiplication by the scalar function r. The eigenstates of the operator **H** are not eigenstates of **r** and so we need to calculate a mean value<index>mean value</index>. In Dirac notation, for this mean value <**r**>$_{\psi}$ we simply write

$$\langle \hat{\mathbf{r}} \rangle_{\psi} = \frac{\langle \Psi_{n,l,m}|\hat{\mathbf{r}}|\Psi_{n,l,m}\rangle}{\langle \Psi_{n,l,m}|\Psi_{n,l,m}\rangle} \tag{VI-30}$$

This results in great simplification of the formulas and this procedure may be extended to every sort of operators and states. For instance, as we shall see in the chapter dealing with molecular theory, the energy has to be calculated with a given stationary state $|\varphi_i>$, which is not an eigenstate of the Hamiltonian. Dirac notation is thus used, so that

$$\langle E_i \rangle_{\phi_i} = \frac{\langle \phi_i | \mathbf{H} | \phi_i \rangle}{\langle \phi_i | \phi_i \rangle}$$

As an example, let us consider the calculation of the mean value $<\mathbf{r}>_\psi$ on the eigenstate $| \Psi_{n,l,m}>$ of the H_2^+ molecular ion of the atomic radius. Let us choose the fundamental state $| \Psi_{1,0,0} >$, in other words state 1s. The corresponding wave function is Ψ_{1s}

$$\langle \vec{\mathbf{r}} | \Psi_{1s} \rangle = \Psi_{1s}(r, \theta, \varphi)$$

The wave function expression may be found in **Table VI-5**, i.e.

$$\Psi_{1s}(r, \theta, \varphi) = \frac{1}{\sqrt{\pi}} \left(\frac{Z}{a_0} \right)^{\frac{3}{2}} e^{-Z\frac{r}{a_0}}$$

For the H_2^+ molecular ion, we have Z = 1, and, if we use atomic units, a_0 = 1. Then, after simplification of the notation, we have

$$\Psi_{1s}(r) = \frac{1}{\sqrt{\pi}} e^{-r} \tag{VI-31}$$

Using the polar coordinates, the volume element is

$$dv = r^2 \sin\theta dr d\theta d\phi$$

and the general expression of the mean value given by Eq. (VI-30) takes the form

$$\langle \hat{\mathbf{r}} \rangle_{1s} = \frac{\iiint \Psi_{1s}(r)^* \hat{\mathbf{r}} \Psi_{1s}(r) dv}{\iiint \Psi_{1s}(r)^* \Psi_{1s}(r) dv} \tag{VI-32}$$

Since Ψ_{1s} (r) is real, we may write

$$\langle\hat{\mathbf{r}}\rangle_{1s} = \frac{\iiint \Psi_{1s}(r)^2 \hat{\mathbf{r}} dv}{\iiint \Psi_{1s}(r)^2 dv} \tag{VI-33}$$

Now, replacing Ψ_{1s} (r) by its expression (VI-31), Eq. (VI-33) becomes

$$\langle\hat{\mathbf{r}}\rangle_{1s} = \frac{\iiint \left(\frac{1}{\sqrt{\pi}} e^{-r}\right)^2 \hat{\mathbf{r}} dv}{\iiint \left(\frac{1}{\sqrt{\pi}} e^{-r}\right)^2 dv}$$

by simplifying the above equation and expressing the **r** operator, we get

$$\langle\hat{\mathbf{r}}\rangle_{1s} = \frac{\iiint e^{-2r} r dv}{\iiint e^{-2r} dv}$$

Now, we individually resolve the numerator and the denominator of this expression

$$\langle\hat{\mathbf{r}}\rangle_{1s} = \frac{\iiint e^{-2r} r dv}{\iiint e^{-2r} dv} = \frac{N}{D}$$

$$\langle\hat{\mathbf{r}}\rangle_{1s} = \frac{\int_0^\infty \int_0^\pi \int_0^{2\pi} e^{-2r} r^3 \sin\theta dr d\theta d\phi}{\int_0^\infty \int_0^\pi \int_0^{2\pi} e^{-2r} r^2 \sin\theta dr d\theta d\phi}$$

integrating and simplifying by the angular part, we get

$$\langle\hat{\mathbf{r}}\rangle_{\psi_{1s}} = \frac{\int_0^\infty e^{-2r} r^3 dr}{\int_0^\infty e^{-2r} r^2 dr} = \frac{N}{D}$$

with

$$N = \int_0^{2\pi} e^{-2r} r^3 dr \quad \text{and} \quad D = \int_0^{\infty} e^{-2r} r^2 dr$$

Let us calculate the numerator N and proceed by integration by parts. Starting with the numerator, we put

$$u = r^3 \text{ and } \quad du = 3r^2 dr$$
$$dv = e^{-2r} dr \text{ and } v = -\frac{1}{2} e^{-2r}$$

Thus, we have

$$N = \int_0^{\infty} e^{-2r} r^3 dr = -\frac{1}{2}\left(r^3 \ e^{-2r}\right)_0^{\infty} + \frac{3}{2}\int_0^{\infty} r^2 e^{-2r} dr$$
$$N = 0 + \tfrac{3}{2} D$$

so that

$$\boxed{\langle \hat{\mathbf{r}} \rangle_{1s} = \frac{3}{2}}$$

c. Fluctuations of the mean value of an operator

As in the case of the one-dimensional potential well, we can calculate the fluctuation on the average value of an operator for a three-dimensional atom, like the molecular ion hydrogen. As an example, we shall take the calculation of the fluctuation of the mean value of the atomic radius. The fluctuation Δr_{1s} is, by definition

$$\Delta r_{1s} = \sqrt{\langle \hat{\mathbf{r}}^2 \rangle_{1s} - \langle \hat{\mathbf{r}} \rangle_{1s}^2}$$

We have already calculated the second term $<r>_{1s}$. Let us calculate the first one $<r^2>_{1s}$. Thus, we have

$$\langle \hat{\mathbf{r}}^2 \rangle_{1s} = \frac{\iiint \Psi_{1s}(r)^* \hat{\mathbf{r}}^2 \Psi_{1s}(r) dv}{\iiint \Psi_{1s}(r)^* \Psi_{1s}(r) dv}$$

Passing to the analytic expressions, we get

$$\langle \hat{\mathbf{r}}^2 \rangle_{1s} = \frac{\iiint \left(\frac{1}{\sqrt{\pi}} e^{-r} \right)^2 \hat{\mathbf{r}}^2 dv}{\iiint \left(\frac{1}{\sqrt{\pi}} e^{-r} \right)^2 dv}$$

and

$$\langle \hat{\mathbf{r}}^2 \rangle_{1s} = \frac{\iiint \left(\frac{1}{\sqrt{\pi}} e^{-r} \right)^2 r^4 \sin\theta dr d\theta d\phi}{\iiint \left(\frac{1}{\sqrt{\pi}} e^{-r} \right)^2 r^2 \sin\theta dr d\theta d\phi}$$

After simplification and integration of the angular part, we get

$$\langle \hat{\mathbf{r}}^2 \rangle_{1s} = \frac{\int_0^\infty e^{-2r} r^4 dr}{\int_0^\infty e^{-2r} r^2 dr} = \frac{N}{D}$$

We shall treat the numerator N because it is of a higher degree than the denominator D. Let us write

$$u = r^4 \text{ and } \quad du = 4r^3 dr$$
$$dv = e^{-2r} dr \text{ and } v = -\tfrac{1}{2} e^{-2r}$$

so that

$$N = \int_0^\infty e^{-2r} r^4 dr = -\tfrac{1}{2} \left(r^4 e^{-2r} \right)_0^\infty + \tfrac{4}{2} \int_0^\infty e^{-2r} r^3 dr$$
$$N = 0 + 2 \int_0^\infty e^{-2r} r^3 dr$$
$$N = 2 \int_0^\infty e^{-2r} r^3 dr$$

We have already calculated this r^3 degree integral

$$\int_0^\infty e^{-2r} r^3\, dr = \tfrac{3}{2} D$$

so that

$$N = 3D$$

then

$$\langle \hat{\mathbf{r}}^2 \rangle_{1s} = 3$$

The fluctuation of the mean value of **r** is thus

$$\boxed{\Delta r_{1s} = \sqrt{3 - \frac{9}{4}} = \frac{\sqrt{3}}{2}}$$

8. Graphical representation of wave functions: the atomic orbitals (AOs)

In the previous paragraphs, we solved the Schrödinger equation of the hydrogen atom and hydrogenic atoms. We are now faced with the question of representing graphically the results concerning the eigenfunctions of the Hamiltonian, i.e. the natural atomic orbitals.

To represent the orbitals, we can use several types of representation. For example:

(i) Representation by angular distribution of the wave function modulus $\|\Psi\|$ or of the probability density Ψ^2.

(ii) Representation by isoamplitude surfaces or isodensity surfaces of probability.

(iii) Representation by radial density.

All these representations are complementary.

It is useful to have a good understanding of the way in which orbitals are constructed and now it is possible to make full use of the advanced computing abilities available to achieve beautiful representations.

a. Representation by angular distribution

Application to the 1s orbital

Given the separation of the variables, the wave function $\Psi(r,\theta,\phi)$, the solution of the Schrödinger equation, can be represented, as we saw above, by a product of three sub-functions $R(r)$,$\Theta(\theta)$ and $\Phi(\phi)$

$$\Psi(r,\theta,\varphi) = \mathbf{R}(r).\,\mathbf{\Theta}(\theta).\,\mathbf{\Phi}(\varphi)$$

In **Table VI-5**, we find some examples of stationary wave-functions. These functions can be represented graphically, but this would really require four-dimensional space.

Reduction in the number of variables

To set up the method, we take the trivial example of the 1s orbital of the hydrogen atom ($Z = 1$).

We reduce the number of variables, starting with r and φ. We vary θ, with the two other space variables being arbitrarily fixed, for example at $r = 1a_0$ and at $\varphi = \pi/2$ (yOz plane).

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

Taking into account the fixed variables, we have

$$\Psi_{1s} = \frac{1}{\sqrt{\pi}} \exp(-1) = 0.207\,553\,7$$

Angle θ variation

We vary θ from 0 to 180° and obtain **Fig. VI-a**. Then, we transfer the value of $\|\Psi_{1s}\|$ to **Fig. VI-6b**. Each vector represents a value of $\|\Psi_{1s}\|$ for a value of the angle θ.

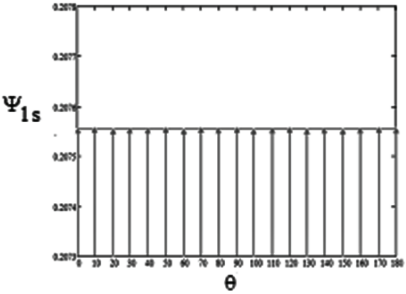


Figure VI-6a: $\|\Psi_{1s}\|$ versus θ.

In **Fig. VI-6b** we have plotted each vector $\|\Psi_{1s}\|$ on a directional graph in the corresponding direction θ_i (polar representation) and the ends of the vectors describe a semicircle.

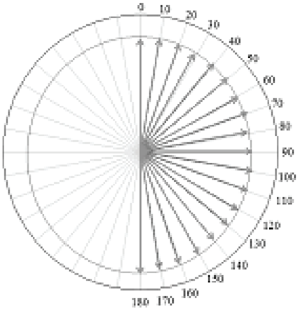


Figure VI-6b: Polar representation of $\|\Psi_{1s}\|$.

Angle φ variation

We can now vary the angle φ from 0 to 360°, which creates the spherical surface seen in **Fig. VI-6c**. The graph bears the name, like the wave function from which it comes, of orbital 1s.

The sign + in the center of the 1s orbital means that the wave function always has the same sign (+) in all directions. We say that the 1s orbital has spherical symmetry. But it is not always so, as we can see in the graph of the $2p_z$ orbital.

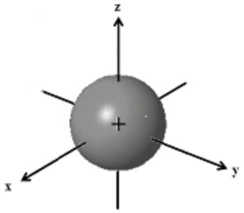


Figure VI-6c: 1s orbital by angular distribution of the amplitude function.

Application to the 2p$_z$ orbital

Reduction in the number of variables

Let us consider the 2p$_z$ orbital the expression of which is given in **Table VI-5**

$$\Psi_{2p_z} = \frac{1}{4\sqrt{2\pi}}\left(\frac{Z}{a_0}\right)^{\frac{5}{2}} r \exp\left(-\frac{Zr}{2a_0}\right) c$$

Angle θ variation

We vary angle θ from 0 to 180° and plot the value of $\|\Psi_{2pz}\|$ on the graph. Each vector represents the value of Ψ_{2pz} for the angle θ_i. The graph in **Fig. VI-7a** shows this evolution.

Fig. VI-7b presents a polar representation and we carry each vector of length $\|\Psi_{2pz}\|$ in the corresponding direction.

Then, we join the ends of each vector and get two semicircles tangential to the origin. We then report the sign that the function takes in each area of space.

Angle φ variation

We can now vary the angle φ from 0 to 360°, which generates the two spherical surfaces tangentially to O in **Fig. VI-7c**.

The graph bears the name, like the wave function from which it comes, of the 2p$_z$ orbital.

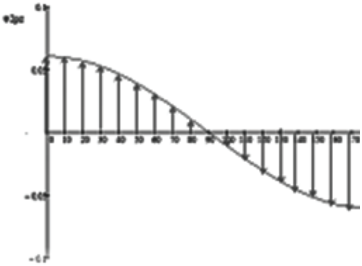


Figure VI-7a: Ψ_{2pz} versus θ.

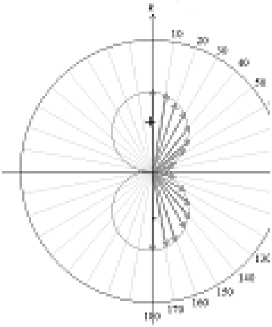


Figure VI-7b: Polar representation.

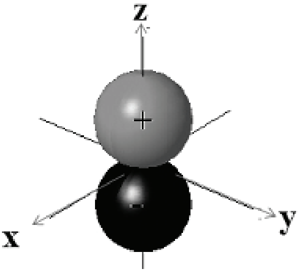


Figure VI-7c: 2pz orbital.

The signs on the lobes recall the sign of the function in this area of space.

Applying this method to other wave functions, we get the results in **Fig. VI-8**.

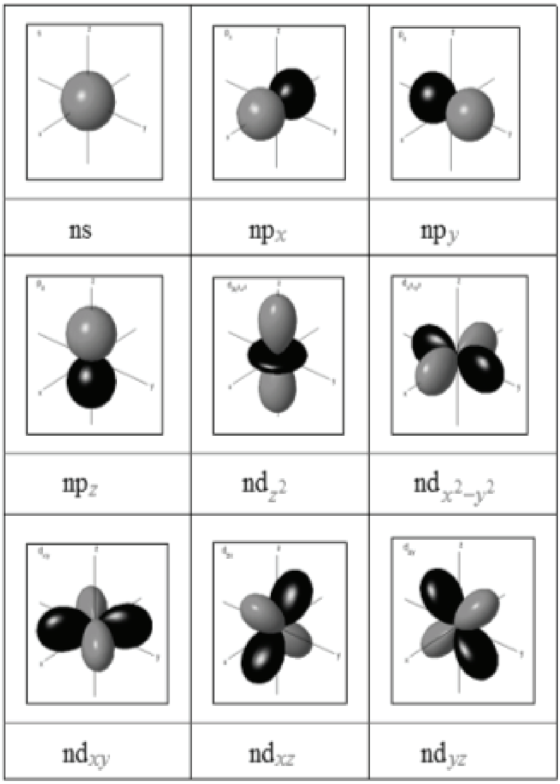


Figure VI-8: The first atomic orbitals of hydrogenic atoms represented by the angular distribution of ‖Ψ‖.

b. Representation by isodensity surfaces

This mode of representation provides information on probability density and topology. This concept is borrowed from cartography. Consider how a mountain can be represented on a map.

For this, it is necessary to cut out planes at different altitudes, h_0, h_1, h_2... and project the trace of the intersection of the mountain with these planes. We then obtain contour lines that translate a three dimensional relief into two dimensions, as shown in **Fig. VI-9**.

The construction of the isodensity curves of an orbital follows the same procedure as that already applied to the $2p_z$ orbital.

Let us start by writing the orbital expression

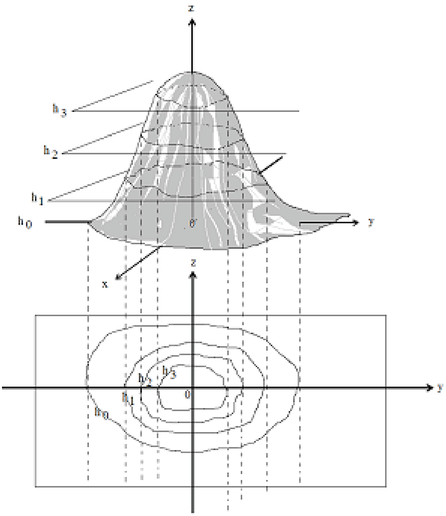


Figure VI-9: The contour line principle.

$$\Psi_{2p_z} = \frac{1}{4\sqrt{2\pi}}\left(\frac{Z}{a_0}\right)^{\frac{3}{2}} r\exp\left(-\frac{Zr}{2a_0}\right)\cos\theta$$

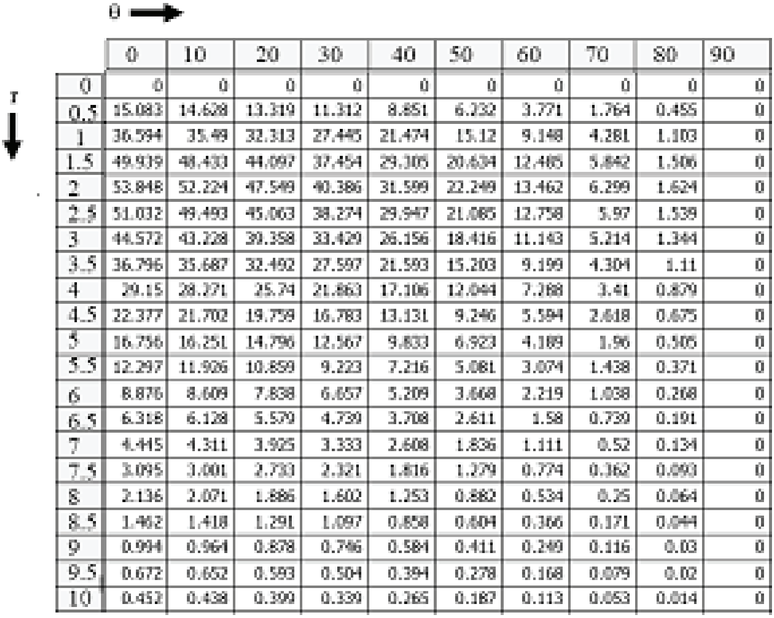
Taking Z = 1 and $a_0 = 1$, we get

$$\Psi_{2p_z} = \frac{1}{4\sqrt{2\pi}} r\exp\left(-\frac{r}{2}\right)\cos\theta \text{ so that } \Psi_{2p_z} = 6.049\times 10^{-2}\times r\cos\theta$$

We shall now represent the probability density, i.e. $(\Psi_{2pz})^2$.

1. First, let r and θ evolve simultaneously, for example $0<r<10$ and $0<\theta<90°$. We obtain the following **Table VI-7**, in which the values of $(\Psi_{2pz})^2$ are multiplied by 10^4.

Table VI-7: Values of $(\Psi_{2pz})^2$ multiplied by 10^4



θ →

r ↓

	0	10	20	30	40	50	60	70	80	90
0	0	0	0	0	0	0	0	0	0	0
0.5	15.083	14.628	13.319	11.312	8.851	6.232	3.771	1.764	0.455	0
1	36.594	35.49	32.313	27.445	21.474	15.12	9.148	4.281	1.103	0
1.5	49.939	48.433	44.097	37.454	29.305	20.634	12.485	5.842	1.506	0
2	53.848	52.224	47.549	40.386	31.599	22.249	13.462	6.299	1.624	0
2.5	51.032	49.493	45.063	38.274	29.947	21.085	12.758	5.97	1.539	0
3	44.572	43.228	39.358	33.429	26.156	18.416	11.143	5.214	1.344	0
3.5	36.796	35.687	32.492	27.597	21.593	15.203	9.199	4.304	1.11	0
4	29.15	28.271	25.74	21.863	17.106	12.044	7.288	3.41	0.879	0
4.5	22.377	21.702	19.759	16.783	13.131	9.246	5.594	2.618	0.675	0
5	16.756	16.251	14.796	12.567	9.833	6.923	4.189	1.96	0.505	0
5.5	12.297	11.926	10.859	9.223	7.216	5.081	3.074	1.438	0.371	0
6	8.876	8.609	7.838	6.657	5.209	3.668	2.219	1.038	0.268	0
6.5	6.318	6.128	5.579	4.739	3.708	2.611	1.58	0.739	0.191	0
7	4.445	4.311	3.925	3.333	2.608	1.836	1.111	0.52	0.134	0
7.5	3.095	3.001	2.733	2.321	1.816	1.279	0.774	0.362	0.093	0
8	2.136	2.071	1.886	1.602	1.253	0.882	0.534	0.25	0.064	0
8.5	1.462	1.418	1.291	1.097	0.858	0.604	0.366	0.171	0.044	0
9	0.994	0.964	0.878	0.746	0.584	0.411	0.249	0.116	0.03	0
9.5	0.672	0.652	0.593	0.504	0.394	0.278	0.168	0.079	0.02	0
10	0.452	0.438	0.399	0.339	0.265	0.187	0.113	0.053	0.014	0

2. Now, let us draw graphs $(\Psi_{2pz})^2$ for a certain number of values of the angle θ as a function of the variable r. Thus, we obtain **Fig. VI-10a**

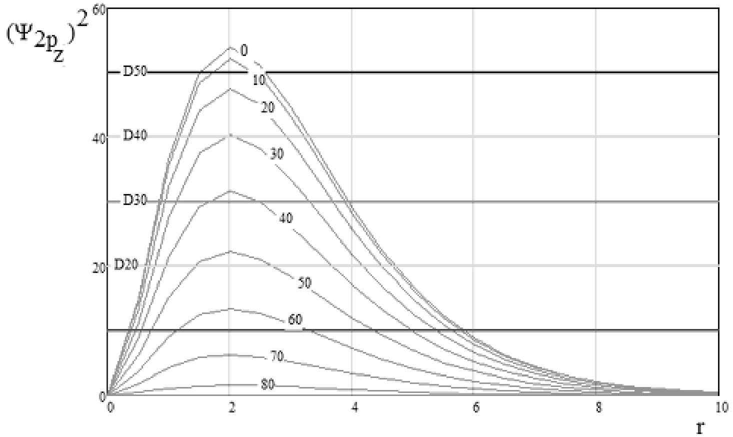


Figure VI-10a: AO $2p_Z$: Probability densities versus θ and r.

3. We draw straight lines parallel to the axis of distance at different probability densities. Each straight line intersects the curves at two points: a point close to O (point 1) and another distant from O (point 2), as given in **Table VI-8**.

Table VI-8: $2p_z$ orbital: points of same density and corresponding angles

θ	Density 50		Density 40		Density 30		Density 20		Density10	
	Point 1	Point 2	Point 1	Point 2	Point 1	Point 2	Point 1	Point 2	Point1	Point 2
0°,180°	1.504	2.595	1.098	3.297	0.833	3.942	0.608	4.699	0.384	5.820
10°,170°	1.611	2.447	1.137	3.218	0.855	3.879	0.621	4.645	0.392	5.773
20°,160°			1.279	2.951	0.931	3.680	0.666	4.478	0.415	5.629
30°,150°			1.810	2.202	1.098	3.297	0.755	4.174	0.461	5.372
40°,140°					1.578	2.491	0.934	3.673	0.543	4.972
50°,130°							1.416	2.726	0.700	4.357

Each axis corresponds to an orientation θ and will thus have 2 points—one near the origin of the referential and the other away far from it. We then join all the points with the same probability density and obtain **Fig. VI-10b**.

Here, we have varied θ from 0 to 360°, bringing out the isodensity curves.

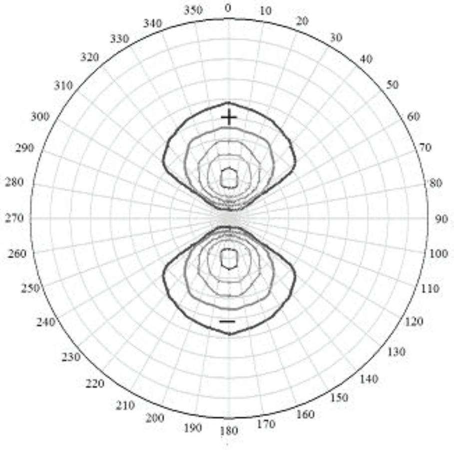


Figure VI-10b: Isodensity curves for the 2p_{z} AO.

The $2p_z$ orbital thus represented is reminiscent of an onion cut lengthwise.The + and - recall the sign of the wave function in the area of the figured space.If we now vary φ from 0 to 360°, we obtain a series of nested isodensity surfaces. The outermost surface finally gives an appearance for the $2p_z$ orbital, which is similar to that observed in the case of representation by angular distribution of the wave function (**cf. Fig. VI-7c**).

This second type of representation is more complete than the first because it simultaneously gives information on the distance and the probability density. The distance from a point on the surface to the center of the frame of reference represents the distance from the nucleus at which the density represented by the surface is obtained.

It is of course necessary to know what we are talking about when we deal with graphical representation of orbitals.

d. Representation by radial density

We now move on to the representation of the orbitals, making it possible to show the degree of exteriority of an orbital. This degree of exteriority measures the probability density along the r coordinate, in other words, the distance for which the probability density of the electron is the greatest. It also gives an idea of the radius of the atom.

Consider the volume element in the spherical polar coordinates given by Eq. (VI-21), i.e.

$$dv = r^2 \sin\theta dr d\theta d\phi$$

Let there be a wave function $\Psi(r,\theta,\varphi)$ describing a stationary state of the hydrogen atom. The probability of finding the electron inside the volume dv is

$$dP = (\Psi(r,\theta,\phi))^2 r^2 \sin\theta dr d\theta d\phi$$

Knowing that the wave function is the product of three sub-functions $R(r)\Theta(\theta)\Phi(\varphi)$ because of the separation of variables

$$dP = (R(r)\Theta(\theta)\Phi(\phi))^2 r^2 \sin\theta dr d\theta d\phi$$

We can group the parts with the same variables

$$dP = R(r)^2 r^2 dr \Theta(\theta)^2 \sin\theta d\theta \ \ \Phi(\phi)^2 d\phi$$

then, we can calculate the probability δP of finding the electron in a spherical film of radius r and thickness dr, as is shown in **Fig. VI-11a**.

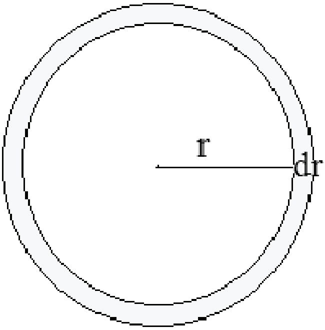


Figure VI-11a: Spherical film of radius r and thickness dr.

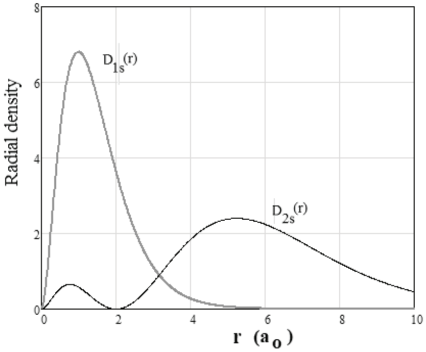


Figure VI-11b: Radial densities of the 1s and 2s orbitals.

If we integrate with respect to all the angular space, we get

$$\delta P = R(r)^2 r^2 dr \int_0^{\pi} (\Theta)^2 \sin\theta d\theta \int_0^{2\pi} \Phi(\phi)^2 d\phi$$

Of course, the angular part of the solution is normalized, i.e.

$$\int_0^{\pi} (\Theta)^2 \sin\theta d\theta \int_0^{2\pi} \Phi(\phi)^2 d\phi = 1$$

so that the elementary probability δP takes the form

$$\delta P = R(r)^2 r^2 dr \text{ so that } \frac{\delta P}{dr} = R(r)^2 r^2$$

This quantity is named the *radial probability density* and is symbolized by the function D(r), so that

$$\mathcal{D}(r) = R(r)^2 r^2$$

We can now express the radial density probability for the atomic orbitals 1s and 2s, and with the distance r expressed in a_0 units, i.e.

$$R(r)_{1s} = 2\exp(-r) \quad \text{and} \quad R_{2s}(r) = \frac{1}{2\sqrt{2}}(2-r)\exp\left(-\frac{r}{2}\right)$$

Thus, for the radial densities of the 1s and 2s orbitals we have, respectively

$$\mathcal{D}_{1s}(r) = 4r^2 \exp(-2r) \text{ and } \mathcal{D}_{2s}(r) = \frac{1}{8}r^2(2-r)^2 \exp(-r)$$

We can draw the radial densities 1s and 2s on the same graph. As can be seen in **Fig.VI-11b**, the radial density 1s has a maximum of r = 1a_0, while 2s has a maximum distance r = 5.24a_0. This shows that the exteriority of orbital 2s is larger than that of orbital 1s. Consider now the probability P of observing the electron inside a sphere of radius r centered on the nucleus. This probability is equal to

$$P = \int_0^r \mathcal{D}(r)_{ns} dr$$

For a sphere of radius 2a_0, the probability for the 1s state is

$$P = \int_0^2 \mathcal{D}(r)_{ns} dr = \int_0^2 4r^2 \exp(-2r) dr = 0.762$$

For the 2s state, this probability is weak for the same distance

$$\Psi_{2s}(r) = \int_0^2 \frac{1}{8}r^2(2-r)^2 \exp(-r) dr = 0.052$$

However, if we consider the section of the radius of the sphere between 2 a_0 and 10 a_0, it is much more important

$$\Psi_{2s}(r) = \int_2^{10} \frac{1}{8}r^2(2-r)^2 \exp(-r) dr = 0.888$$

There is good evidence that an electron in a 2s orbital has greater externality than an electron in a 1s orbital.

9. The orbital momentum and its relationship with the quantum numbers l and m

In **Fig. VI-12a**, consider the electron rotating around the nucleus in a classical model.

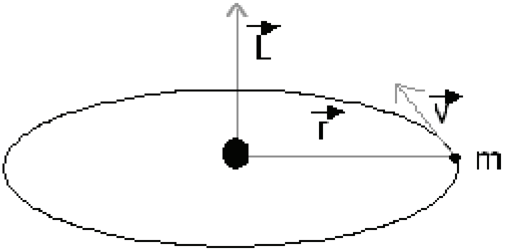
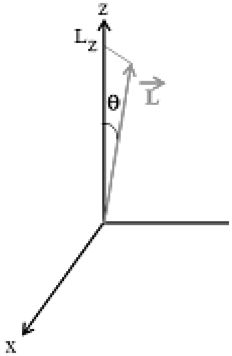


Figure VI-12a : Classical momentum.



FigureVI-12b : Momentum components.

This movement generates a vector, the angular momentum $\vec{L}$, which is perpendicular to the plane formed by the vector position $\vec{r}$ and speed $\vec{v}$, so that

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

where $\vec{p}$ is the momentum of the particle, i.e.

$$\vec{p} = m\vec{v}$$

Momentum, being a vector, is defined by its three components, L_x , L_y, and L_z, and by its square L^2, as shown in **Fig. VI-12b**.

In quantum mechanics, we can only know the momentum by the square of its length and one of the components, L_z for example, the other components being unknown.

The length of the angular momentum, i.e. the modulus of $\vec{L}$, is related to the *secondary quantum number* l by the relation

$$\left\| \vec{L} \right\| = \hbar\sqrt{l(l+1)}$$

Its component along the z axis is related to the *magnetic quantum number* m

$$L_z = m\hbar$$

then, for the angle θ, we have

$$\cos\theta = \frac{m\hbar}{\hbar\sqrt{l(l+1)}} = \frac{m}{\sqrt{l(l+}}$$

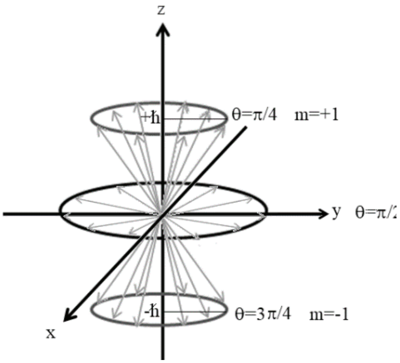


Figure VI-12c: Orbital momentum orientations.

We can thus see (**Fig. VI-12c**) that there are preferred directions for the angular momentum, for example, in the case of a 2p state (l = 1 and m = 0, +1, -1).

The angular momentum L takes 3 directions, that is to say the angular momentum is really quantized. Only one component L_z (m = -1, +1, and 0), for example, is known. The components L_x and L_y cannot be known. It follows that they can take all the values. This uncertainty is expressed by the tracing of the cones (θ = π/4) and (θ = 3π/4) and of the central disc (θ = 0). There are therefore 2l+1 possible orientations of the orbital angular momentum.

10. The 4th quantum number: spin

Since 1920, the notion of spin has presented a difficult problem to solve.

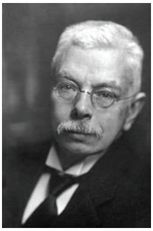
a. The anomalous Zeeman effect[7]

The Zeeman effect concerns the hyperfine structure of observed spectral lines and designates the separation of a defined energy level of an atom or a molecule into several sublevels of distinct energies under the effect of an external magnetic field, as depicted in **Fig. VI-13**. There is therefore a

---

[7] Peter Zeeman (1865-1943). Dutch physicist known for his work on the emission of light by excited atoms, the propagation of light signals in moving media, and the discovery of the effect that bears his name. He won the Nobel Prize in Physics in 1902.

degeneration in the energy levels. This effect is easily observed using spectroscopy: when a light source is immersed in a static magnetic field, its spectral lines separate into several components.



P. Zeeman

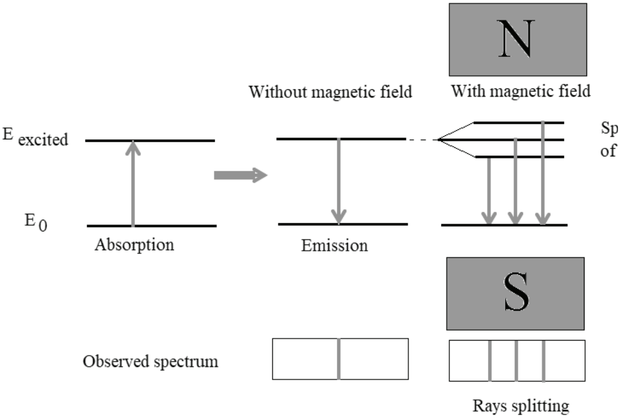


Figure VI-13: Zeeman effect.

b. The Stern-Gerlach experiment (1922)

The Stern[8]-Gerlach[9] experiment is an experiment in quantum mechanics that highlights the existence of spin. The experiment was developed by Otto Stern and Walther Gerlach in February 1922 and is described in **Fig. VI-14**.

It consists of passing silver atoms through a non-uniform magnetic field in a vertical direction. Silver atoms in their ground state have zero angular momentum and their associated orbital magnetic moment is also zero. As such, the beam should not be influenced by the magnetic field.

However, experience shows that the beam is split in two parts. One cannot attribute this result to an orbital kinetic momentum and has to explain this phenomenon by introducing an essentially quantum observable: the kinetic moment of spin, or more simply “spin”. Spin is comparable to intrinsic

---

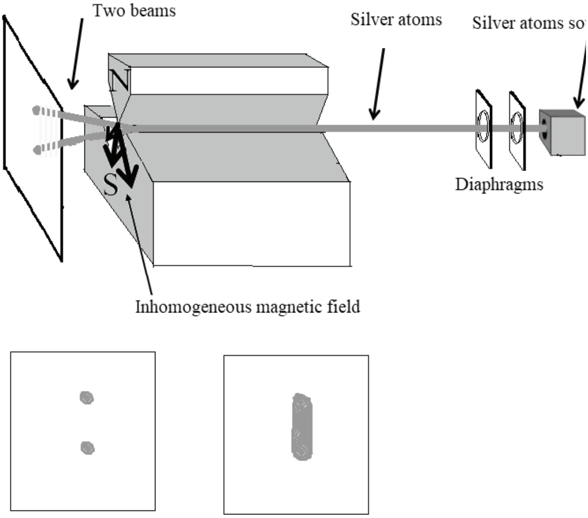
[8] Otto Stern (1888-1969). German physicist known for his discovery of the magnetic moment of the electron. He won the Nobel Prize in Physics in 1943.

[9] Walther Gerlach (1889-1979). German physicist known for his discovery of the magnetic moment of the electron.

angular momentum, but the classical analogy is very limited as it makes no sense to speak of an electron rotating around its axis.

In the case of the silver atom, its separation into two beams reveals that there are two possible states for the spin of the atom. The study of spin operators as angular momentum operators leads to the value 1/2 (in units of $\hbar$) for the total spin, to which the two possible states (projections) correspond: +1/2 and -1/2.

O. Stern



Quantum physics

Classical physics

Figure VI-14: Stern-Gerlach experiment.

W. Gerlach

c. The concept of spin

S. Goudsmit

G. Uhlenbeck

The discovery of the concept of spin by Goudsmit[10] and Uhlenbeck[11] in September 1925 was revolutionary. In an article published in the journal Nature[12] they presented their ideas, providing the origin of “spintronics”.

In quantum physics spin is an intrinsic property of particles, just like mass or electric charge. Like other quantum quantities, its measurement gives discrete values and is subject to the principle of uncertainty. It is the only quantum observable that does not have a classical equivalent, unlike, for example, the position, the pulse, or the energy of a particle.

It is, however, often assimilated to the intrinsic angular momentum of the electron, just like the intrinsic magnetic moment (of spin), and both are confused under the term of spin.

Spin has important theoretical and practical implications and has influenced practically everything in physics. It is responsible for the magnetic spin moment and therefore for the anomalous Zeeman effect (sometimes incorrectly described as “abnormal”) that results.

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[10] Samuel Goudsmit (1902-1978). Dutch-American physicist known for his work on spin with Georges Uhlenbeck.

[11] George Uhlenbeck (1900-1988). Dutch-American physicist known for his work on spin in collaboration with Samuel Goudsmit.

[12] G. E. Uhlenbeck, S. Goudsmit, “Spinning Electrons and the Structure of Spectra”, Nature, vol. 117, 264-265, February 20, 1926.

W. Pauli

P. A. M. Dirac

Based on W. Pauli's[13] non-relativistic spin system, in 1928, Paul Dirac[14] developed a relativistic equation describing the electron and spin. Today, this is called the Dirac equation.

This equation describes the behavior of elementary particles of half-integer spins, like electrons. Dirac sought to transform the Schrödinger equation in order to make it invariable to the action of the Lorentz group, in other words, to make it compatible with the principles of special relativity.

This equation naturally takes into account the notion of spin, which was developed shortly before, and made it possible to predict the existence of antiparticles.

To schematize, we can say that when we introduce a fourth coordinate in the Schrödinger equation, the four quantum numbers relative to the movement of the electron, we must solve a four-dimensional system. It must correspond to these four dimensions, i.e. four quantum numbers:

(i) the *principal quantum number n* related to the energy of the electron;

(ii) the *secondary quantum number l* related to the magnitude of the orbital angular momentum;

(iii) the *magnetic quantum number m*, related the value of the projection of the angular momentum on the z axis;

(iv) the *4th quantum number, the magnetic quantum number of spin s*, the characteristics of which will be described further.

---

[13] Wolfgang Pauli (1900-1958). Austrian physicist known for his definition of the principle of exclusion in quantum mechanics, or the Pauli principle, which earned him the 1945 Nobel Prize in Physics.

[14] Paul Adrien Maurice Dirac (1902-1984) was a British mathematician and physicist. He is one of the fathers of quantum mechanics and predicted the existence of antimatter. With Erwin Schrödinger, he was a co-winner of the Nobel Prize in Physics in 1933 "for the discovery of new and useful forms of atomic theory".

In **Fig. VI-15a**, we compare the situation of an electron moving around the nucleus and that of an electron “rotating” by itself.

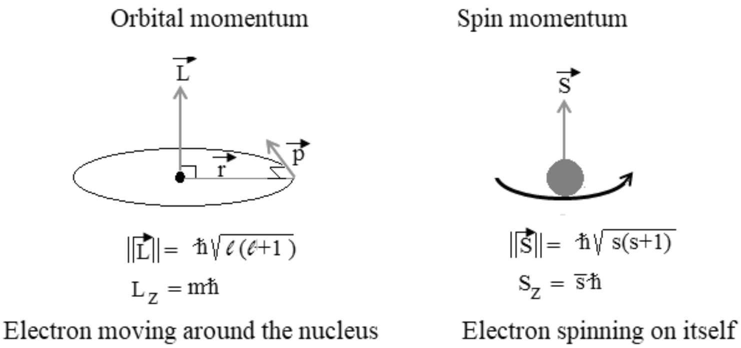


Figure VI-15a: Comparison between orbital and spin angular momentum.

In both cases a kinetic momentum is generated. We have already seen that orbital angular momentum and spin angular momentum are comparable, leading to two new quantum numbers: the quantum number of spin s and the magnetic quantum number of spin. s is related to the modulus of the angular spin momentum while $\bar{s}$ is related to the projection along z of the spin angular momentum.

Unlike ℓ, the spin quantum number s only takes the value 1/2. It characterizes the nature of the corpuscle, of which there are two elementary types: fermions and bosons. Recall that fermions are corpuscles with a half-integer quantum number of spin. The bosons, on the other hand, correspond to particles with a quantum number of whole spin (a photon for example).

Thus, by continuing the correspondence with the orbital angular momentum, we can say that there will be 2s+1 possible orientations for the spin angular momentum. As s only takes the value 1/2, it follows that the possible orientations correspond to s = +1/2 and s = -1/2, as can be seen in **Fig. VI-15b**. For the same reasons as in the case of the orbital angular momentum,

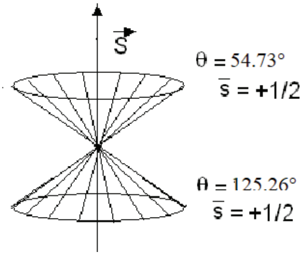


Figure VI-15b: Orientations of electronic spin momentum.

the other components of $\vec{S}$ are not known.

To conclude, we can state that the spin momentum can only have 2 orientations characterized by the values of the electron magnetic moment quantum number s = ±(1/2).

VI-III. Extension of the Model to Polyelectronic Atoms

The model of stationary states of hydrogenic atoms can be extended to atoms with several electrons; however, we should remain aware that this model is only an approximation. The difference between hydrogenic atoms and polyelectronic atoms lies in the presence of the other electrons. The latter result in such perturbation that the resolution of the Schrödinger equation is impossible. This is due to the existence of Coulomb repulsion energy between electrons whose respective positions cannot be known.

Nevertheless, the experimentally derived facts show that an approximation can be made, leading to a satisfactory description of polyelectronic atoms within the framework of the hydrogenic atom model.

1. General principles

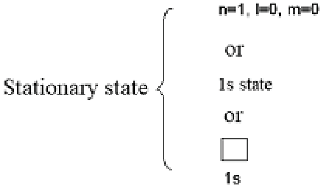
The electrons of a polyelectronic atom are distributed in energy levels, which are, more or less, the stationary states of hydrogenic atoms.

a. Orbital box notation

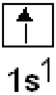
By definition, an *orbital box* is a stationary state defined by three quantum numbers: n, ℓ, and m.

Orbital box notation is used in **Table VI-8** to represent these states in addition to two further ones.

Table VI-8: Stationary state notations



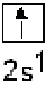
In this stationary state, an electron can exist with a magnetic quantum number of spin equal to +1/2. We say that we have an orbital box occupied by an electron with spin 1/2:



This is the electronic configuration of the hydrogen atom in its ground state.

Examples of other possible states include

n = 2; ℓ = 1; m=0; s = +1/2, for which we write:

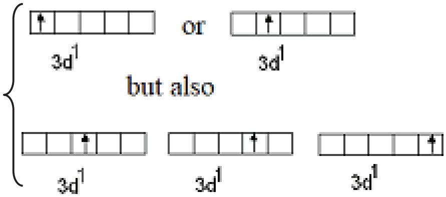


This is an excited state of the hydrogen atom.

Another example is the state characterized by n = 2; ℓ = 1; m = 0, ±1; s = +1/2:

For the same value of l corresponding to a given value of n, the orbital boxes are placed in a contiguous manner to mark the triple degeneracy of the state l = 1 (same energy for contiguous orbital boxes).

Other cases: n = 3; ℓ = 3; m = 0, ±1; ±2; s = +1/2, which will be written:



In conclusion, the orbital boxes corresponding to the same value of ℓ are shown joined together. Their number represents the different values of m, that is to say the different orientations of the orbital angular momentum for the same value of ℓ. These stationary states correspond to the same energy value.

b. The Pauli exclusion principle

According to the laws of classical physics, an atom having several electrons should have all of its electrons in the lowest level, i.e. level 1s.

If this were the case, atoms in their ground state should have an identical radius and identical physicochemical properties.

However, this is not the case meaning that the electrons are not all in the same energy level. This leads us to state the principle, known as the *Pauli exclusion principle*, that:

"Two electrons belonging to the same atom cannot have four identical quantum numbers. They must differ by at least one quantum number value".

Let us consider two electrons belonging to the same atom. Suppose that these electrons are described by three quantum numbers, n, l, and m, identical and placed two by two

$$n_1 = n_2 \;;\; l_1 = l_2 \;;\; m_1 = m_2$$

If this is the case, then we must should have

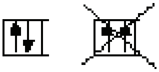
$$\bar{s}_1 \neq \bar{s}_2$$

Since there are only two possible values for $\bar{s}$, we have

$$\bar{s}_1 = +\frac{1}{2} \text{ and } \bar{s}_2 = -\frac{1}{2} \text{ or vice-versa}$$

According to the Pauli exclusion principle, we deduce that there cannot be more than two electrons per stationary state, that is to say per orbital box.

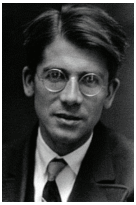
Example: two electrons in a 1s state:



We can thus predict the maximum number of electrons per energy level, as in **Table VI-9**.

Table VI-9: Quantum numbers and atomic shells

$n = 1, l = 0, m = 0 \quad \Rightarrow$	maximum 2 electrons	K shell
$n = 2, l = 0 \quad \Rightarrow$	maximum 2 electrons	
$n = 2, l = 0, m = 0, \pm 1 \quad \Rightarrow$	maximum 6 electrons	
	Total 8 electrons	L shell
$n = 3, l = 0 \quad \Rightarrow$	maximum 2 electrons	
$n = 3, l = 1, m = 0, \pm \quad \Rightarrow$	maximum 6 electrons	
$n = 3, l = 2; m = 0, \pm 1, \pm 2 \quad \Rightarrow$	maximum 10 electrons	
	Total 18 electrons	M shell



F. Hund

c. Hund's rule

We can distinguish three simple rules, which are used to determine what the fundamental spectroscopic term of the atom considered is. They were proposed by Hund[15].

The first of these rules is particularly important in chemistry and we often refer to it as "Hund's rule".

Hund's rule:

If two electrons belonging to the same atom have different quantum numbers, n, l, and m, but their energies are equal or very close, then their magnetic quantum numbers of spin $\bar{s}$ will be equal.

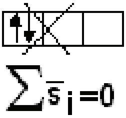
Electrons 1		Electron 2
Energy E_1		Energy E_2
n_1	$\neq$	n_2
l_1	$\neq$	l_2
m_1	$\neq$	m_1
If $E_1 = E_2$	then	$\bar{s}_1 = \bar{s}_2$

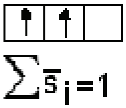
---

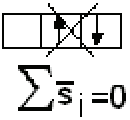
[15] Friedrich Hund (1886-1997). German physicist known for his work on the rule that bears his name and his contributions to the study of the tunnel effect.

Consequently, for a particular case where we have

$$n_1 = n_2 = 2$$
$$l_1 = l_2 = 1$$





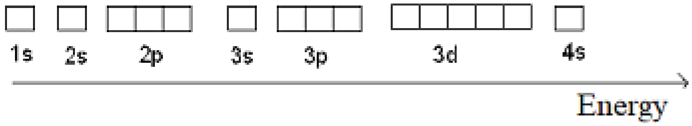


Hund's rule is respected in the middle case where we find the most stable arrangement, which corresponds to the maximum sum of the magnetic spin quantum numbers.

d. The Pauli construction principle and Klechkowski's rule[16]

The Pauli construction principle proposes that one builds the "skeleton" of the configuration by placing the orbital boxes in the natural order of growth of the quantum numbers, which corresponds to the increasing order of the energy levels. For reasons of space, the levels are represented horizontally with increasing energy from left to right.

For example, we arrange the orbital boxes in the following manner.



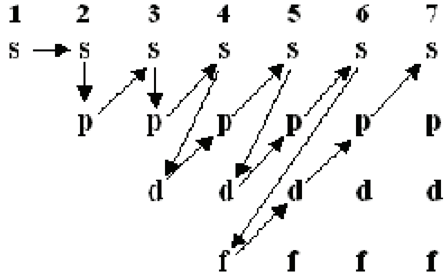
---

[16] Also called Madelung's rule or Aufbau principle

Klechkowski's rule[17]

As given in **Table VI-10**, this is a mnemonic process to remember the order of filling the orbital boxes and not the energetic order of energy levels.

Table VI-10: Klechkowski's rule

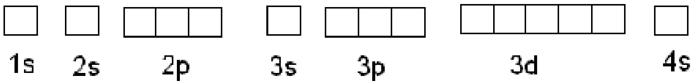


So we shall follow the order given by this table to fill the orbital boxes already arranged.

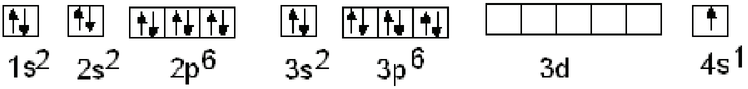
e. The writing of electronic structures

Let us take the example of potassium (K).

1. The empty orbital boxes are disposed in the number necessary to contain the electrons (the Pauli construction principle).



2. The electrons are placed, starting from the left and following the different rules (the Pauli exclusion principle, Hund's rule, and Klechkowski's rule).



The 3d sub-shells remain unoccupied. These are virtual levels. It is possible to not represent them and write the configuration as follows

---

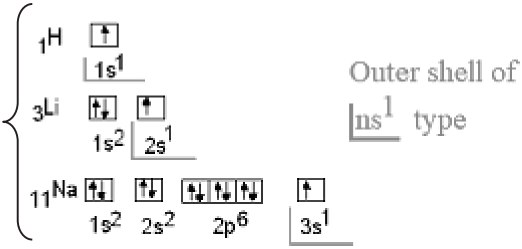
[17] Vsevolod Kletchkovski (1900-1972). Russian chemist known for his work on radioisotopes and for the rule that bears his name.

2. Electronic structures and periodic classification

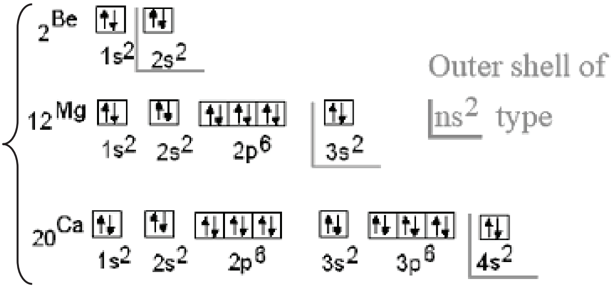
We previously saw how the periodic classification was based on the periodicity of the physicochemical properties.

Groups

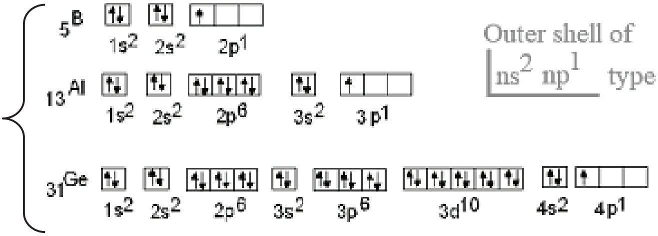
Hydrogen and alkalines



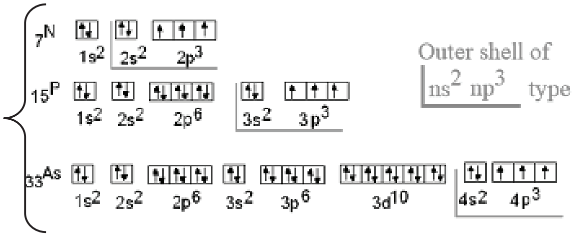
Alkaline-earth



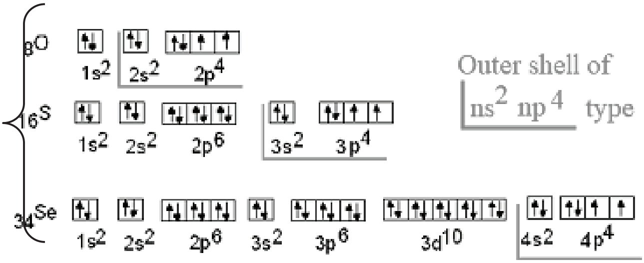
Boron group



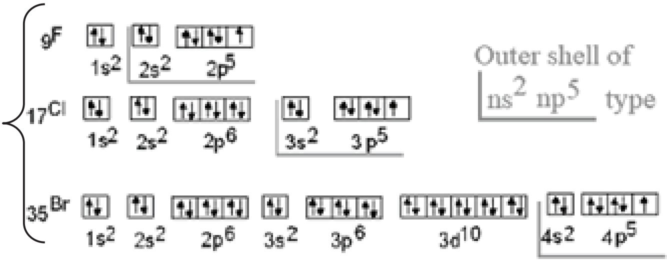
Nitrogen group



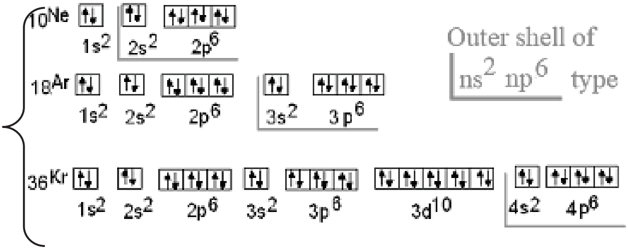
Oxygen group



Halogen group

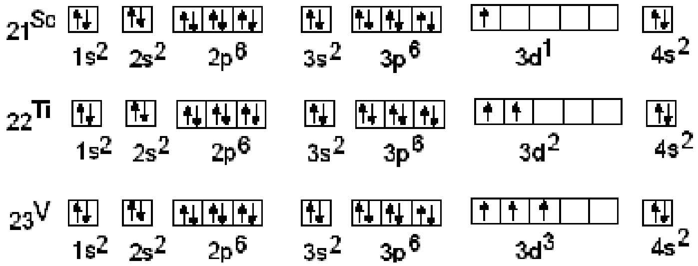


Rare gas group

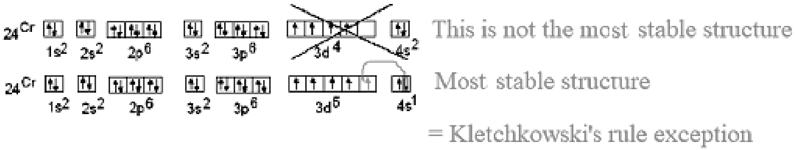


Transition elements

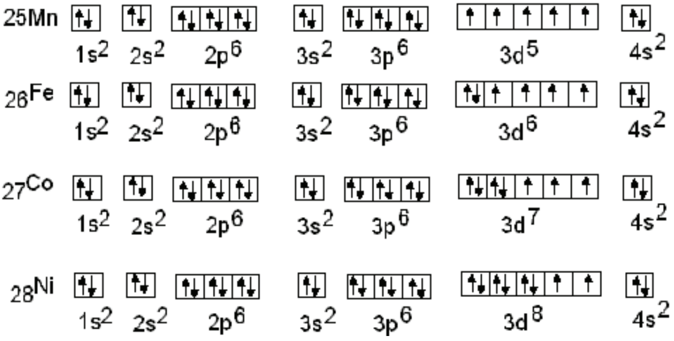
Located between the elements of block s and those of block p, the elements of block d are also called “transition elements” because they mark the transition between blocks s and p. They are characterized by the filling of their d sub-shells and constitute a *category* of elements and *not a family*.



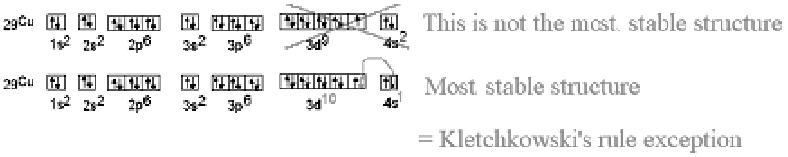
For chromium, we see a peculiarity.



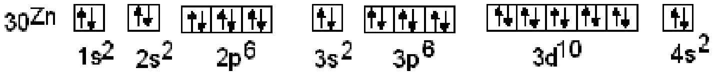
The other transition elements follow Klechkowski's rule.



However, for copper there is also a peculiarity

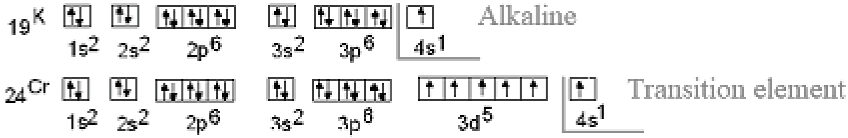


Finally, zinc corresponds to a normal filling.



We must be aware of possible confusion regarding the name of the family to which an element belongs due to the similarity of their outer shells.

See, for example, the following elements, which have the same type of outer shells.



Always check whether the d orbital boxes just below the outer shell are occupied or not before saying whether or not it is an alkaline.

3. The periodicity of physicochemical properties enlightened by electronic configurations

a. Experimental evolution of the first ionization potential

The first ionization potential (IP_1) and second ionization potential (IP_2) (or ionization energies) of the elements have been measured from the first to the fourth period of the periodic table.

The *first ionization potential* is, by definition, the energy that must be supplied to an atom to extract an electron from it

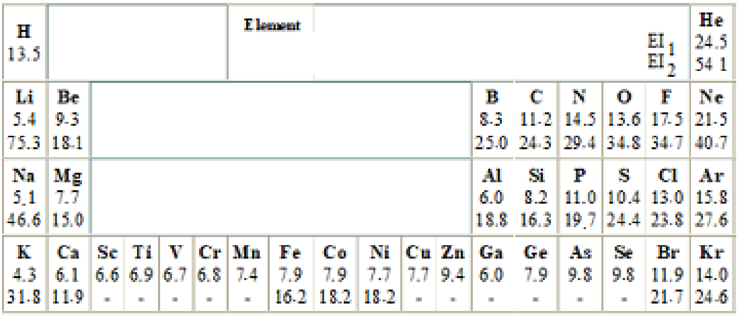
$$IP_1 + X \rightarrow X^+ + e^-$$

The *second ionization potential* is the energy that must be supplied to the ion X^+ to extract an electron, such as

$$IP_2 + X^+ \rightarrow X^{2+} + e^-$$

Table VI-11 gives the first and second ionization potentials, expressed in electron volts, for each element.

Table VI-11: first and second ionization potentials (in eV)



H 13.5						Element										EI$_1$ EI$_2$	**He** 24.5 54.1
Li 5.4 75.3	**Be** 9.3 18.1											**B** 8.3 25.0	**C** 11.2 24.3	**N** 14.5 29.4	**O** 13.6 34.8	**F** 17.5 34.7	**Ne** 21.5 40.7
Na 5.1 46.6	**Mg** 7.7 15.0											**Al** 6.0 18.8	**Si** 8.2 16.3	**P** 11.0 19.7	**S** 10.4 24.4	**Cl** 13.0 23.8	**Ar** 15.8 27.6
K 4.3 31.8	**Ca** 6.1 11.9	**Sc** 6.6 -	**Ti** 6.9 -	**V** 6.7 -	**Cr** 6.8 -	**Mn** 7.4 -	**Fe** 7.9 16.2	**Co** 7.9 18.2	**Ni** 7.7 18.2	**Cu** 7.7 -	**Zn** 9.4 -	**Ga** 6.0 -	**Ge** 7.9 -	**As** 9.8 -	**Se** 9.8 -	**Br** 11.9 21.7	**Kr** 14.0 24.6

Experimental evolution

In **Fig. VI-16** we can trace the evolution[18] of IP_1 versus the atomic number Z.

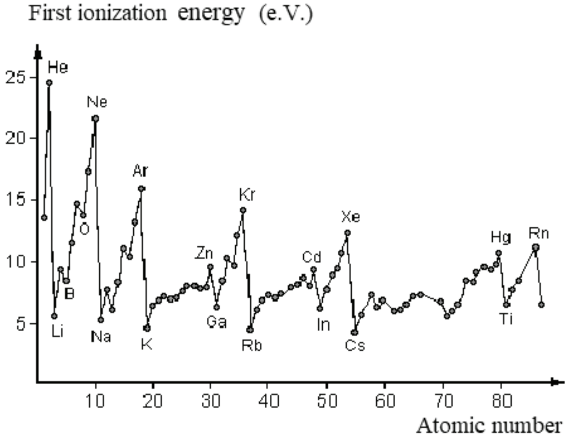


Figure VI-16: First ionization potential versus the atomic number Z.

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[18] From https://cdn.britannica.com/38/6038-050-DC1FDAEA/ionization-energy-element-atom-electron-energies-nonmetal.jpg

b. Qualitative explanation of IP_1 evolution versus the atomic number Z

We can qualitatively explain this evolution by assimilating the ionization energy IP_1 to the energy of an electron belonging to the outer shell with a changed sign.

Since the energy of an electron belonging to the outer shell is characterized by the quantum number n, for a polyelectronic atom we have

$$E(n) = -\frac{13.6}{n^{*2}} Z^{*2}$$

where n* denotes the effective quantum number of this electron and Z* is the effective atomic number with which an electron of this outer shell “sees” the nucleus.

The effective atomic number Z* depends on the environment of a given electron, as well as the effective quantum number n*.

These parameters are determined by computation. For the moment, as we wish to understand the evolution of IP_1, we shall content ourselves with using the usual values given by the energy formula of the levels of the hydrogenic atoms for these quantities, namely

$$E(n) = -\frac{13{,}6}{n^2} Z^2$$

Given what we have said above, IP_1 can be assimilated to -E(n), where n is the principal quantum number of the outer shell

$$IP_1 \backsim +\frac{13{,}6}{n^2} Z^2$$

We therefore see why, overall, IP_1 increases within a period: when we travel through a period the main quantum number of the peripheral shell remains constant. The variation of IP_1 is then dictated by the evolution of the atomic number Z. However, as Z increases from alkalis to rare gases in a period, we can understand why IP_1 correlatively increases.

$$IP_1 = \frac{13{,}6}{n^2} Z^2 \text{ is increasing because } n\text{=constant and } Z \nearrow$$

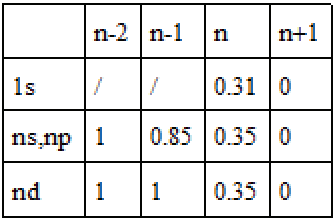
When we change the period, Z continues to increase; however, this increase will be controlled by the increase in the quantum number of the outer shell, which increases by one unity. This results in a denominator that increases sharply and, therefore, by a decrease in IP_1, which falls when one passes from the rare gas of one period to the alkaline of the following period

$$IP_1 = \frac{13,6}{n^2}Z^2 \text{ is decreasing because } n \nearrow$$

c. A more quantitative explanation: Slater's rule

J. Slater

Table VI-12: Screen constants



	n-2	n-1	n	n+1
1s	/	/	0.31	0
ns,np	1	0.85	0.35	0
nd	1	1	0.35	0

According to Slater[19], the electrons of the internal shells and those of the same shell as the considered electron, characterized by the quantum number n, exert a *screen effect*. The electron being studied will then not "see" the nucleus with its Z protons, but rather with a lower number, much like a person wearing a wide-brimmed hat in a movie theater can hide the screen from those next to or behind them. Slater evaluated these effects as follows.

The screen constants σ_i are given in **Table VI-12**, where n represents the principal quantum number of the electron of a given shell; n-1 represents the situation in the level below that of the considered electron; and n-2, … etc., represent deeper situations. Their values depend on the situation of electrons other than the one considered.

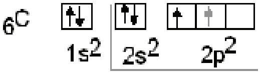
---

[19] John Clarke Slater (1900-1976). American physicist and theoretical chemist. He devised a relevant method for the expression of antisymmetric wave functions for fermions in the form of determinants. These functions are known as *Slater determinants*. John Slater stood out again in 1930 by introducing exponential functions to describe atomic orbitals. These functions are now known as Slater orbitals.

The values of σ_i are proton charge fractions, which are deducted from the atomic number Z

$$Z^* = Z - \sum \sigma_i$$

Thus, if we wish to know the effective number of an electron in the outermost shell of carbon, we start by identifying the electron in the environment that we wish to determine, represented here in gray.



Then, we deduce from the atomic number of carbon (Z = 6) the sum of the screen constants of the electrons of the environment of the red electron, which can be grouped as follows:

- electrons belonging to the same shell as it (shell n = 2): of which there are 3;
- electrons from shell n-1, i.e. shell n = 1: of which there are 2.

$$Z^* = 6 - 0.35 \times 3 - 0.85 \times 2 = 3.25$$

We can deduce that the energy of an electron in the outer shell of carbon will be

$$E(2) = -13.6\frac{(3.25)^2}{2^2} = -35.913 \ e.V$$

Slater extended this method of calculating the energies of electrons to the more precise calculation of the first ionization potential IP_1

$$IP_1 + X \rightarrow X^+ + e^-$$

He considered the ionization energy or ionization potentials given by the relation

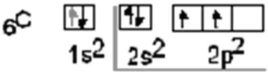
$$IP_{1_X} = E_{X^+} - E_X$$

where E_{X^+} is the energy of the ion X^+ and E_X is that of the atom X. Let us take the example of carbon.

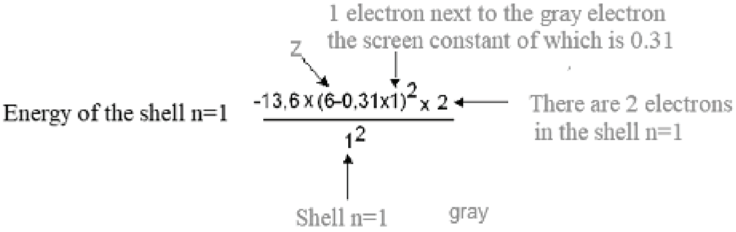
First calculate the energy of the atom C

$$E_X = \text{Energy of the shell } n = 1 + \text{Energy of the shell } n = 2$$

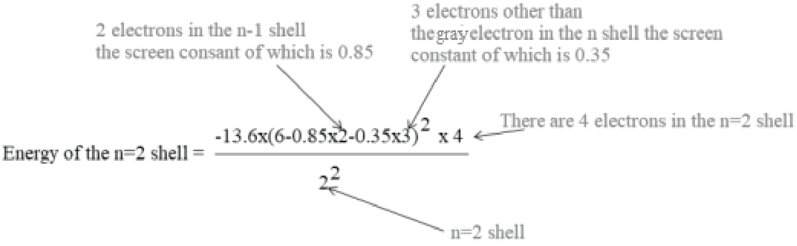
Energy of the shell n = 1: energy of an electron (gray electron) of this shell × the number of electrons in this shell, i.e. 2.



The energy of the “gray” 1s electron in this shell is found using the screen constants, i.e.



Energy of the n = 2 shell = energy of an electron of this shell × the number of electrons in this shell, i.e. 4 (no distinction is made between s and p electrons).

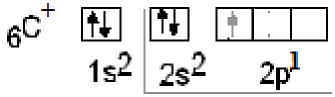


Therefore, we have

$$E_C = -\frac{13.6}{1^2}[6 - 0.31 \times 1]^2 \times 2 - \frac{13.6}{2^2}[6 - 0.85 \times 2 - 0.35 \times 3]^2 \times 4$$

Second: calculate the energy of the ion C^+

Consider the outer shell of this ion



There will be one electron less on the shell n = 2; hence, the calculation

$$E_{C^+} = -\frac{13.6}{1^2}[6-0,.31\times 1]^2\times 2-\frac{13.6}{2^2}[6-0.85\times 2-0.35\times 2]^2\times 3$$

Ultimately, for the IP_1 of carbon we have

$$IP_{1_C} = E_{C^+}-E_C = \frac{13.6}{2^2}\Big[[6-0.85\times 2-0.35\times 3]^2\times 4-[6-0.85\times 2-0.35\times 2]^2\times 3\Big]$$

which is

$$IP_{1_C} = 11.46\ e.V$$

and the result can be compared to the experimental value of 11.20 eV.

Qualitative improvement of the result

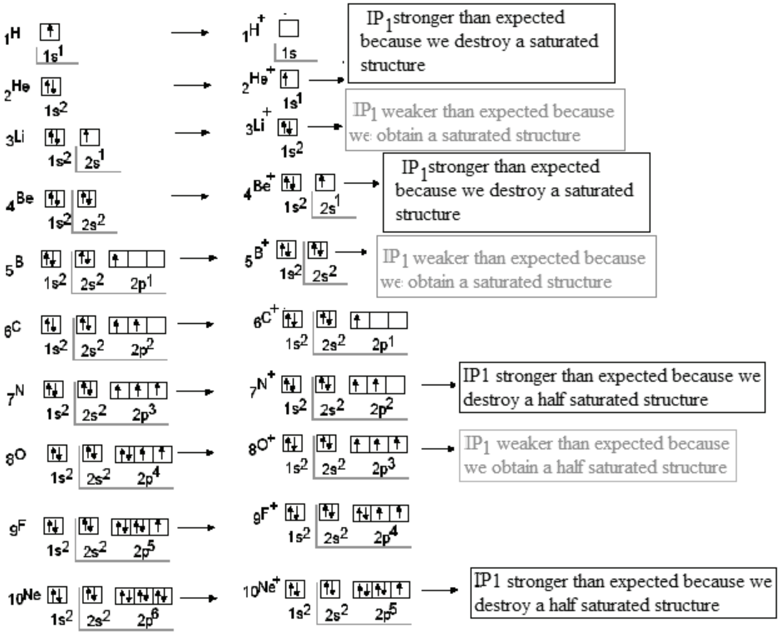
However, calculation of the Slater ionization energies does not address local variations in IP_1; it only presents the general evolution. To explain “accidents” in global evolution, we must engage in intuitive reasoning.

It is an experimentally proven fact that the energies of saturated or half-saturated shells have a certain stability. As such, it takes more energy to extract an electron from a saturated or half-saturated structure than it does to extract an electron from a structure that does not have these characteristics.

We should also note that, if, by extracting an electron from a structure, we obtain a saturated structure, it will take less energy than expected.

We can therefore predict these corrections and match them to the evolution of IP_1 by looking at the electronic structures before and after ionization, as shown in **Table VI-13**.

Table VI-13: Qualitative explanation of accidents during the evolution of IP_1



d. Electron affinity (EA)

Electron affinity, denoted EA or A, is the amount of energy released following the capture of an electron by an isolated atom. The greater the electronic affinity, the more energy the electron captured by the atom has and the more stable the resulting negative ion. A negative electronic affinity, on the contrary, means that it would be necessary to supply energy to the atom to attach an electron to it.

$$X + 1e^{-} \rightarrow X^{-} + EA$$

By definition[20], the electron affinity is

$$E_{EA} = (E_X - E_{X^-})$$

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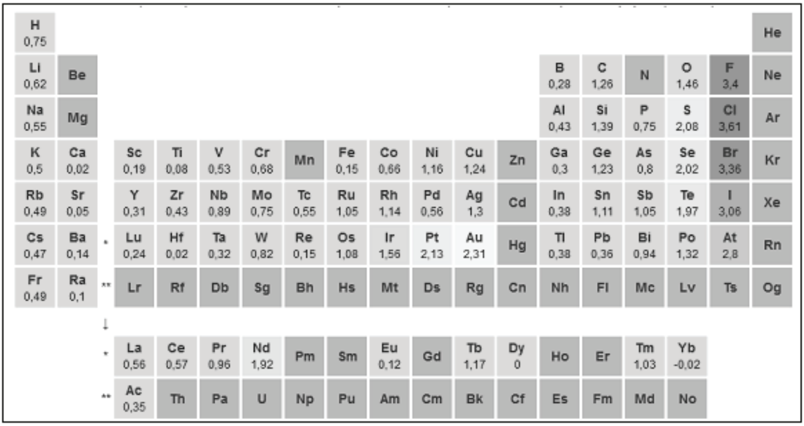
[20] CRC Handbook of Chemistry and Physics, 91st Edition (Internet Version 2011), W. M. Haynes, ed., CRC Press/Taylor and Francis, Boca Raton, FL., 10-147.

Fig. VI-17a gives the experimental EA values.



H 0,75																		He
Li 0,62	Be												B 0,28	C 1,26	N	O 1,46	F 3,4	Ne
Na 0,55	Mg												Al 0,43	Si 1,39	P 0,75	S 2,08	Cl 3,61	Ar
K 0,5	Ca 0,02		Sc 0,19	Ti 0,08	V 0,53	Cr 0,68	Mn	Fe 0,15	Co 0,66	Ni 1,16	Cu 1,24	Zn	Ga 0,3	Ge 1,23	As 0,8	Se 2,02	Br 3,36	Kr
Rb 0,49	Sr 0,05		Y 0,31	Zr 0,43	Nb 0,89	Mo 0,75	Tc 0,55	Ru 1,05	Rh 1,14	Pd 0,56	Ag 1,3	Cd	In 0,38	Sn 1,11	Sb 1,05	Te 1,97	I 3,06	Xe
Cs 0,47	Ba 0,14	*	Lu 0,24	Hf 0,02	Ta 0,32	W 0,82	Re 0,15	Os 1,08	Ir 1,56	Pt 2,13	Au 2,31	Hg	Tl 0,38	Pb 0,36	Bi 0,94	Po 1,32	At 2,8	Rn
Fr 0,49	Ra 0,1	**	Lr	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn	Nh	Fl	Mc	Lv	Ts	Og
		↓																
		*	La 0,56	Ce 0,57	Pr 0,96	Nd 1,92	Pm	Sm	Eu 0,12	Gd	Tb 1,17	Dy 0	Ho	Er	Tm 1,03	Yb -0,02		
		**	Ac 0,35	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No		

Figure VI-17a: Experimental EAs of elements.

If we graph the EAs of various elements against their atomic numbers Z (**Fig. VI-17b**), we can see that the minimum electronic affinities occur for alkaline earth metals and rare gases, while the maximums occur for halogens. This is understandable if we consider that the addition of an electron to a saturated or semi-saturated shell is contrary to stability and therefore the electron affinity of this element will be low or zero. Conversely, if a captured electron reinforces the stability of a shell by making it saturated or half saturated, the electron affinity will be high.

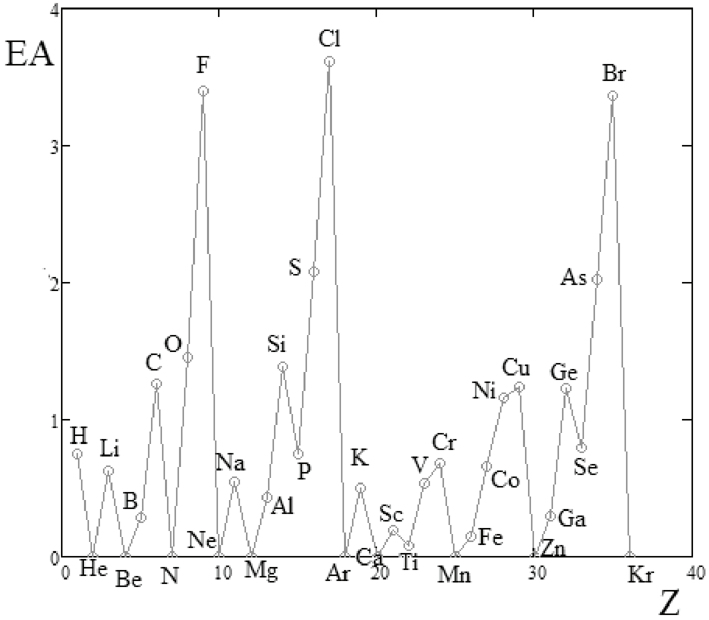
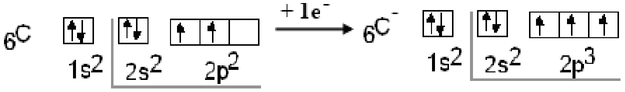


Figure VI-17b: Electron affinities of elements.

We can try to calculate the electron affinity using Slater's method, as described above. For example, we have already calculated the energy of a carbon atom, i.e.



according to Slater's method, for the energies of C and C$^-$ respectively we have

$$E_C = -\frac{13.6}{1^2}[6 - 0.31 \times 1]^2 \times 2 - \frac{13.6}{2^2}[6 - 0.85 \times 2 - 0.35 \times 3]^2 \times 4$$

$$E_{C^-} = -\frac{13.6}{1^2}[6 - 0.31 \times 1]^2 \times 2 - \frac{13.6}{2^2}[6 - 0.85 \times 2 - 0.35 \times 4]^2 \times 5$$

Then, according to the definition of electron affinity

$$E_{EA} = (E_X - E_{X^-})$$

we may write

$$EA = -\frac{13.6}{2^2}[6 - 0.85 \times 2 - 0.35 \times 3]^2 \times 4 + \frac{13.6}{2^2}[6 - 0.85 \times 2 - 0.35 \times 4]^2 \times 5$$

so that

$$EA = +\frac{13.6}{2^2}\left((6 - 0.85 \times 2 - 0.35 \times 4)^2 \times 5 - (6 - 0.85 \times 2 - 0.35 \times 3)^2 \times 4\right) = -0.68\ e.V.$$

The experimental value is thus 1.26 eV and we can see that Slater's method is too crude to be applied in the calculation of electron affinities.

e. Electronegativity

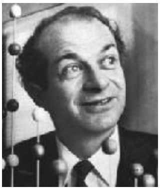
Electronegativity is a relative quantity, which depends on how it is defined, like a temperature scale. This notion, introduced in chemistry, is applied to non-isolated atoms. For molecules, which are assemblies of atoms, it expresses the greater or lesser ability of an atom to attract an electron from the chemical bond that binds it to another atom. There are several definitions of electronegativity, but we shall only talk here about those given by Mulliken[21] and Pauling[22] because they are the most commonly used.

R. S. Mulliken

Note that, recently, a new revision of Pauling's electronegativity scale has been proposed[23].

According to Mulliken, the electronegativity χ_x of an element X is

$$\chi_X = \frac{1}{2}[IP_{1X} + EA_X] \times 0{,}317$$



L. Pauling

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[21] Robert Sanderson Mulliken (1896-1986). American physicist and chemist. He is mainly known for his work on the concept of the molecular orbital, explaining the structure of molecules, for which he won the Nobel Prize in Chemistry in 1966.

[22] Linus Carl Pauling (1901-1994). American chemist and physicist. He won the Nobel Prize in Chemistry in 1954 for his work on the nature of the chemical bond and the Nobel Peace Prize in 1962.

[23] A. Oganov and C. Tantardini, Nature Communication, 12, (2021) 2087.

where IP_{1_X} and EA_X are, respectively, the first ionization potential and the electron affinity of X. The factor 0.317 is used to make Mulliken's scale coincide with that of Pauling, which is based on the dissociation energies of diatomic molecules.

We can thus see that electronegativity increases when we move from left to right along a row of the periodic table. Furthermore, electronegativity decreases from top to bottom in a column of the periodic table. **Fig. VI-18** gives an idea of the evolution of electronegativity: the larger the circle, the greater the electronegativity.

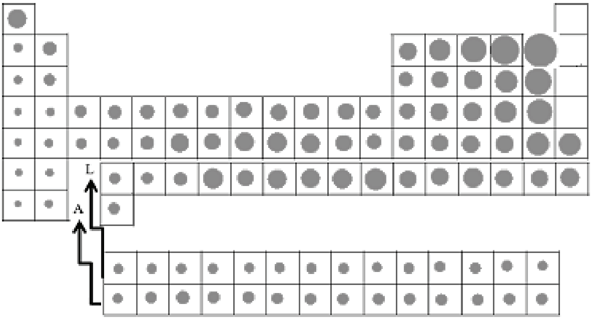

Figure VI-18: Relative Electronegativity magnitudes according to Pauling.

f. Atomic radius

The atomic radius can be experimentally obtained indirectly by measuring the distance between the centers of the atoms of a diatomic molecule. Indeed, if R_e is the internuclear distance at equilibrium, we can write that the atomic radius r_e of an atom is at least equal to half the distance of R_e

$$R_e \leq 2r_e \text{ from which we deduce } r_e \backsimeq \frac{R_e}{2}$$

and the "experimental" atomic radii of some elements may be calculated[24] (**see Table VI-14**).

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[24] For rare gases the values are of course calculated using quantum mechanics

Table VI-14: Calculated radii of some atoms

Element	Li	Be	B	C	N	O	F	Ne	Na	Mg	Al	Si	P
Z	3	4	5	6	7	8	9	10	11	12	13	14	15
$r_e(\text{Å})$	1.23	0.89	0.80	0.77	0.70	0.66	0.64	1.57	1.37	1.26	1.17	1.10	1.04

As can be seen in **Fig. VI-19**, the atomic radius decreases in the same row of the periodic table as we move from alkalines to rare gases.

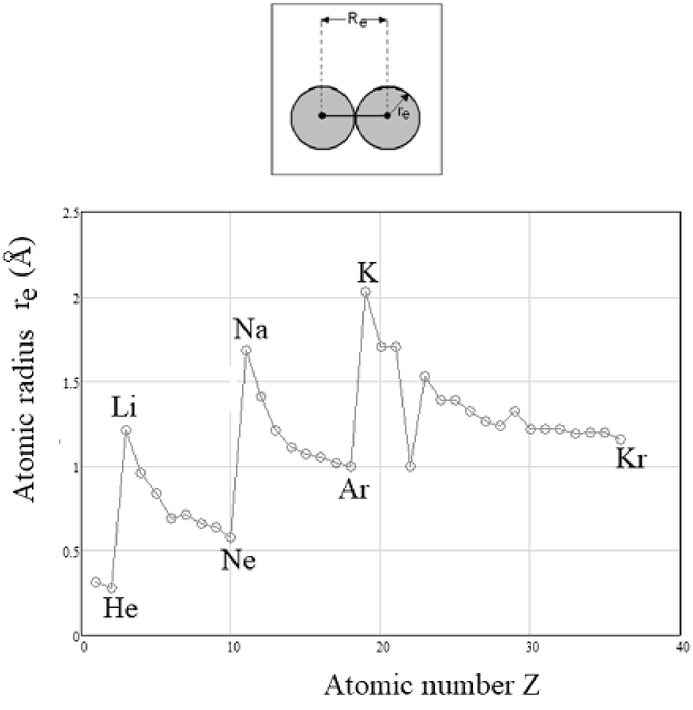


Figure VI-19: Atomic radius r_e versus Z.

The theoretical explanation of this behavior is easily understood, but requires the notion of *orbital radius*. It will be shown later that the atomic radius can be estimated using the quantum properties of the electron. The electron of the peripheral shell of an atom is at a mean distance <r> from the nucleus.

Quantum mechanics tells us that

$$r_e \backsimeq < r > = Cst\frac{3n^2 - l(l+1)}{2Z^*}a_0$$

where Cst is a constant; a_0 is the radius of the first Bohr orbit, i.e 0.529 A; and Z* is the effective atomic number, which evolves like Z.

We can thus see that, within a period where n is constant and Z increases, r_e will decrease as we move from an alkaline to a rare gas.

VI-IV. Tutorial for Chapter VI

T-VI-1. The one-dimensional atomic model

a) Recall the properties of a stationary wave

ANSWER

A stationary wave is a wave that has amplitude dependent on the spatial coordinates. The square of this amplitude has physical meaning, for example, in the case of electronic interferences: it represents the probability of impact of a particle at a point along the electronic interference plane.

b) Give the expression of the equation relating the energy of a particle to its amplitude wave function.

ANSWER

This expression is the Schrödinger equation. For a one-dimensional system, we have the following equation

$$\frac{d^2\Psi(x)}{dx^2} + \frac{2m}{\hbar^2}(E - V)\Psi(x) = 0$$

where E is the total energy of the particle and V is the operator potential energy, which is zero in the case of the model of the particle in a well of infinite potential.

c) What do the boundary conditions imposed on the wave-particle in the potential well correspond to physically?

ANSWER

It is the imposing of a space of the order of magnitude of its associated wavelength is imposed on the wave-particle.

d) Express the energy E_n of the particle in a well of infinite potential. What remark can we make?

ANSWER

A quick glance at Chapter VI gives the energy of a particle in a potential well as

$$E_n = \frac{h^2}{8ma^2}n^2$$

where h is the Planck constant; m is the mass of the particle; a is the size of the one-dimensional space; and n is an integer that takes values from n = 1 to infinity.

It is a purely kinetic energy since the potential energy is hypothetically null.

This energy is quantized because it depends on an integer n called a quantum number. It depends on the size of the space and since we have here one-dimensional space, there is a unique quantum number.

e) Give the expression of the energy difference between two successive energy levels of the potential well.

ANSWER

The gap between two successive levels corresponding to n and n+1 is

$$\Delta E_n = E_{n+1} - E_n$$

then

$$\Delta E_n = \frac{h^2}{8ma^2}(n+1)^2 - \frac{h^2}{8ma^2}(n)^2$$

and

$$\Delta E_n = \frac{h^2}{8ma^2}(2n+1)$$

f) Show that the wavelength associated with the particle in the potential well is of the order of magnitude of the width of the well.

ANSWER

Let us first express the wavelength of the wave associated with the particle

$$\lambda_n = \frac{h}{p_n}$$

Now let us express the kinetic energy Ek_n of the particle. This is equal to the total quantized energy E_n because the potential energy is zero

$$E_{k_n} = E_n = \frac{h^2}{8ma^2}n^2$$

In addition, the kinetic energy can be put into the form

$$E_{k_n} = \frac{1}{2}mv_n^2 = \frac{p_n^2}{2m}$$

where p is the momentum of the particle. By equalizing the two expressions of the kinetic energy, we get

$$\frac{p_n^2}{2m} = \frac{h^2}{8ma^2}n^2$$

$$\text{so that } p_n^2 = \frac{h^2}{4a^2}n^2 \quad \text{i.e. } p_n = \frac{h}{2a}n$$

We deduce the relation between the width a and λ_n

$$\lambda_n = \frac{h}{p_n} = \frac{h}{\frac{h}{2a}n} = \frac{2a}{n}$$

We can see that the wavelength is indeed of the order of magnitude of size a of the space.

h) What is the origin of the quantization of energy in microscopic systems?

ANSWER

The expression of the gap ΔE_n between two successive levels shows that the larger the size of the space, the less the quantization is felt. This is the same for the mass of the particle: the lower the mass, the less the energy is quantized. On the other hand, a system will have its energy quantized if the wavelength of the particle is of the order of magnitude of the size of the space in which it is located.

T-VI-2. Applications of the potential well model

a) The nucleus of an atom can be compared to a potential well in which nuclear particles (nucleons) move in a space of the order of one nuclear diameter in length.

A comparison of the situation of a nucleon with that of an electron in the atom, shows that the radiation emitted by the nucleus (γ rays) has an energy of the order of one mega electron-volt (10^6 eV).

Data: mass of a nucleon $\simeq 10^{-27}$ kg; mass of an electron $\simeq 10^{-30}$ kg; diameter of a nucleus $\simeq 10^{-14}$ m; diameter of an atom $+10^{-10}$ m

ANSWER

Let us call m_e the mass of an electron and m_{nu} that of a nucleon. Let a_{at} be the diameter of an atom and a_N the diameter of a nucleus. We can now consider the relation giving the difference between the two successive levels previously obtained

$$\Delta E_n = \frac{h^2}{8ma^2}(2n+1)$$

We know that a transition between the energy levels E_n and E_{n+1} corresponds to a photon of energy $\Delta E_n = h\nu$.

We can then write that in the case of an atom we have

$$h\nu_{UV} = \frac{h^2}{8m_e a_{at}^2}(2n+1)$$

and for a nucleus

$$h\nu_\gamma = \frac{h^2}{8m_{nu}a_N^2}(2n+1)$$

If we consider that the levels concerned are the same in the two systems, then, by finding the ratio of these two relations, we obtain

$$\frac{h\nu_\gamma}{h\nu_{UV}} = \frac{m_e a_{at}^2}{m_{nu}a_N^2}$$

which leads to

$$\frac{h\nu_\gamma}{h\nu_{UV}} = \frac{10^{-30}\times(10^{-10})^2}{10^{-27}\times(10^{-14})^2} = 10^5$$

As the radiations emitted by the atoms are in the ultraviolet domain, and therefore of the order of 10 eV, we can see that the rays emitted by the nucleus have an energy of the order of mega-eV.

b) Construction of a one-dimensional atomic model. In an atom, the kinetic energy T has an expression that resembles that of a particle in a well of infinite potential. Using this resemblance and knowing that the Coulomb energy of electron-nucleus attraction has the expression $V = -Ke^2/r$ where $K = 10^9$ SI

1) Express the total energy E_{Tot} of the system.

ANSWER

The total energy is

$$E_{Tot} = T + V$$

where T is the kinetic energy and V is the potential energy.

If we assimilate the kinetic energy of the electron to the energy of a particle in a well of infinite potential, then we can write, taking the diameter of the atom as the value of a, as shown in **Fig. T-IV-1**.

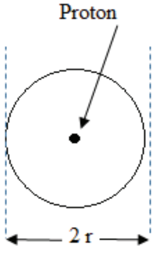


Figure T-VI-1

Setting a = 2r, we get

$$T = \frac{h^2}{8m(2r)^2}n^2 \ \text{ i.e. } \ T = \frac{h^2}{32m(r)^2}n^2$$

Moreover, knowing the expression of the potential energy

$$V = -K\frac{e^2}{r}$$

we can express the total energy as

$$E_{Tot} = \frac{h^2}{32m(r)^2}n^2 - K\frac{e^2}{r}$$

Let us simplify

$$A_n = \frac{h^2}{32m}n^2 \text{ and } B = Ke^2 \ \text{ so that: } \ E_{Tot_n}(r) = \frac{A_n}{(r)^2} - \frac{B}{r}$$

and use the derivative of this expression with respect to r

$$\frac{dE_{Tot_n}(r)}{dr} = -2\frac{A_n}{(r)^3} + \frac{B}{r^2}$$

To obtain the minimum energy for the system, this derivative must be zero. Let r_e be the distance for which this energy is minimum. We then have

$$\left[\frac{dE_{Tot_n}(r)}{dr}\right]_{r=r_e} = -2\frac{A_n}{(r_e)^3} + \frac{B}{(r_e)^2} = 0$$

which will be verified if

$$r_e = \frac{2A_n}{B}$$

By introducing this value into the expression of the energy, we obtain

$$E_{Tot} = \frac{A_n}{(r_e)^2} - \frac{B}{r_e}$$

$$E_{Tot_n}(r) = E_n = \frac{A_n}{\left(\frac{2A_n}{B}\right)^2} - \frac{B}{\frac{2A_n}{B}} = -\frac{B^2}{4A_n}$$

By replacing A_n and B in the expressions of r_e and E_n, we obtain

$$r_e = \frac{2\frac{h^2}{32m}n^2}{Ke^2} = \frac{h^2}{16me^2K}n^2$$

so that

$$E_n = -\frac{(Ke^2)^2}{4\frac{h^2}{32m}n^2} = -\frac{8mK^2e^4}{h^2}\frac{1}{n^2}$$

We see that the energy is quantized and resembles that found for the hydrogen atom according to Bohr’s theory. We can now numerically evaluate these quantities.

$$r_e = \frac{h^2}{16me^2K}n^2 \text{ i.e. } r_e = \frac{(6.6\times 10^{-34})^2}{16\times(9.1\times 10^{-31})\times(1.6\times 10^{-19})^2\times 9\times 10^9}n^2$$

and

$$r_e = 1.2985\times 10^{-10}n^2 meter$$

or in angstrom

$$r_e = 1.2985n^2\mathring{A}$$

$$E_n = -\frac{(Ke^2)^2}{4\frac{h^2}{32m}n^2} = -\frac{8\times 9.1\times 10^{-31}(9\times 10^9)^2(1.6\times 10^{-19})^4}{(6.6\times 10^{-34})^2}\frac{1}{n^2}$$

$$E_n = -8.8717\times 10^{-19}\frac{1}{n^2}J$$

or in eV

$$E_n = -5.5448\frac{1}{n^2}e.V$$

These values are slightly different from those found experimentally, but are of the same order of magnitude.

In this approach, it is important to see how the fundamental principles operate. The assumption of the wave-like nature of the electron and the restriction of the space within which this electron is moving are sufficient to make apparent the quantization of energy.

2) Give the expression of the wavenumber of a transition between the levels n_1 and n_2 of this system. Construct the emission spectrum of this one-dimensional atom.

ANSWER

Just as with Bohr's model, using the formula giving E_n, we can reconstitute the electron spectra of this one-dimensional atom.

For the emission spectrum, we have

$$hc\frac{1}{\lambda_{em}} = \frac{8mK^2e^4}{h^2}\left[\frac{1}{n_f^2} - \frac{1}{n_i^2}\right]$$

so that

$$\bar{\nu}_{em} = \frac{1}{\lambda_{em}} = \frac{8mK^2e^4}{h^3c}\left[\frac{1}{n_f^2} - \frac{1}{n_i^2}\right] \text{with } n_f < n_i$$

and for absorption

$$\bar{\nu}_{abs} = \frac{1}{\lambda_{em}} = \frac{8mK^2e^4}{h^3c}\left[\frac{1}{n_i^2} - \frac{1}{n_f^2}\right] \text{with } n_f > n_i$$

The value of the constant, which is analogous to Rydberg's constant, is

$$r_H = \frac{8mK^2e^4}{h^3c} = \frac{8.8717 \times 10^{-19}}{6.6 \times 10^{-34} \times 3 \times 10^8} = 4.4807 \times 10^6 m^{-1}$$

We can then construct the spectra by varying n_i and n_f, just as in the case of the hydrogen atom.

T-VI-3: Extension to three dimensions: the hydrogen atom and hydrogenic atoms

a) Recall where the 3 quantum numbers that characterize the situation of the electron in the atom come from.

ANSWER

They come from the solution of the Schrödinger equation in three dimensions and are independent of time: n is the principal quantum number $n = 1, 2, \ldots \infty$; l is the secondary quantum number; $l = 0.1 \ldots n-1$; m is the magnetic quantum number: $m = 0, \pm 1, \ldots \pm l$

b) What do orbitals represent?

ANSWER

They represent the amplitude function of the electron or the square of this function, which is called the probability density. They depend on the space variables used for the solution of the three-dimensional Schrödinger equation, namely the spherical polar coordinates r, θ, and φ. r is the radial coordinate, which varies from 0 to ∞; θ and φ are the angular coordinates, which vary, respectively, as $0 \leq \theta \leq \pi$ and $0 \leq \varphi \leq 2\pi$.

c) Draw the orbitals freehand using the angular distribution of the amplitude function $|\Psi|$. The atomic orbitals:

1s, 2s, $2p_x$, $2p_y$, $2p_z$, $3d_{z^2}$,$3d_{x2-y2}$, $2d_{xy}$, $3d_{xz}$, $3d_{yz}$

ANSWER

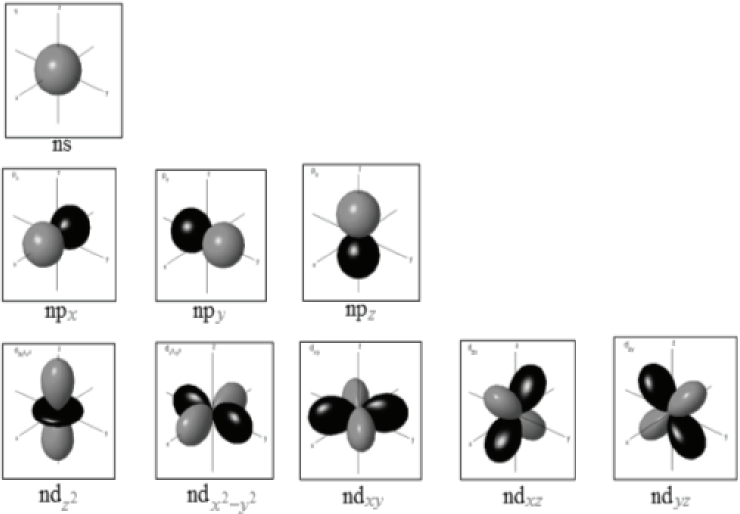


Figure T-IV-2: Hydrogenic atomic orbitals.

d) Give the outermost shell electronic structure of an alkaline, an alkaline earth, a halogen, and a rare gas.

ANSWER

Alkaline: outermost shell of ns^1 type

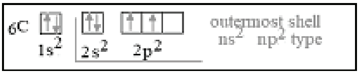
Alkaline earth: outermost shell of ns^2 type

Halogen: outermost shell of ns^2np^5 type

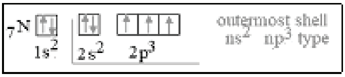
Rare gas (except helium): outermost shell of ns^2np^6 type

e) Give the electronic structure of the following elements and indicate those that belong to the same group:

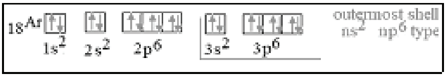
${}_6C$, ${}_{15}P$, ${}_{18}Ar$, ${}_{14}Si$, ${}_{33}As$, ${}_{24}Cr$, ${}_{10}Ne$



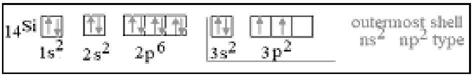
Carbon family



Nitrogen family

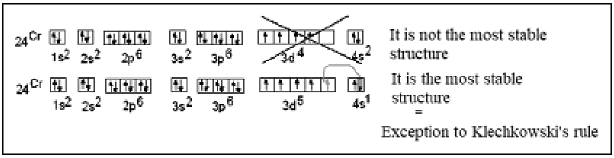


Rare gas family



Carbon family

Nitrogen family



Transition element

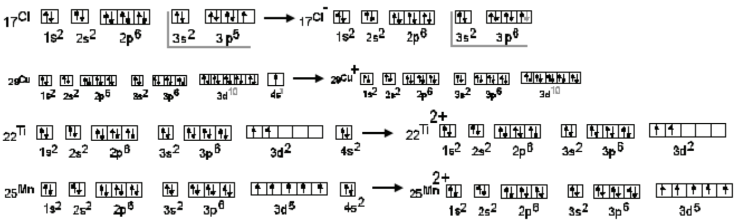
The outermost shell is $4s^1$, but there are electrons in the d orbitals of the previous shell. As such, it is not an alkaline, but a transition element.

f) Give the electronic structure of the following ions:

$_{17}Cl^-$, $_{29}Cu^+$, $_{22}$Ti^{2$^+$}, $_{25}Mn^{2+}$

ANSWER

The principle of constructing ion structures implies that we first build the structure of the neutral element, then we remove (ion +) or add (ion -) electrons.



g) We define the valence of an element as the number of electrons that it is able to give up or receive when it binds with other elements.

Using this definition, predict the valence of the elements of the first three periods of the periodic table from their electronic configuration. Plot the evolution of the valence as a function of the atomic number Z on a graph.

ANSWER

H: valence 1, He: valence 0, Li: valence 1, Be: valence 2, B: valence 3, C: valence 4, N: valence 3, O: valence 2, F: valence 1, Ne: valence 0.

Then, changing the period,

Na: valence 1, Mg: valence 2, Al: valence 3, Si: valence 4, P: valence 3, S: valence 2, Cl: valence 1, Ar: valence 0.

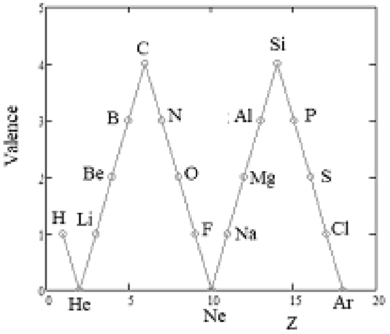


Figure T-IV-3. Valence evolution with Z.

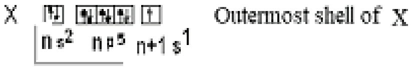
h) An element of the 4th period by double ionization gives an ion that has the electronic structure of a halogen. What is its atomic number?

ANSWER

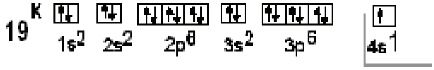
Two solutions are possible depending on whether the ion is positive or negative.

Positive ion. Ionization removes 2 electrons from the X atom resulting in an ion with the outermost shell of a halogen.

To reconstitute the element it is necessary to add 2 electrons, i.e.



We must therefore give the electronic structure of the alkaline of period 4. It is the alkaline of atomic number 19, which is potassium.



Negative ion. We start from the ion

and subtract 2 electrons.

We need to reconstruct the electronic structure of the element of the nitrogen family of the 4th period.

This is arsenic having the atomic number 33.

i) Recall how the first ionization potential (IP_1) evolves experimentally when Z increases.

ANSWER

IP_1 grows globally within one period from the alkalines to the rare gases and decreases sharply when changing from the rare gas of one period to the alkaline of the following period

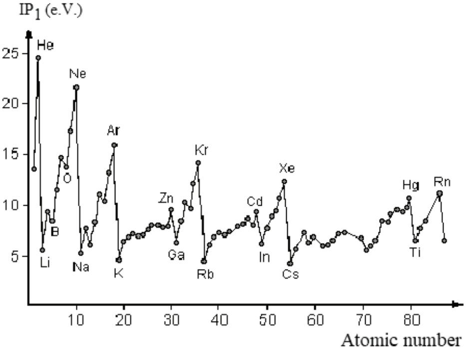


Figure T-VI-4. Experimental IP_1 evolution.

j) Qualitatively predict this evolution. For which values of Z will we see accidents in this evolution?

ANSWER

We can assimilate IP_1 to the energy of the least bonded electron (peripheral shell) with the sign changed. As the energy of the electron in a polyelectronic atom can be likened to the energy of an electron of the outermost shell characterized by the quantum number n of a hydrogenic atom whose atomic number has been corrected by the influence of the environment of the other electrons included in the effective atomic number Z*

$$E_n = -\frac{13.6 \times Z^{*2}}{n^2}$$

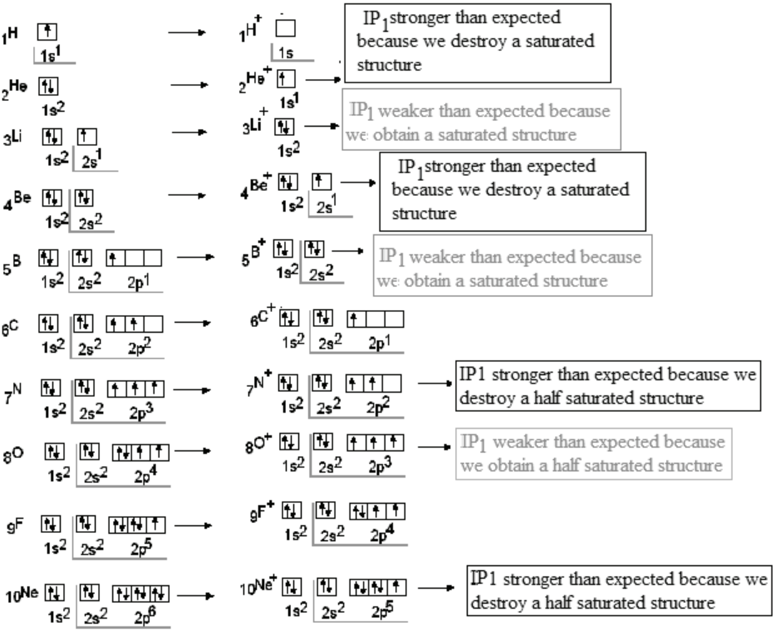
As such, for IP_1, we have

$$IP_1 \backsim \frac{13.6 \times Z^{*2}}{n^2}$$

where n is the quantum number of the outermost shell. We can therefore see that within a period, n is the same. As such, Z imposes the evolution of IP_1 when we go from left to right. When we change the period, the linear evolution of IP_1 conducted by the continuous rising of Z is broken by a sudden change in n, which increases by a unity. As a result, IP_1 drops suddenly.

We can therefore predict the corrections to be made to the evolution of IP_1 by looking at the electronic structures before and after ionization and following the qualitative reasoning presented in **Table T-VI-1**.

Table T-VI-1: Qualitative explanation of accidents along the evolution of IP_1



IP_1 stronger than expected because we destroy a saturated structure

IP_1 weaker than expected because we obtain a saturated structure

IP_1 stronger than expected because we destroy a saturated structure

IP_1 weaker than expected because we obtain a saturated structure

IP1 stronger than expected because we destroy a half saturated structure

IP_1 weaker than expected because we obtain a half saturated structure

IP1 stronger than expected because we destroy a half saturated structure

CHAPTER VII

THE CHEMICAL BOND

This chapter deals with the formation of chemical bonds and the geometry of molecules.

We focus on the successive conceptual contributions that have led to the current vision of a chemical bond starting with the fundamental work of G. Lewis. In order to better understand this work, we shall build on what we have learned from a number of discoveries about the electronic structure of atoms, the Lewis method being a consequence of these structures.

VII-I. The Chemical Bond According to Lewis

The Lewis method[1] is well known through the writing of molecular formulas, which make use of the conventions stated by Lewis. We give here a method for the systematic application of this method.

G. Lewis

1. The chemical bond: principles

A chemical bond is the realization of a bond between two atoms through the pooling of two electrons. This convention began with Lewis and remains the basis of descriptions of the chemical bond. Even modern theories of chemical bonding (molecular orbital theory and the VSEPR method) make

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[1] Gilbert Lewis (1875-1946). American physicist and chemist. He is known for his theory of electron sharing in the chemical bond and for his theory of acids and bases. Lewis developed theoretical physics by studying the application of thermodynamics to chemical equilibrium.

use of this concept of chemical bonding resulting from sharing a pair of electrons.

1. Lewis's rule

By bonding, the atoms acquire the outermost electronic structure of a rare gas.

When we consider the electronic structure of the elements as described in quantum theory, it is easy to understand the method.

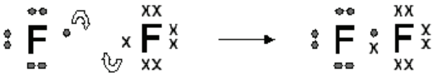
Let us take the fluorine molecule as an example.

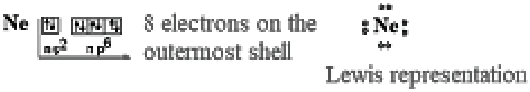
The outermost electronic shell of this element allows us to understand the representation that Lewis made of the fluorine element (F).

In the representation of the element according to Lewis, only the electrons of the outermost shell (the L shell) are represented by points. The electrons are grouped two by two, that is to say in doublets where possible. Thus, fluorine, which contains 7 electrons on its outermost electronic shell, has them arranged in 3 doublets represented by the closed points.

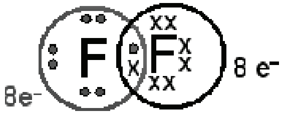
A quick way to represent these doublets is to use lines. Thus the outermost shell of fluorine can be represented as shown on the right.

Now let us examine the union between two atoms. We shall represent their respective electrons differently to distinguish them.



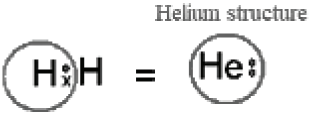


The Lewis rule, which says that through bonding two atoms acquire a saturated outermost shell. This gives the structure of the nearest rare gas belonging to the 2nd period of the periodic table, which is neon.As we can see, there will be 8 electrons around each atom, i.e. an outermost shell of rare gas form.



In general there are 8 electrons on the outermost shell of a rare gas, except for helium, which has only 2.

We may note that the Lewis representation of the hydrogen molecule makes the outermost shell of bonded hydrogen look like that of a helium atom, as shown on the right.



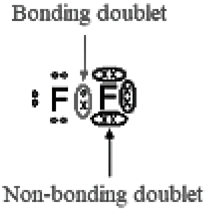
2. Bonding and non-bonding doublets

In the example of fluorine, we can see the difference between bonding and non-bonding doublets.

(i) The Lewis rule places 8 electrons around each atom. As such, for 2 atoms there should be 2 x 8 = 16 electrons for the Lewis rule to be respected.

(ii) The fluorine molecule has only 2 x 7 = 14 electrons in its outermost shell.

(iii) The difference 16 - 14 = 2 then represents the number of electrons counted twice, i.e. the number of electrons that are common to the two atoms.

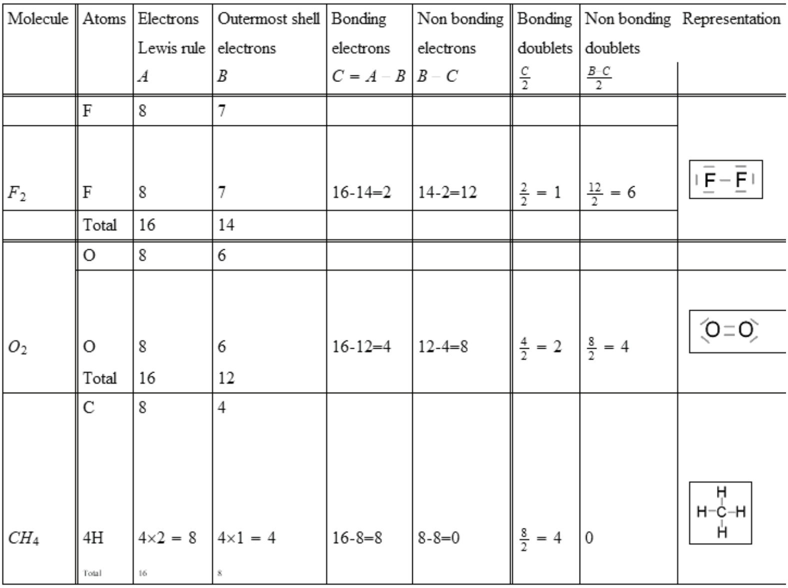


(v) There are 14 - 2 = 12 electrons remaining that do not participate in the bond.

(vi) There are 12/2 = 6 non-bonding doublets.

With fluorine, this procedure seems obvious, but for more complex molecules it can be useful to represent this in the form shown in **tables VII-1** and **VII-2**.

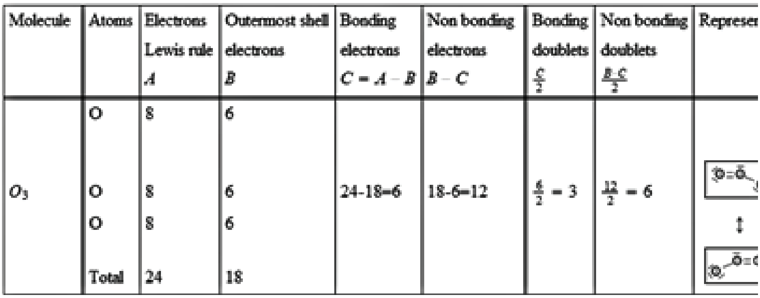
Table VII-1: Systematic method for Lewis structures



Molecule	Atoms	Electrons Lewis rule A	Outermost shell electrons B	Bonding electrons $C = A - B$	Non bonding electrons $B - C$	Bonding doublets $\frac{C}{2}$	Non bonding doublets $\frac{B-C}{2}$	Representation
	F	8	7					
F_2	F	8	7	16-14=2	14-2=12	$\frac{2}{2} = 1$	$\frac{12}{2} = 6$	F – F
	Total	16	14					
	O	8	6					
O_2	O Total	8 16	6 12	16-12=4	12-4=8	$\frac{4}{2} = 2$	$\frac{8}{2} = 4$	O = O
	C	8	4					
CH_4	4H Total	4×2 = 8 16	4×1 = 4 8	16-8=8	8-8=0	$\frac{8}{2} = 4$	0	H H–C–H H

Let us now look at the ozone molecule. This molecule has the formula O_3, is bent, and the distances between the oxygen atoms are of equal length. An analysis of the electronic structure of this molecule gives the following results.

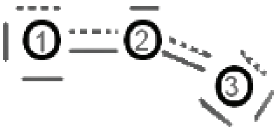
Table VII-2: Systematic method for the Lewis structure



Molecule	Atoms	Electrons Lewis rule A	Outermost shell electrons B	Bonding electrons $C = A - B$	Non bonding electrons $B - C$	Bonding doublets $\frac{C}{2}$	Non bonding doublets $\frac{B-C}{2}$	Represen
	O	8	6					
O_3	O O	8 8	6 6	24-18=6	18-6=12	$\frac{6}{2} = 3$	$\frac{12}{2} = 6$	O=O ↕ O–O=
	Total	24	18					

As bonds 12 and 23 must be of equal length, it should be envisaged that a bonding doublet is delocalized on the whole of the molecule. This phenomenon is called *mesomerism* or *resonance* The resonance structures are connected by a double entry arrow, i.e. ↔. This arrow does not mean that we are dealing with an equilibrium, but ratehr that the structure of the molecule is intermediate between two resonance structures.

We can globalize this representation in the following way with a hybrid structure. For ozone, we have a superposition of the two resonance forms, giving the representation on the right, with the delocalized doublet shown by dotted lines.



3. Exceptions to the Lewis rule

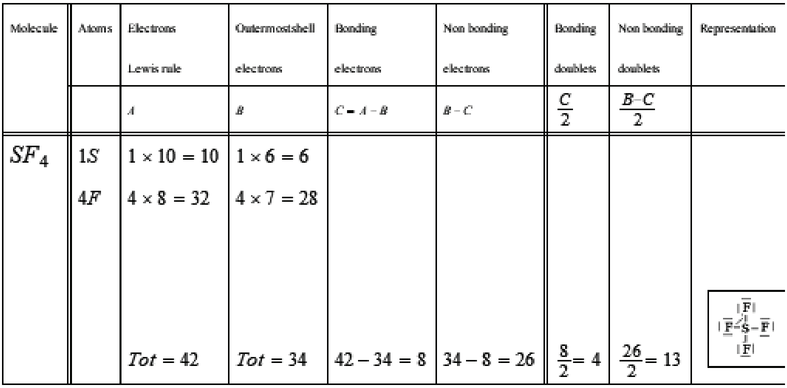
Atoms in column 13 of the periodic classification (boron, aluminum, etc.) are often electro-deficient, which is a default violation of the octet rule. These atoms have exactly 6 electrons around them. We speak of a “gap” (represented by a small empty rectangle), which both boron and carbocations have. The gap gives the atom a particular acidity for neighboring electrons (Lewis acidity).

With the element silicon, atoms can override the octet rule. We can then speak of *hypervalence* (for example PCl_5, SF_4). The atoms particularly concerned are sulfur, phosphorus, and xenon.

Hydrogen atoms have a maximum of 2 electrons around them and thus we speak of the *duet rule* in relation to them.

For example, we have the case of the SF_4 molecule where the hypervalence of sulfur states that this atom will accept 10 electrons on its outermost shell when it binds with other atoms. The Lewis rule then results in 10 electrons (see **Table VII-3**).

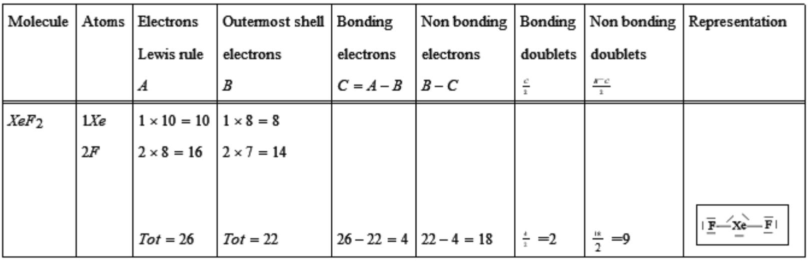
Table VII-3: Systematic method for SF_4



Molecule	Atoms	Electrons Lewis rule	Outermostshell electrons	Bonding electrons	Non bonding electrons	Bonding doublets	Non bonding doublets	Representation
		A	B	$C = A - B$	$B - C$	$\frac{C}{2}$	$\frac{B-C}{2}$	
SF_4	$1S$ $4F$	$1 \times 10 = 10$ $4 \times 8 = 32$ $Tot = 42$	$1 \times 6 = 6$ $4 \times 7 = 28$ $Tot = 34$	$42 - 34 = 8$	$34 - 8 = 26$	$\frac{8}{2} = 4$	$\frac{26}{2} = 13$	

Another example is the case of the XeF_2 molecule where the hypervalence of neon states that this atom will accept 10 electrons on its outermost shell when it binds with other atoms. The Lewis rule thus results in 10 electrons.

Table VII-4: Systematic method for the Lewis structure of XeF_2



Molecule	Atoms	Electrons Lewis rule A	Outermost shell electrons B	Bonding electrons $C = A - B$	Non bonding electrons $B - C$	Bonding doublets $\frac{C}{2}$	Non bonding doublets $\frac{B-C}{2}$	Representation
XeF_2	$1Xe$ $2F$	$1 \times 10 = 10$ $2 \times 8 = 16$ $Tot = 26$	$1 \times 8 = 8$ $2 \times 7 = 14$ $Tot = 22$	$26 - 22 = 4$	$22 - 4 = 18$	$\frac{4}{2} = 2$	$\frac{18}{2} = 9$	

4. Formal charges

Another interesting notion of the Lewis method is the calculation of formal charges. Formal charges are local charges reflecting the non-uniformity of the electronic distribution in a molecule. The sum of these local charges is zero if the molecule is neutral or equal to the charge of the ion if the molecule is electrically charged.

By definition, the formal charge carried by an atom X is

$$f_X = Z - \left(\text{core electrons+Non-bonding electrons}\right) - \frac{\text{Bonding electrons}}{2}$$

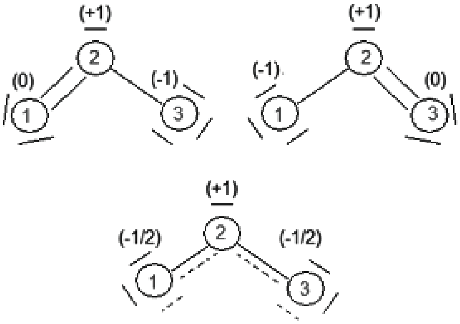
For example, consider the ozone molecule described above and more particularly one of its resonance forms.

Table VII-5 gives the formal charges on each atom of ozone. For the other limit forms, the same calculations are given in the figure below on the right in which the formal charges are represented by numbers within parenthesis, above the atoms of both resonance structures and the hybrid form after delocalization of the electrons.

Table VII-5: Formal charges on O_3

Atom	f_X
O_1	$f_{O_1} = 8 - (2+6) - \frac{2}{2} = -1$
O_2	$f_{O_2} = 8 - (2+2) - \frac{6}{2} = +1$
O_3	$f_{O_3} = 8 - (2+4) - \frac{4}{2} = \ \ 0$

For the hybrid form, the changing formal charges are averaged.



For instance, in the case of ozone, for atoms 1 and 3 we have the average formal charge of (-1) divided by the number of atoms concerned, i.e. (-1/2).

5. Failures of the Lewis method

There are certain molecules that do not respect the Lewis rule; however, we still use Lewis notation to represent them. These molecules have an electronic deficit on one of the atoms or molecules where the d orbitals play an important role.

An example is the BH_3 molecule for which the systematic method indicates that 2 electrons are missing if we were to obtain a conventional Lewis structure; however, BH_3 violates the Lewis rule (Table VII-6).

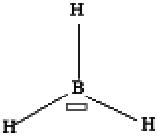


Table VII-6: **Lewis rule failure for BH3**

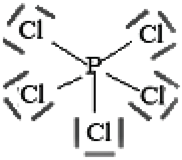
Molecule	Atoms	Lewis	Outer	Bonded	Non-bonded	Bonding dbts	Non-bonding dbts
BH_3	B	$1 \times 8 = 8$	$1 \times 3 = 3$				
	$3H$	$3 \times 2 = 6$	$3 \times 1 = 3$				
		$Total = 14$	$Total = 6$	$14 - 6 = 8$	$6 - 8 = -2$		

Another example is phosphorus pentachloride (PCl_5). In **Table VII-7**, we apply the systematic method to it.

Table VII-7: Lewis method failure for PCl_5

Molecule	Atoms	Lewis	Outer	Bonded	Non-bonded	Bonding dbts	Non-bonding dbts
	$1P$	$1 \times 8 = 8$	$1 \times 5 = 5$				
PCl_5	$5Cl$	$5 \times 8 = 40$	$5 \times 7 = 35$				
		Total 48	Total 40	$48 - 40 = 8$	$40 - 8 = 32$	$\frac{8}{2} = 4$	$\frac{32}{2} = 16$

In this case, there are not enough bonding doublets to bind the 5 ligands of the phosphorus. However, if we consider that P has what is called hypervalence, the Lewis rule is satisfied if phosphorus can have 10 electrons in its outermost shell.



Then, the number of bonding doublets becomes equal to five, giving us the figure on the right.

There are many other examples of such failures to account for electronic structure according to Lewis's octet rule.

As such, a need to develop other more relevant theories of the chemical bond was recognized.

VII-II. The Chemical Bond according to Molecular Orbital (MO) Theory

The theory of molecular orbitals (MO) is the modern theory of chemical bonding. It builds on the definition of the chemical bond by Lewis that an electronic doublet shared in common between two atoms is equivalent to a chemical bond.

The theory of molecular orbitals builds on the *valence bond theory* (1927) and was developed in the work of F. Hund, R. Mulliken, J. C. Slater, and J. Lennard-Jones[2].

Sir Lennard-Jones

This theory was originally called the *Hund-Mulliken theory*. The term orbital was introduced by Mulliken in 1932 and in 1933 the theory of molecular orbitals was accepted as a valid and practical theory.

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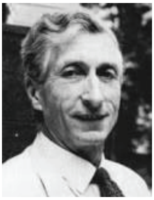
[2] Sir John Lennard-Jones (1894-1954) was a British mathematician, theoretical physicist, and theoretical chemist. He is considered to be the initiator of modern quantum chemistry.

E. Hückel

According to the physicist and physicochemist Erich Hückel[3], the first quantitative use of the theory of molecular orbitals is in a 1929 article by Lennard-Jones[4].

The first precise calculation of a molecular wave function was carried out in 1938 by Charles Coulson[5] for the dihydrogen molecule.

In 1950, molecular orbitals were definitively defined as eigenfunctions (wave functions) of the Hamiltonian of the self-coherent field and it was from this moment that the theory of molecular orbitals became fully rigorous and consistent. This rigorous approach is known as the Hartree[6]-Fock[7] method for molecular orbitals, although it is based on atomic calculations. In these calculations, molecular orbitals are developed on a basis set[8] of atomic orbitals, represented by the Roothaan's equations[9].



C. Coulson

V. Fock

D. Hartree

C. Roothan

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[3] Erich Hückel (1896-1980) was a German physicist and chemist. He is known for two major contributions: the Debye-Hückel theory on electrolytic solutions and Hückel's method of approximation for the calculation of molecular orbitals.

[4] J. E. Lennard-Jones, Trans. Faraday Soc., 25 (1929), p. 668.

[5] Charles Alfred Coulson (1910-1974). British theoretical chemist known for his contribution to theoretical chemistry.

[6] Douglas Hartree (1897-1958) was an English mathematician and physicist. He is known for his development of numerical analysis and its application to atomic physics.

[7] Vladimir Fock (1898-1974). Russian physicist known for his work on quantum mechanics and quantum electrodynamics.

[8] A basis set in quantum chemistry is a set of atomic wave functions used to construct molecular orbitals by their linear combination.

[9] Clemens Roothaan (1918-2019) was a Dutch physicist. He is known for his contributions to molecular calculations.

This led to the development of many *ab initio methods* of quantum chemistry. In parallel to these rigorous developments, the theory of molecular orbitals is also applied in an approximate form using empirically established parameters in what is known as a *semi-empirical quantum method*.

1. Principles

Molecular orbital theory envisions an interaction between the atomic orbitals of two different atoms, resulting in molecular orbitals. Just like the light interferences that we studied in Chapter II, this interaction has two types of solutions: a constructive solution that favors the chemical bond and a destructive interaction that does not favor it. As such, depending on the interfering orbitals, there will be two types of molecular orbitals: molecular bonding orbitals and molecular anti-bonding orbitals. This method is known as the *simple LCAO method* (linear combination of atomic orbitals). This method can be improved by adding a variational parameter in the wave function used, but the principle remains the same.

a) Referential

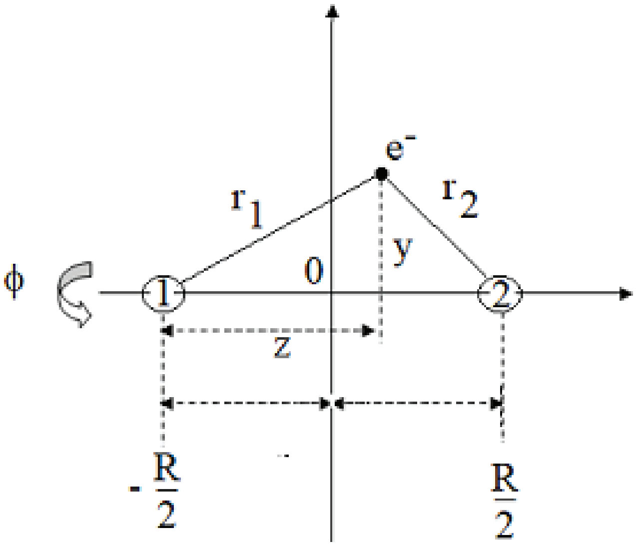


Figure VII-1: Coordinates for the H_2^+ ion.

Let us consider two orbitals ϕ_1 and ϕ_2 of the same kind, centered respectively on two nuclei, which we shall call 1 and 2. We call φ the angle of rotation around the z axis, which passes through the nuclei. This angle can vary from 0 to 2π and is shown in **Fig. VII-1**.

What is the wave function that describes the movement of the electron? We can answer this question immediately if we mentally increase the distance R separating the two nuclei. The electron can then belong to the zone of influence of nucleus 1 or to that of nucleus 2. The first case will be described by the atomic wave function ϕ_1 and the second case by the atomic wave function ϕ_2.

b) Molecular energy

We know the principle for calculating the energy of the electron when it is in any orbital. For this, the energy operator H or Hamiltonian of the system and the wave function Ψ must be known. The energy is then formally written

$$\langle E \rangle = \frac{\iiint \Psi^* \mathbf{H} \Psi dv}{\iiint \Psi^* \Psi dv} \qquad \text{(VII-1)}$$

where Ψ^* is the *conjugate complex* of Ψ.

using the LCAO method, we can construct the molecular wave function Ψ as a linear combination of the atomic wave functions ϕ_1 and ϕ_2, so that

$$\Psi = C_1\varphi_1 + C_2\varphi_2 \qquad \text{(VII-2)}$$

where C_1 and C_2 are the coefficients associated to each atomic orbital, i.e. the respective "weights" of the orbitals ϕ_1 and ϕ_2 in the combination. By introducing this expression of Ψ in Eq. (VII-1), we get

$$\langle E \rangle = \frac{\iiint (C_1\varphi_1 + C_2\varphi_2)\mathbf{H}(C_1\varphi_1 + C_2\varphi_2)dv}{\iiint (C_1\varphi_1 + C_2\varphi_2)^2 dv} \qquad \text{(VII-3)}$$

in which we consider, for reasons of simplicity, that the wave function Ψ is real.

We can rewrite the expression (VII-3) by developing the two terms of this fraction, knowing that C_1 and C_2 are constants.

$$\langle E\rangle = \frac{C_1^2 \iiint \varphi_1 \mathbf{H} \varphi_1 dv + C_2^2 \iiint \varphi_2 \mathbf{H} \varphi_2 dv + C_1 C_2 \iiint \varphi_1 \mathbf{H} \varphi_2 dv + C_1 C_2 \iiint \varphi_2 \mathbf{H} \varphi_1 dv}{C_1^2 \iiint \varphi_1^2 dv + C_2^2 \iiint \varphi_2^2 dv + C_1 C_2 \iiint \varphi_1 \varphi_2 dv + C_1 C_2 \iiint \varphi_2 \varphi_1 dv} \tag{VII-4}$$

We can simplify its writing as

$$\iiint \varphi_1 \mathbf{H} \varphi_1 dv = E_{11} \quad \text{and} \quad \iiint \varphi_2 \mathbf{H} \varphi_2 dv = E_{22}$$

E_{11} and E_{22} are, respectively, the *Coulomb energies* of the electron in the state ϕ_1 of hydrogen atom 1 and in the state ϕ_2 of hydrogen atom 2, and the crossed term E_{12} is called the *exchange energy*.

$$\iiint \varphi_1 \mathbf{H} \varphi_2 dv = \iiint \varphi_2 \mathbf{H} \varphi_1 dv = E_{12}$$

The term S is the *overlap integral* between atomic orbitals ϕ_1 and ϕ_2

$$\iiint \varphi_1 \varphi_2 dv = \iiint \varphi_2 \varphi_1 dv = S \tag{VII-5}$$

If one considers that ϕ_1 and ϕ_2 are *normalized wave functions*, i.e. if

$$\iiint \varphi_1^2 dv = \iiint \varphi_2^2 dv = 1$$

then Eq. (VII-4) becomes

$$\langle E\rangle = \frac{C_1^2 E_{11} + C_2^2 E_{22} + C_1 C_2 E_{12} + C_1 C_2 E_{21}}{C_1^2 + C_2^2 + C_1 C_2 S + C_1 C_2 S}$$

and as such, we may write

$$\langle E\rangle (C_1^2 + C_2^2 + C_1 C_2 S + C_1 C_2 S) = C_1^2 E_{11} + C_2^2 E_{22} + C_1 C_2 E_{12} + C_1 C_2 E_{21} \tag{VII-6}$$

We now perform what is called the *variation method*. In order to determine the best coefficients to obtain the lowest energy, we successively derive this expression with respect to C_1 and C_2 to obtain

$$\frac{\partial\langle E\rangle}{\partial C_1}(C_1^2 + C_2^2 + C_1C_2S + C_1C_2S) + \langle E\rangle\frac{\partial(C_1^2 + C_2^2 + C_1C_2S + C_1C_2S)}{\partial C_1}$$

$$= \frac{\partial}{\partial C_1}(C_1^2E_{11}+C_2^2E_{22} + C_1C_2E_{12} + C_1C_2E_{21})$$

giving

$$\frac{\partial\langle E\rangle}{\partial C_1}(2C_1 + C_2S + C_2S) + \langle E\rangle(2C_1 + C_2S + C_2S) = 2C_1E_{11} + C_2E_{12} + C_2E_{21}$$

by rearranging, we get

$$\frac{\partial\langle E\rangle}{\partial C_1}(C_1 + C_2S) + \langle E\rangle(C_1 + C_2S) = C_1E_{11} + C_2E_{12}$$

As we wish to find the minimum energy with respect to C_1, we have ∂<E>)/$\partial C_1 = 0$, so that

$$\langle E\rangle(C_1 + C_2S) = C_1E_{11} + C_2E_{12}$$

by rearranging, we get

$$C_1(E_{11} - \langle E\rangle) + C_2(E_{12} - \langle E\rangle S) = 0$$

Now, let us derive Eq. (VII-6) with respect to C_2. We thus obtain

$$C_1(E_{12} - \langle E\rangle S) + C_2(E_{22} - \langle E\rangle) = 0$$

We then have the following system of two simultaneous equations to solve

$$\begin{bmatrix} (E_{11} - \langle E\rangle) & (E_{12} - \langle E\rangle S) \\ (E_{12} - \langle E\rangle S) & (E_{22} - \langle E\rangle) \end{bmatrix} = 0 \tag{VII-7}$$

and have

$$(E_{11} - \langle E \rangle)(E_{22} - \langle E \rangle) - (E_{12} - \langle E \rangle S)^2 = 0 \quad \text{(VII-8)}$$

Let us simplify Eq. (VII-8) in the case of the hydrogen atom where $E_{11} = E_{22}$ because the two atoms are identical

$$(E_{11} - \langle E \rangle)(E_{11} - \langle E \rangle) - (E_{12} - \langle E \rangle S)^2 = 0$$

rearranging this equation leads to

$$(E_{11} - \langle E \rangle)^2 = (E_{12} - \langle E \rangle S)^2$$

This equation has two solutions

$$(E_{11} - \langle E \rangle)^2 = (E_{12} - \langle E \rangle S)^2 \quad \text{(VII-9)}$$

and

$$(E_{11} - \langle E \rangle_{II}) = (E_{12} - \langle E \rangle_{II} S) \quad \text{(VII-10)}$$

We shall see later why we chose the sign for the first solution. Thus, we can deduce

$$\langle E \rangle_I (1 + S) = E_{11} + E_{12}$$
$$\langle E \rangle_{II} (1 - S) = E_{11} - E_{12}$$

and obtain the two following solutions

$$\langle E \rangle_I = \frac{E_{11} + E_{12}}{(1 + S)} \quad \text{(VII-11)}$$

$$\langle E \rangle_{II} = \frac{E_{11} - E_{12}}{(1 - S)} \quad \text{(VII-12)}$$

We need to evaluate the different quantities in the equations to access the energies of the molecular orbitals, namely the Coulomb energy of the atomic orbitals E_{11}, the exchange integral E_{12}, and the overlap integral S. This integral depends on the distance R between the nuclei, which is neglected if R is not too small. Under these conditions, the molecular energies are simply reduced to

$$\langle E \rangle_I \backsimeq E_{11} + E_{12} \tag{VII-13}$$

$$\langle E \rangle_{II} \backsimeq E_{11} - E_{12} \tag{VII-14}$$

As E_{11} and E_{12} are both negative, it can be seen that E_I is more negative than E_{II}. Necessarily being lower in energy than the atomic energy E_{11}, it therefore corresponds to a more favorable situation from the energetic point of view. E_{II} is thus energetically higher than the atomic energy E_{11} and the system will be destabilized if the electron is in the state characterized by E_{II}.

c) Orbital coefficients

To fully describe the system, we need to know the coefficients of the linear combinations. For this, consider the secular equations

$$\begin{cases} C_1(E_{11} - \langle E \rangle) + C_2(E_{12} - \langle E \rangle S) = 0 \\ C_1(E_{12} - \langle E \rangle S) + C_2(E_{22} - \langle E \rangle) = 0 \end{cases} \tag{VII-14}$$

In the case of the lower energy orbital Ψ_I, for the first equation we can write

$$C_1^I(E_{11} - \langle E \rangle_I) + C_2^I E_{12} = 0$$

where C_1^I and C_2^{II}, respectively, denote the coefficients of the atomic orbitals in the linear combination.

We can write

$$C_1^I(E_{11} - \langle E \rangle_I) = -C_2^I E_{12} \tag{VII-15}$$

so that

$$\frac{C_1^I}{C_2^I} = -\frac{E_{12}}{E_{11} - \langle E \rangle_I}$$

Let us replace the energy $\langle E \rangle_I$ by its expression (VII-13). This leads to

$$\frac{C_1^I}{C_2^I} = 1 \text{ so that } C_1^I = C_2^I$$

Let us do the same with the energy <E>$_{\text{II}}$

$$C_1^{II}(E_{11} - (E_{11} - E_{12})) + C_2^{II}E_{12} = 0$$

then

$$C_1^{II}E_{12} + C_2^{II}E_{12} = 0 \quad \text{and} \quad C_1^{II} = -C_2^{II}$$

We can thus deduce the expression of the molecular orbitals

$$\Psi_I = C_1^I(\varphi_1 + \varphi_2)$$
$$\Psi_{II} = C_1^{II}(\varphi_1 - \varphi_2)$$

It just remains to evaluate C_1^{I} and C_1^{II}. For this we introduce a physical condition into the problem. When it is in an orbital, the electron must have a probability of 1 (certainty) to be in the molecule. In other words

$$\int\int\int \Psi_I^* \Psi_I dv = 1$$

If the wave functions are real, as is the case here, we have the condition

$$\int\int\int \Psi_I^2 dv = 1$$

For the wave function Ψ_{I}, we can write

$$(C_1^I)^2 \int\int\int (\varphi_1 + \varphi_2)^2 dv = 1$$

As C_1^{I} is a constant, we have

$$(C_1^I)^2 \int\int\int (\varphi_1 + \varphi_2)^2 dv = 1$$

so that, by developing the integral

$$(C_1^I)^2 \iiint (\varphi_1^2 + \varphi_2^2 + 2\varphi_1\varphi_2)dv = 1$$

or

$$(C_1^I)^2 \left(\iiint \varphi_1^2 dv + \iiint \varphi_2^2 dv + 2\iiint \varphi_1\varphi_2 dv\right) = 1$$

Given that the orbitals ϕ_1 and ϕ_2 are normalized, and using the notation for the overlap integral (VII-5), we have

$$(C_1^I)^2(1 + 1 + 2S) = 1$$

which leads to

$$2(C_1^I)^2(1 + S) = 1$$

and

$$(C_1^I)^2 = \frac{1}{2(1 + S)} \tag{VII-16}$$

The expression of the coefficient C_1^I may be deduced

$$C_1^I = \frac{1}{\sqrt{2(1 + S)}} \tag{VII-17}$$

Similarly, with Ψ_{II} for the coefficient C_1^{II} we obtain

$$C_1^{II} = \frac{1}{\sqrt{2(1 - S)}} \tag{VII-18}$$

If the overlap integral S is neglected, these coefficients become

$$C_1^I = \frac{1}{\sqrt{2}} \quad \text{and} \quad C_1^{II} = \frac{1}{\sqrt{2}}$$

Hence, the expressions of the molecular wave functions are

$$\boxed{\Psi_I = \frac{1}{\sqrt{2}}(\varphi_1 + \varphi_2)} \qquad \text{(VII-19)}$$

and

$$\boxed{\Psi_{II} = \frac{1}{\sqrt{2}}(\varphi_1 - \varphi_2)} \qquad \text{(VII-20)}$$

2. Graphical representations of molecular orbitals

One way to represent molecular orbitals is to use isodensity surfaces, which have the merit of providing information on both probability density and topology. To make the information provided more complete, we use the representation that gives the value of the wave function including its sign in the different areas of the space. This method is similar to that used for atomic orbitals with the difference that there are now two nuclei and therefore a different referential, the origin of which will be taken as the middle of the internuclear axis.

We start from the expression of molecular orbitals with linear combinations of atomic orbitals

$$\Psi_I = \frac{1}{\sqrt{2}}(\varphi_1 + \varphi_2) \quad \text{and} \quad \Psi_{II} = \frac{1}{\sqrt{2}}(\varphi_1 - \varphi_2)$$

in which φ_1 and φ_2 constitute a basis set of wave functions.

From the geometrical point of view, the establishment of a chemical bond supposes a direction. Usually, we consider that the chemical bonds between two atoms start by establishing themselves along the axis z'0z giving us the interaction pattern in **Fig. VII-2**.

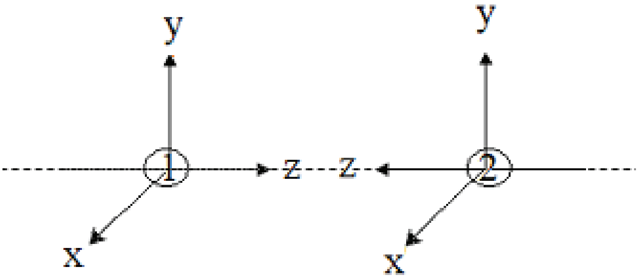


Figure. VII-2: interaction scheme between AOs.

a. Interaction between atomic orbitals ns: molecular orbitals σ_s

Consider the case of the linear combination of two orbitals 1s, the expression of which is given in **Table VI-2**. If $a_0 = 1$ and Z = 1, we have

$$\phi(r_1) = \frac{1}{\sqrt{\pi}}\exp(-r_1) \quad \text{and} \quad \phi(r_2) = \frac{1}{\sqrt{\pi}}\exp(-r_2)$$

where r_1 and r_2 are the distances from the electron to nucleus 1 and 2, respectively.

First consider the problem in two dimensions. The coordinates will then be as shown in **Fig. VII-1**.

For nucleus 1, we have

$$z^\circ{}_1 = -\frac{R}{2},\ y^\circ{}_1 = 0$$
$$z^\circ{}_2 = \frac{R}{2},\ y^\circ{}_2 = 0$$

so that

$$\Psi_I = \frac{1}{\sqrt{2\pi}}(\exp(-r_1) + \exp(-r_2))$$
$$\Psi_{II} = \frac{1}{\sqrt{2\pi}}(\exp(-r_1) - \exp(-r_2))$$

Using the Pythagorean theorem we can write

$$r_1 = \sqrt{(z - z°_1)^2 + (y - y°_1)^2}$$

$$r_2 = \sqrt{(z - z°_2)^2 + (y - y°_2)^2}$$

So, replacing r₁ and r₂ with their respective values, we have

$$\Psi_I = \frac{1}{\sqrt{2\pi}}\left(\exp\left(-\left|\sqrt{(z - z°_1)^2 + (y - y°_1)^2}\right|\right) + \exp\left(-\left|\sqrt{(z - z°_2)^2 + (y - y°_2)^2}\right|\right)\right)$$

$$\Psi_{II} = \frac{1}{\sqrt{2\pi}}\left(\exp\left(-\left|\sqrt{(z - z°_1)^2 + (y - y°_1)^2}\right|\right) - \exp\left(-\left|\sqrt{(z - z°_2)^2 + (y - y°_2)^2}\right|\right)\right)$$

For a value of the distance between the nuclei, for example R = 2, it then suffices to vary z and y, for example, between -3 and 3, and we obtain a table of values of Ψ_I and Ψ_{II}, respectively, the 3-D representation of which (the two space variables and the function) are given in **figs. VII-3a** and **VII-4a** for the two molecular wave functions. In order to better visualize the orbital, we use contour lines (**figs. VII-3b** and **VII-4b**), which projects the trace of the wave function at a certain value in the z0y plane. These curves are called *isoamplitude curves*.

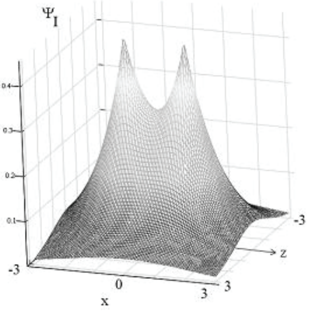


Figure. VII-3a: Amplitude function for σ₁ₛ.

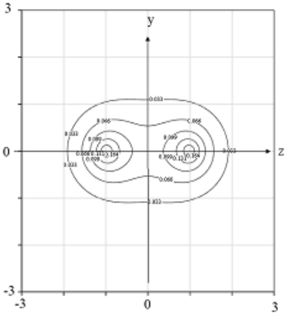


Figure. VII-3b: Amplitude contours for σ₁ₛ.

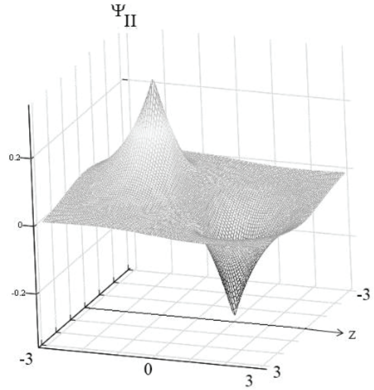


Figure VII-4a: Amplitude function for σ^*_{1s}.

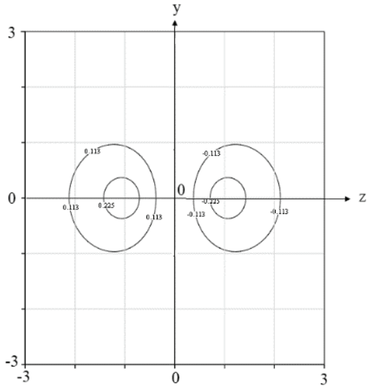


Figure VII-4b: Amplitude contours for σ^*_{1s}.

Note that the sign of the function is reversed in the case of the orbital Ψ_{II} after being canceled in the internuclear zone.

A similar representation given in **Fig. VII-5** uses the probability density Ψ_{II}^2, rather than the wave function Ψ_{II}. In this case, the orbital is represented by isodensity curves the shapes of which are similar to those shown above. This representation allows us to realize the probability density of the electron in the space around the nuclei. We can then see that the probability density in the internuclear zone is not zero, which favors the existence of a chemical bond between the nuclei. There is symmetry in the revolution of the orbital around the axis σ, which merges with the axis z'Oz; we shall call this orbital σ_{1s} because it comes from the interference between two atomic orbitals 1s. As it promotes chemical bonding due to the non-zero probability density in the internuclear zone, this orbital is called the *bonding orbital*.

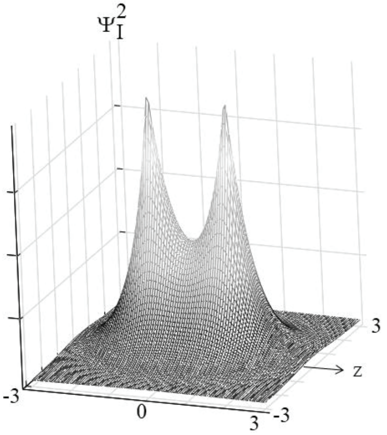


Figure VII-5a: Probability density for σ_{1s}.

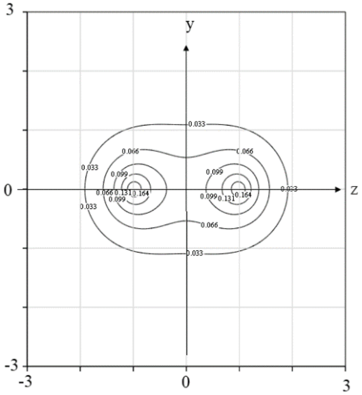


Figure VII-5b: Probability density for σ^*_{1s}.

When we represent the orbital Ψ_{II}, which corresponds to a combination of the function of opposite sign, we obtain the orbital σ^*_s for the symmetry of the revolution around the axis z'Oz, which has a zero probability density between the nuclei. This is not favorable to the establishment of a chemical bond between the nuclei, hence it takes the name *anti-bonding molecular orbital* (**Fig. VII-6**).

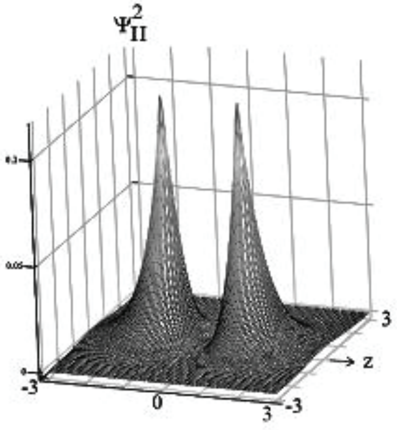


Figure VII-6a: Probability density for σ^*_{1s}.

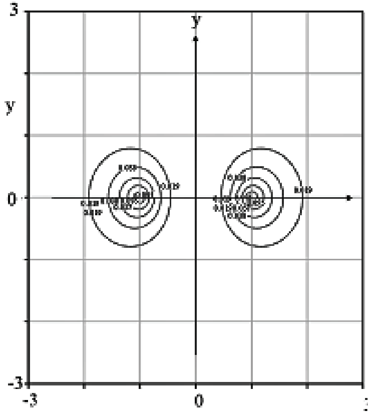


Figure VII-6b: Probability density contours for σ^*_{1s}.

The representation of the orbital is complete once we have varied the third variable, the angle φ of rotation around the axis z'oz.

In the case of the orbital σ_{1s} or σ^*_{1s}, we obtain an elongated volume representing an isodensity surface according to the diagram: the constructive combination gives the bonding orbital σ_{ns} and the destructive combination gives the anti-bonding orbital σ^*_{ns} (**Fig. VII-7**).

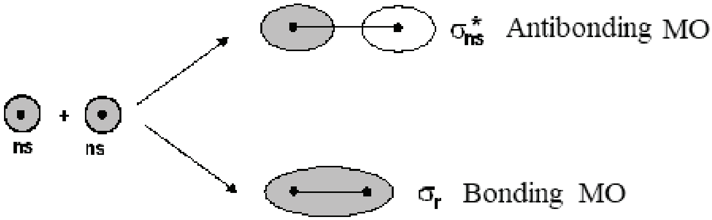


Figure VII-7: Schematic representation of the interaction between two AO ns.

The sign of the wave function is represented by a color—gray for the "+" and white for the "-" signs.

This type of orbital is met in the case of axial interactions between ns orbitals and also between np_z orbitals. There are also other types of interactions between p orbitals.

b. Interaction between np atomic orbitals

There are three np atomic orbitals, i.e. $2p_x$ $2p_y$, and $2p_z$; there are two sorts of interactions between them. An axial interaction between np_z AOs and two lateral interactions for the $2p_x$ and $2p_y$ respectively. **Fig. VII-8** presents the interaction scheme between these orbitals.

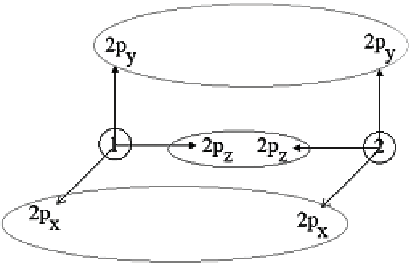


Figure VII-8: Interaction scheme between np AOs.

σ_z orbital

Looking at **Fig. VII-8**, we can see that once we complete the linear combination along the z axis, generating the two orbitals σ_z and σ^*_z, the only possibility of interaction between the np AOs is lateral and perpendicular to the z axis, while the only possibility of interaction between the 2p orbitals is lateral. Let us look first at the axial combination between the atomic orbitals $2p_z$.

Consider the expression of the $2p_z$ wave function

$$\phi_{2pz} = \frac{1}{4\sqrt{2\pi}} \exp\left(-\frac{r}{2}\right) \frac{r}{2} \cos\theta$$

in which we recognize the expression of the z coordinate and write

$$\phi_{2pz} = \frac{1}{8\sqrt{2\pi}} z \exp\left(-\frac{r}{2}\right)$$

The wave function linear combinations of atomic orbitals for σ_z are thus

$$\Psi\sigma_z = \frac{1}{\sqrt{2}}(\Psi_{2pz_1} - \Psi_{2pz_2})$$

and for the anti-bonding σ^*_z

$$\Psi\sigma_z^* = \frac{1}{\sqrt{2}}(\Psi_{2pz_1} + \Psi_{2pz_2})$$

which leads to

$$\Psi\sigma_z = \frac{1}{\sqrt{2}}\left(\frac{1}{8\sqrt{2\pi}} z_1 \exp\left(-\frac{r_1}{2}\right) - \frac{1}{8\sqrt{2\pi}} z_2 \exp\left(-\frac{r_2}{2}\right)\right)$$

The orbital will initially be constructed in the z0y plane. To do this, we have to locate the coordinates of the nuclei in the coordinate system, the origin of which is in the middle of the internuclear axis, i.e.

$$z_1 = -\frac{R}{2}; \quad y_1 = 0 \quad \text{and} \quad z_2 = \frac{R}{2}; \quad y_2 = 0$$

Then, we have the expressions for the two molecular orbitals

$$\Psi\sigma_z = \frac{1}{16\sqrt{2\pi}}(z-z_1)\exp\left(-\frac{\left|\sqrt{(z-z_1)^2+(y-y_1)^2}\right|}{2}\right) - \frac{1}{16\sqrt{2\pi}}(z-z_2)\exp\left(-\frac{\left|\sqrt{(z-z_2)^2+(y-y_2)^2}\right|}{2}\right)$$

$$\Psi\sigma_z^* = \frac{1}{16\sqrt{2\pi}}(z-z_1)\exp\left(-\frac{\left|\sqrt{(z-z_1)^2+(y-y_1)^2}\right|}{2}\right) + \frac{1}{16\sqrt{2\pi}}(z-z_2)\exp\left(-\frac{\left|\sqrt{(z-z_2)^2+(y-y_2)^2}\right|}{2}\right)$$

We represent the contour lines of the $\Psi\sigma_z$ and $\Psi\sigma^*_z$ OM amplitudes respectively in **figs. VII-9a** and **VII-9b**.

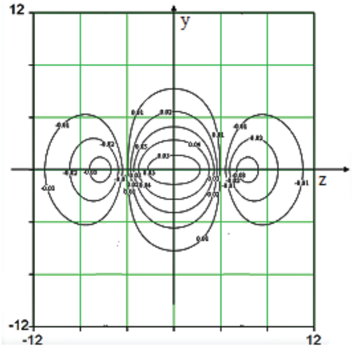


Figure VII-9a: bonding σ_z MO contour lines.

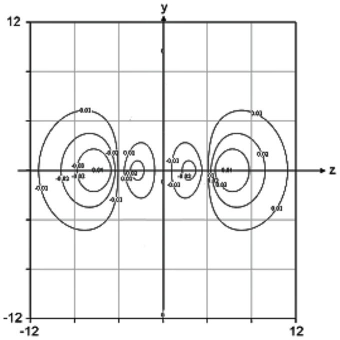


Figure VII-9b: bonding σ^*_z MO contour lines.

We can see that for the orbital σ_z the wave function is not null in the internuclear zone, implying electronic density in this area and thereby favorable connective conditions for the two nuclei. The orbital σ_z has axial symmetry with respect to the axis z'oz and is symmetrical with respect to a plane perpendicular to z'Oz in the middle of the internuclear distance. It has a positive phase in this area, but a negative phase beyond the nuclei.

On the contrary, the orbital σ^*_z does not favor a connection between the two nuclei since the probability density between the nuclei is zero. The orbital has axial symmetry with respect to z'Oz and is asymmetric with respect to the plane perpendicular to z'Oz passing through the middle of the internuclear axis.

Fig. VII-10 gives a schematic representation of the molecular orbitals σ_z and σ^*_z.

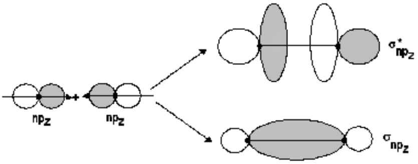


Figure VII-10: Interaction scheme of two np_z AOs.

π_x and π_y orbitals

These orbitals result from the lateral interaction of two atomic orbitals np_x or np_y. For this, we have to work in the xOz or yOz plane. We preferably study the orbital resulting from the interference in the yOz plane for reasons of convenience, but the orbitals obtained in the xOz plane are identical to those obtained in the yOz plane with a rotation of π/2. We have the following interactions in **Figs. VII-11**.

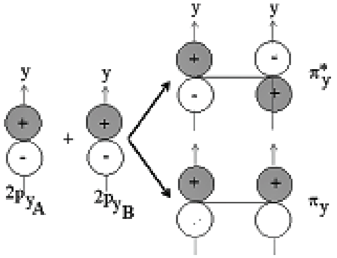


Figure VII-11a: Lateral interactions of two np_y AOs.

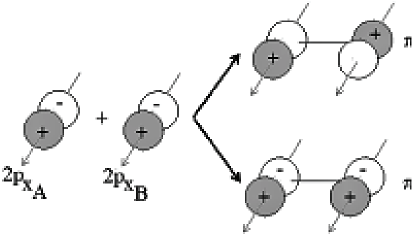


Figure VII-11b: Lateral interactions of two np_y AOs.

If we draw the isoamplitude curves for the π_y molecular orbital, which are easier to represent, we obtain the following result for the π_y binding orbitals (**Fig. VII-12a**) and the π^*_y anti-binding orbitals (**Fig. VII-12b**).

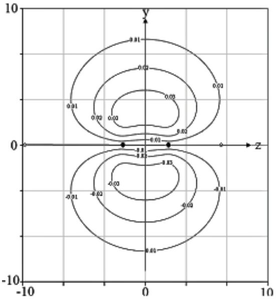


Figure VII-12a: π_y MO contour lines.

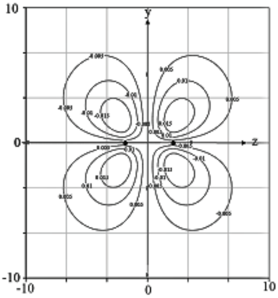


Figure VII-12a: π^*_y MO contour lines.

The π_{npx} orbitals can be deduced from π_{npy} by a rotation of $\pi/2$ in the plane perpendicular to the sheet.

3. Energy level diagrams

Above we saw that the interaction of two atomic orbitals leads to two molecular orbitals—one binding, the other non-binding. The binding orbital has lower energy than the energy of the starting atomic orbitals, while the anti-binding orbital has an energy greater than that of the starting atomic orbitals.

In **Fig. VII-13**, we represent these results in a diagram of energy levels, which should be read as follows: on the left and right followed by the vertical energy axes, we can see the situation of the system before the molecular interaction. In the center, we find the situation that results from this interaction: the atomic levels of the same energy $E_1 = E_2$ are split into molecular levels of different energies E_I and E_{II}. This diagram is diachronic (before-after) and is called an *orbital correlation diagram*.

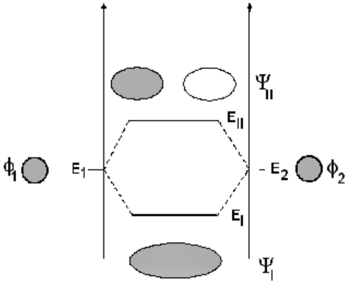


Figure VII-13: Correlation diagram of AOs and MOs.

It can be seen that the OMs obtained are of different energies. The lowest energy is the binding Ψ_I, while the highest is the anti-binding Ψ_{II}. It can be noted that the electronic density (the density probability of the presence of the electron) is large in the internuclear zone of the binding OM, thus favoring a bond between the nuclei; in the case of the anti-binding OM, the electronic density is zero, which is unfavorable for a connection between the nuclei.

4. Interference principles

If we consider the interaction between all the atomic orbitals of one atom with all the atomic orbitals of another atom, we can have two types of diagrams. These diagrams can be predicted by looking at the outermost electronic structure of the interacting atoms. We shall limit our study to that of homonuclear diatomic molecules.

If an atom that has n orbitals is interacting with an atom that also has n atomic orbitals, we get 2n molecular orbitals.

The interacting orbitals must all be of the same symmetry or of neighboring symmetry and their energies must not be too far apart, or their respective interaction, although possible, will remain negligible.

The correlation diagram for the set of molecular orbitals resulting from the interference between the atomic s or p orbitals takes into account the energy of the starting atomic orbitals, which is the basis of the linear combination. If we start from the basis of the atomic orbitals, including the 1s, 2s, $2p_x$, $2p_y$, and $2p_z$ orbitals, for each atom, we get 10 molecular orbitals. Each molecular orbital is created based on the symmetry and the energy gap between the initial atomic orbitals. Thus, we shall be able to see several groups of atomic orbitals, which will interfere. If A and B are the atoms with atomic orbitals that interfere, we mainly have the following interactions.

$$(1s_A + 1s_B) \rightarrow \left(\sigma_{1s} \text{ and } \sigma^*_{1s}\right)$$

$$(2s_A + 2s_B) \rightarrow \left(\sigma_{2s} \text{ and } \sigma^*_{2s}\right)$$

$$(2p_{z_A} + 2p_{z_B}) \rightarrow \left(\sigma_{2pz} \text{ and } \sigma^*_{2p_z}\right) \text{ or, to simplify } \left(\sigma_z \text{ and } \sigma^*_z\right)$$

$$(2p_{x_A} + 2p_{x_B}) \rightarrow \left(\pi_{2px} \text{ and } \pi^*_{2p_x}\right) \text{ or, to simplify} \left(\pi_x \text{ and } \pi^*_x\right)$$

$$(2p_{y_A} + 2p_{y_B}) \rightarrow \left(\pi_{2p_y} \text{ and } \pi^*_{2p_y}\right) \text{or, to simplify} \left(\pi_y \text{ and } \pi^*_y\right)$$

From the energy point of view, we have the *a priori* arrangement given in **Fig. VII-14**.

The double lines on the vertical axes mean that the energy scale has been shortened to include the orbitals on the diagram. The 1s and 2s orbitals therefore have no significant interaction even if they are of the same symmetry because they are energetically too far apart. Regarding the anti-bonding orbitals (marked with an asterisk *), they will always be higher on the energy scale than the corresponding bonding orbitals.

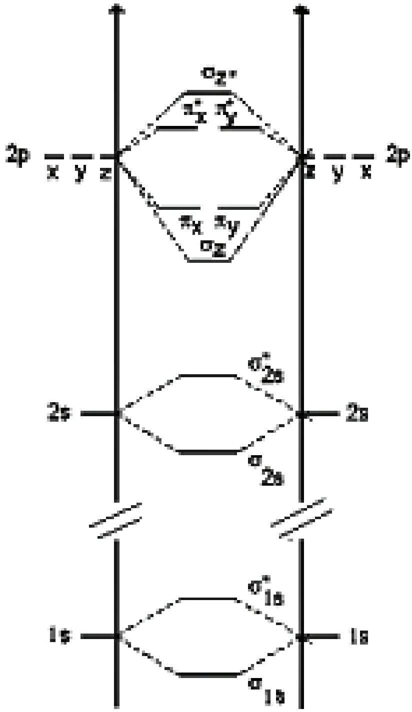


Figure VII-14: a priori diagram.

The σ type orbitals are *a priori* more stable than the π type orbitals and therefore come below them on the energy scale. However, as we shall see, this last detail has to be reconsidered. The orbitals π_x and π_y have the same energy and are said to be degenerate, as are π^*_x and π^*_y. It is for this reason that they are represented by lines on the same level.

5. Extension to polyelectronic molecules

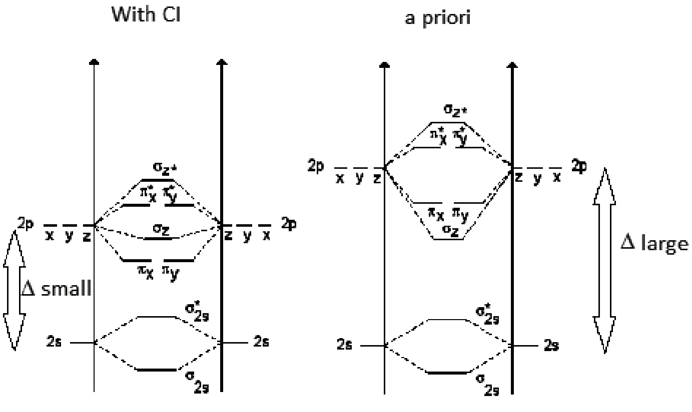
As with the results obtained in the case of the hydrogen atom (monoelectronic atom), which have been extended to atoms with several electrons (polyelectronic atoms), we can use the same principles to molecules other than the molecular hydrogen ion. This supposes certain rules, specified due to the presence of several electrons, which govern the electronic structures of molecules with several electrons.

a. Types of diagrams encountered

In order to facilitate the rapid use of the correlation diagrams of molecular orbitals to build the electronic structures of molecules, we state the following procedures the reasons for which will be made apparent later.

Filling the molecular energy levels with electrons, we must obey the following rules:

- when the outermost shell of an atom constituting a homonuclear diatomic molecule does not have doublets in the np orbitals, we have what is called a *diagram with configuration interaction (CI)*.
- when there are doublets in the np atomic orbitals, we have an *a priori diagram*, which we have already defined and that we can qualify as natural. These types of diagrams occur periodically and they intervene as soon as the atomic orbitals np are occupied by electrons (**Fig. VII-15**).


With CI

a priori

Figure VII-15: Both types of diagrams for homonuclear diatomic molecules.

The difference between these diagrams is related to the gap Δ between the energies of the orbitals s and p in the same atom. The gap Δ is significant when there is a strong repulsion between the s and p orbitals of the outermost shells of the same atom, occurring when there are doublets in the p orbitals. The order of the energy levels is that given by the a priori diagram. This term means that it is the natural order of molecular energy levels.

The difference Δ is small when there is little repulsion between the electrons in the outermost shell of orbital s and p, that is to say when there are no electron doublets in the p orbitals. We then have the diagram with configuration interaction. These terms mean that, due to their energetic proximity, there is an interaction between the molecular orbitals σ_{2s} and σ_z; an interaction that raises the level of the orbital σ_z and lowers that of the orbital σ_{2s}. The orbital σ_z then passes over the orbitals π_x and π_y. We say that there is a permutation of the levels σ and π.

b. Interference between atomic orbitals of different energies

The energy level of the interfering orbitals is not always the same. Let us examine the case where the basis orbitals that interfere do not have the same energy.

We consider the result of the interaction between two normalized orbitals characterized by ϕ_1 and ϕ_2. The molecular wave function can be represented within the framework of the LCAO method, i.e.

$$\Psi = C_1\varphi_1 + C_2\varphi_2$$

where the C_i is the respective weight of orbital ϕ_i.

Using the same notations as in our treatment of the molecular ion H_2^+, we have

$$\iiint \phi_1 \mathbf{H} \phi_1 \, dv = E_{11} \quad \text{and} \quad \iiint \phi_2 \mathbf{H} \phi_2 \, dv = E_{22}$$

We suppose that

$$E_{11} >> E_{22}$$

and E_{12}, the interaction energy, has the form

$$\iiint \phi_1 \mathbf{H} \phi_2 \, dv = \iiint \phi_2 \mathbf{H} \phi_1 \, dv = E_{12}$$

whereas the overlap integral is written

$$\iiint \phi_1 \phi_2 \, dv = S_{12}$$

Furthermore, since ϕ_1 and ϕ_2 are normalized, we have

$$\iiint \phi_1 \phi_1 \, dv = \iiint \phi_2 \phi_2 \, dv = 1$$

and then, for the energy (VII-11) we write

$$\langle E \rangle = \frac{C_1^2 E_{11} + C_2^2 E_{22} + 2C_1 C_2 E_{12}}{C_1^2 + C_2^2 + 2C_1 C_2 S_{12}}$$

Let us now apply the variation method we used previously

$$\begin{cases} \dfrac{\partial \langle E \rangle}{\partial C_1} = 0 \\[2ex] \dfrac{\partial \langle E \rangle}{\partial C_1} = 0 \end{cases}$$

which leads to the system of secular equations

$$\begin{cases} C_1 (E_{11} - \langle E \rangle) + C_2 (E_{12} - \langle E \rangle S_{12}) = 0 \\ C_1 (E_{12} - \langle E \rangle S_{12}) + C_2 (E_{22} - \langle E \rangle) = 0 \end{cases}$$

For the system to be solved, the secular determinant must be zero

$$\begin{vmatrix} (E_{11} - \langle E \rangle) & (E_{12} - \langle E \rangle S_{12}) \\ (E_{12} - \langle E \rangle S_{12}) & (E_{22} - \langle E \rangle) \end{vmatrix} = 0$$

i.e.

$$(E_{11} - \langle E \rangle)(E_{22} - \langle E \rangle) - (E_{12} - \langle E \rangle S_{12})^2 = 0$$

by developing this expression we get

$$(E_{11}E_{22} - \langle E \rangle E_{22}) - \langle E \rangle E_{11} + \langle E \rangle^2 - \left(E_{12}^2 + \langle E \rangle^2 S_{12}^2 - 2\langle E \rangle S_{12}\right) = 0$$

i.e.

$$(E_{11}E_{22} - \langle E \rangle E_{22}) - \langle E \rangle E_{11} + \langle E \rangle^2 - E_{12}^2 - \langle E \rangle^2 S_{12}^2 + 2\langle E \rangle S_{12} = 0$$

or

$$\langle E \rangle^2 (1 - S_{12}^2) - \langle E \rangle (E_{11} + E_{22} - 2S_{12}) + (E_{11}E_{22} - E_{12}^2)$$

The resolution of this equation leads to

$$\langle E \rangle = \frac{1}{2(1 - S_{12}^2)}\left((E_{11} + E_{22} - 2S_{12}) \pm \sqrt{(E_{11} + E_{22} - 2S_{12})^2 - 4(1 - S_{12}^2)(E_{11}E_{22} - E_{12}^2)}\right)$$

To simplify, consider that S_{12} is negligible and the equation then becomes

$$\langle E \rangle = \frac{1}{2}\left((E_{11} + E_{22}) \pm \sqrt{(E_{11} + E_{22})^2 - 4(E_{11}E_{22} - E_{12}^2)}\right)$$

Let us consider the discriminant

$$\Delta = (E_{11} + E_{22})^2 - 4(E_{11}E_{22} - E_{12}^2)$$

and develop it

$$\Delta = E_{11}^2 + E_{22}^2 + 2E_{11}E_{22} - 4E_{11}E_{22} + 4E_{12}^2$$

or

$$\Delta = E_{11}^2 + E_{22}^2 - 2E_{11}E_{22} + 4E_{12}^2$$

which may be also written

$$\Delta = (E_{11}^2 + E_{22}^2 - 2E_{11}E_{22}) + 4E_{12}^2$$

or

$$\Delta = (E_{11} - E_{22})^2 + 4E_{12}^2$$

Now, put the first term of the expression into common factors

$$\Delta = (E_{11} - E_{22})^2 \left[1 + \frac{4E_{12}^2}{(E_{11} - E_{22})^2} \right]$$

Note that the numerator of the fraction in this expression is small with respect to the denominator because the difference (E_{11}-E_{22}) is positive and of the order of ten eV, while E_{12}^2 is of the order of magnitude of 1 eV. Consequently, one can write that the expression between square brackets is of the type 1+ε.

Let us take now the square root of the discriminant

$$\sqrt{\Delta} = (E_{11} - E_{22}) \sqrt{\left[1 + \frac{4E_{12}^2}{(E_{11} - E_{22})^2} \right]}$$

given that

$$\sqrt{1+\varepsilon} \backsimeq 1 + \frac{\varepsilon}{2}$$

we may write

$$\sqrt{\Delta} \backsimeq (E_{11} - E_{22}) \left[1 + \frac{2E_{12}^2}{(E_{11} - E_{22})^2} \right]$$

so that

$$\langle E \rangle = \frac{1}{2} \left((E_{11} + E_{22}) \pm (E_{11} - E_{22}) \left[1 + \frac{2E_{12}^2}{(E_{11} - E_{22})^2} \right] \right)$$

or

$$\langle E \rangle_I = \frac{1}{2} \left((E_{11} + E_{22}) - \left[(E_{11} - E_{22}) + \frac{2E_{12}^2}{(E_{11} - E_{22})} \right] \right)$$

and

$$\langle E\rangle_{II} = \frac{1}{2}\left((E_{11} + E_{22}) + \left[(E_{11} - E_{22}) + \frac{2E_{12}^2}{(E_{11} - E_{22})} \right]\right)$$

The first solution $<E>_I$ is

$$\langle E\rangle_{I} = \frac{1}{2}\left((E_{11} + E_{22}) - (E_{11} - E_{22}) - \frac{2E_{12}^2}{(E_{11} - E_{22})} \right)$$

$$\langle E\rangle_{I} = \frac{1}{2}\left(E_{11} + E_{22} - E_{11} + E_{22} - \frac{2E_{12}^2}{(E_{11} - E_{22})} \right)$$

so that

$$\langle E\rangle_{I} = \frac{1}{2}\left(2E_{22} - \frac{2E_{12}^2}{(E_{11} - E_{22})} \right)$$

and finally

$$\langle E\rangle_{I} = E_{22} - \frac{E_{12}^2}{(E_{11} - E_{22})}$$

Likewise, for $<E>_{II}$ we find

$$\langle E\rangle_{II} = E_{11} + \frac{E_{12}^2}{(E_{11} - E_{22})}$$

Note that the expression $E_{12}^2/(E_{11}-E_{22})$ is positive because E_{12}^2 is a square and $E_{11}-E_{22}>0$.

We deduce that <E>$_I$ is the most negative of the solutions. It therefore corresponds to the energy of the binding orbital while <E>$_{II}$ corresponds to the energy of the anti-bonding orbital. In **Fig. VII-16** we schematize this by drawing a diagram of the energy levels.

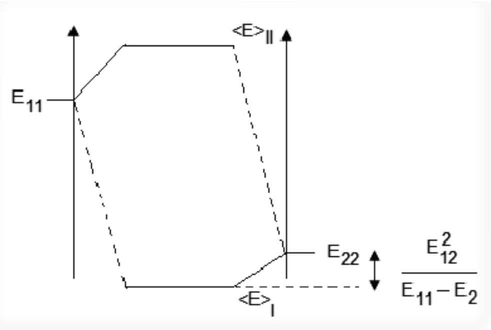


Figure VII-16: Interaction between two orbitals of different energies.

Let us consider the secular equations in which we have neglected the overlap integrals

$$\begin{cases} C_1(E_{11}-\langle E\rangle)+C_2(E_{12}) = 0 \\ C_1(E_{12})+C_2(E_{22}-\langle E\rangle) = 0 \end{cases}$$

These equations can also be written

$$\begin{cases} C_1(E_{11}-\langle E\rangle) = -C_2(E_{12}) \\ C_1(E_{12}) = -C_2(E_{22}-\langle E\rangle) \end{cases}$$

$$\frac{C_1}{C_2} = -\frac{E_{12}}{(E_{11}-\langle E\rangle)} = \frac{E_{12}}{(\langle E\rangle - E_{11})}$$

$$\frac{C_1}{C_2} = -\frac{(E_{22}-\langle E\rangle)}{E_{12}} = \frac{(\langle E\rangle - E_{22})}{E_{12}}$$

Let us make the product of these two last expressions

$$\left(\frac{C_1}{C_2}\right)^2 = \frac{(E_{22}-\langle E\rangle)}{(E_{11}-\langle E\rangle)}$$

So, for the energy binding orbital <E>$_I$, we have

$$\left(\frac{C_1^I}{C_2^I}\right)^2 = \frac{(E_{22} - \langle E\rangle_I)}{(E_{11} - \langle E\rangle_I)}$$

while for the anti-binding orbital $<E>_{II}$, we have

$$\left(\frac{C_1^{II}}{C_2^{II}}\right)^2 = \frac{(E_{22} - \langle E\rangle_{II})}{(E_{11} - \langle E\rangle_{II})}$$

c. Dipole moment

A quick glance at the molecular orbital diagram shows that

$(E_{22}-<E>_I) < (E_{11}-<E>_I)$ and that $(E_{22}-<E>_{II}) < (E_{11}-<E>_{II})$.

So that

$$\left(\frac{C_1^I}{C_2^I}\right)^2 < 1 \quad \text{and} \quad \left(\frac{C_1^{II}}{C_2^{II}}\right)^2$$

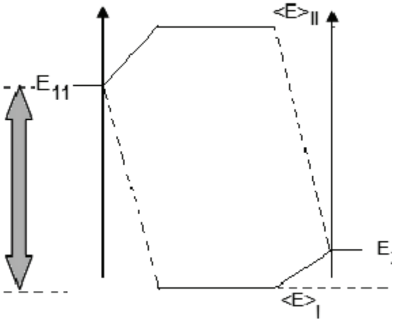


Figure VII-17: Dissymmetry of coefficients.

We can thus see that in the bonding MO, the most important coefficient is found on the right atom, while this is the opposite for the anti-bonding orbital. This means that the probability of the presence of the bond doublet is greater on atom 2 than on atom 1. The situation is the opposite for the anti-bonding MO.

We deduce that the electronic charge carried by atom 2 and atom 1 are, respectively

$$Q_2 = 2e^-(C_2^I)^2 \quad \text{and} \quad Q_1 = 2e^-(C_1^I)^2$$

Compared to a so-called covalent situation where the electrons of the bond doublet are exactly shared between the two atoms, we can say that the excess of negative charge on atom 2 or a positive charge on atom 1 will be, respectively

$$-\delta Q = |Q_2 - 1|e^- \quad \text{and} \quad +\delta Q = e|1^- - Q_2|$$

i.e.

$$\delta Q_2 = \left(2(C_2^I)^2 - 1\right)e^- \text{ and } \delta Q_1 = -e\left(1 - 2(C_2^I)^2\right)$$

In both cases, we can see that the quantity δQ is the same except for the sign. We can therefore say that the molecule formed corresponds to a dipole.

The system formed by two equal charges, but with opposite signs separated by distance R_e is called a dipole. A dipole is characterized by its electric dipole moment **μ** such as that given in **Fig. VII-18**.

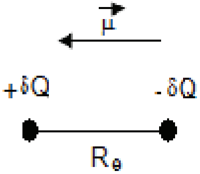


Figure VII-18: Dipole moment definition.

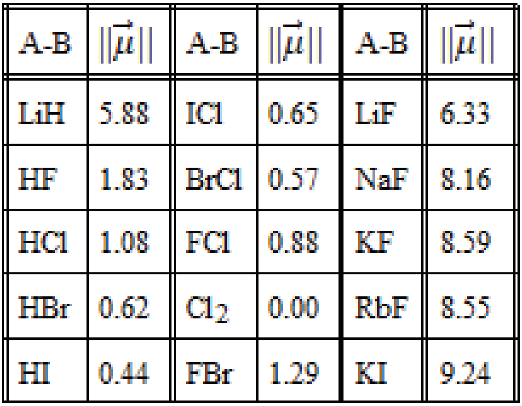
$$||\vec{\mu}|| = R_e\delta Q \tag{VII-21}$$

||μ|| is expressed in Coulomb meter (C.m). It is often also expressed in Debye, i.e. 1 Debye = $0.33.10^{-29}$ C.m.

The dipole moment is an experimentally measured quantity. The existence of a dipole moment in a molecule has its origin in the difference of electronegativity between atoms. We have seen that the electron density is higher in the vicinity of the most electronegative atom, which leads to an asymmetry in the distribution of the binding electrons. The molecule is said to be polar because the barycenter of positive charges is no longer confused with the barycenter of negative charges. The molecule is therefore comparable to a dipole.

By convention, the experimental dipole moment vector is oriented from the negative charge to the positive charge. We can thus predict the importance of the dipole moment as a function of the energy difference between the orbitals entering into interference. **Table VII-8** gives the values of the experimental dipole moment for several diatomic molecules. We shall see later how to calculate a dipole moment using the theory of molecular orbitals.

Table VII-8: Experimental dipole moments



A-B	$\|\|\vec{\mu}\|\|$	A-B	$\|\|\vec{\mu}\|\|$	A-B	$\|\|\vec{\mu}\|\|$
LiH	5.88	ICl	0.65	LiF	6.33
HF	1.83	BrCl	0.57	NaF	8.16
HCl	1.08	FCl	0.88	KF	8.59
HBr	0.62	Cl_2	0.00	RbF	8.55
HI	0.44	FBr	1.29	KI	9.24

d. Explanation of the permutation of the σ and π levels in MO diagrams

We can now give a qualitative explanation[10] of the permutation of the σ and π levels in molecular orbital diagrams.

For this we must remember that two orbitals, whether atomic or molecular, can interfere if they are of the same or almost the same symmetry and of the same or almost the same energy. This is the case of the molecular orbitals 2s and σ_z and 2s* and σ^*_z. It may indeed happen that the difference between these energy levels becomes relatively small allowing such interference to take place. This then leads us to a new interaction diagram, shown in **Fig. VII-19**.

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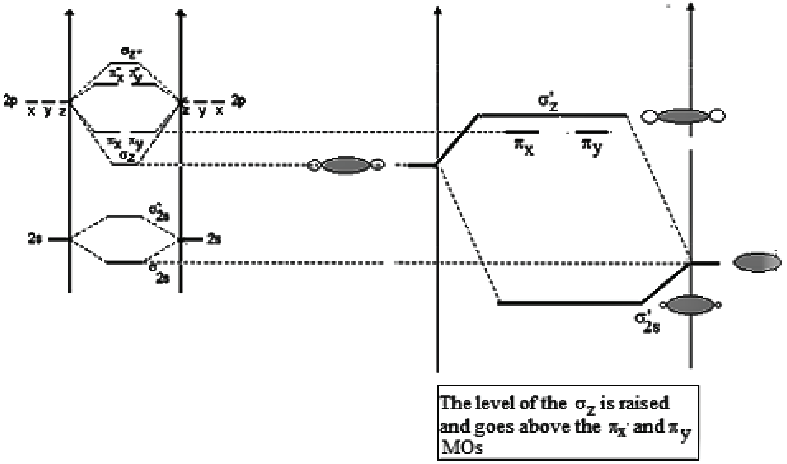
[10] For more details see for instance the paper O. Henri-Rousseau and B. Boulil, "Explanation of the Permutation of the σ(p) and π Levels in Homonuclear Diatomic Molecules". J. Chem. Educ. 55 (1978) 571-73.



The level of the σ_z is raised and goes above the π_x and π_y MOs

Figure VII-19: The permutation of σ_z and π levels.

The molecular orbital σ_z of axial symmetry can interfere with the molecular orbital σ_{2s}, also of axial symmetry, and under certain conditions energetically close to σ_z. This interference causes the raising of σ_z to σ_z' (destructive interference) and the lowering of σ_{2s} to σ_{2s}' (constructive interference). We can thus understand why there is a permutation of the levels σ_{2s} and π_x and π_y. This phenomenon is called a *configuration interaction* (CI) in the language of quantum chemistry. We shall call the diagram of molecular orbitals in these conditions, a diagram with CI, as in **Fig. VII-15**.

e. Molecular electronic structures

These structures are a result of the molecular levels being filled by the electrons of the atoms making up the molecule. For reasons of simplicity, we only represent what is happening on the outermost shell of atoms.

The rules of constructing molecular electronic structures are almost the same as those governing the construction of atomic electronic structures, applying the following:

- The Pauli construction principle: we trace the empty orbital boxes.
- The Pauli exclusion principle: no more than 2 electrons per molecular stationary state.

- Hund's rule: the distribution at the same energy levels of the electrons with the same quantum magnetic spin number.

To represent the MO diagram of a diatomic homonuclear molecule X_2, we may use the following procedure:

(i) We give the electronic configuration of the atom X.

(ii) We establish the necessary orbital basis (in general, the AOs occupied by electrons)

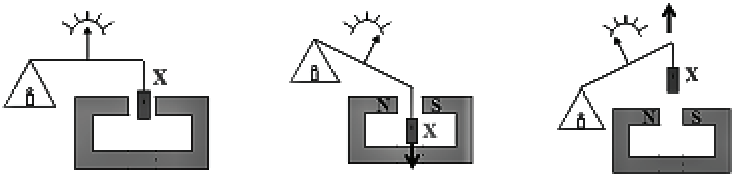
(iii) We note whether or not there are electron doublets in the np orbitals of the outermost shell of the atom X. If yes, then the diagram used is of the a priori type. If not, the diagram used is of the CI type.

(iv) The electrons are placed in the molecular levels starting with the lower energy levels, respecting the Pauli exclusion principle and Hund's rule.

(v) We calculate the bond index I, which is the difference between the number of electrons in bonding orbitals and the number of electrons in anti-bonding orbitals all divided by 2.

(vi) If i is different to zero, then the molecule may exist and we then give its electronic configuration.

(vii) One can predict its magnetic properties. The molecule is *paramagnetic* if there are single electrons in the molecule; otherwise it is *diamagnetic*.



a) Without electromagnetic field.

b) With electromagnetic field. X is paramagnetic.

c) With electromagnetic field. X is diamagnetic.

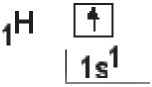
Figure VII-20: Behavior of paramagnetic and diamagnetic samples in an electromagnetic field.

Fig. VII-20 gives the behavior of a paramagnetic sample (b) and of a diamagnetic sample (c) placed within the poles of an electromagnet. If the electromagnet moves into the air gap, it means that the sample is paramagnetic. On the contrary, movement away from the field implies diamagnetic behavior.

Examples

The hydrogen (H_2) molecule

(i) The electronic structure of hydrogen



(ii) The basis orbital is {1s}. An interaction between two 1s orbitals is performed.

(iii) There are no p orbitals concerned in the fundamental state.

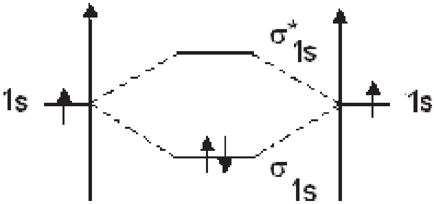


Figure VII-21: MO correlation diagram for the H_2 molecule.

(iv) The diagram is drawn and the electrons are placed respecting the rules (**Fig. VII-21**).

(v) The bond index is (2-0)/2 = 1.

(vi) The molecule exists.

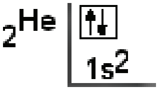
(vii) The molecule is diamagnetic because there are no single electrons on the outermost shell.

(viii) Its electronic configuration is

$$H_2 : \sigma_{1s}^2$$

The helium (He_2) molecule

(i) The electronic structure of helium



(ii) The basis orbital is {1s}. An interaction between two 1s orbitals is performed.

(iii) There are no p orbitals concerned in the fundamental state.

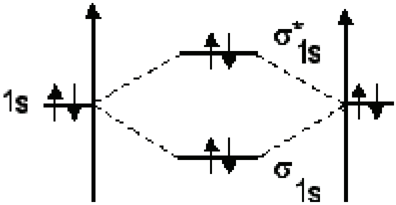


Figure VII-22: MO correlation diagram for the hypothetical He_2 molecule.

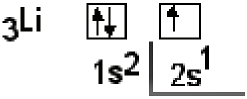
(iv) The diagram is drawn and the electrons are placed respecting the rules stated above (**Fig. VII-22**).

(v) The bond index is (2-2)/2 = 0.

(vi) The molecule cannot exist.

The lithium (Li_2) molecule

(i) The electronic structure of Li



(iv) The diagram is drawn and the electrons are placed respecting the rules stated above (**Fig. VII-23**).

(v) The bond index is (2-0)/2 = 1.

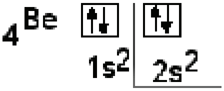
(vi) The molecule can exist.

(vii) The molecule is diamagnetic because there are no single electrons on the outermost shell.

(viii) Its electronic configuration is

$$Li_2 \ : \sigma_{2s}^2$$

The beryllium (Be₂) molecule
(i) The electronic structure of beryllium



(ii) The basis orbital is {2s} because we limit ourselves to the outermost shell. An interaction between two 2s orbitals is performed.

(iii) There are no p orbitals concerned in the fundamental state.

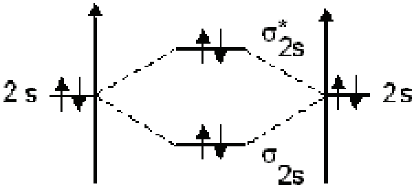


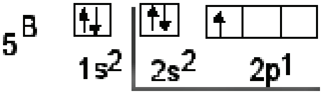
Figure VII-24: MO correlation diagram for the hypothetical Be_2 molecule.

(iv) The diagram is drawn and the electrons are placed respecting the rules stated above (**Fig. VII-24**).

(v) The bond index is (2-2)/2 = 0.

(vi) The molecule cannot exist.

The boron (B_2) molecule
(i) The electronic structure of boron



(ii) The basis orbital is {2s, $2p_x$, $2p_y$, $2p_z$} because we limit ourselves to the outermost shell. Interaction between the 2s orbitals and between the six p orbitals is performed.

(iii) There is a p orbital concerned in the fundamental state. The diagram that must be used is of the CI type because there are no electronic doublets in the 2p orbitals.

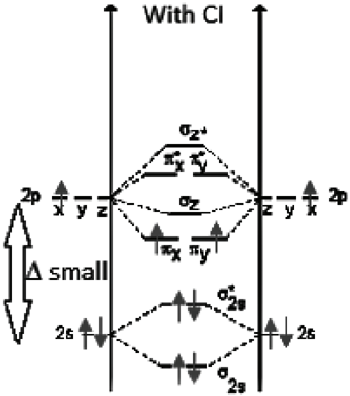


Figure VII-25: MO correlation diagram for the B_2 molecule.

(iv) The diagram is drawn and the electrons are placed respecting the rules stated above (**Fig. VII-25**).

(v) The bond index is (4-2)/2 = 1.

(vi) The molecule can exist.

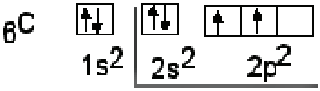
(vii) The molecule is paramagnetic because there are two single electrons on the outermost shell.

(viii) Its electronic configuration is

$$B_2 \ : \sigma_{2s}^2 \sigma_{2s}^{*2} \pi_x^1 \pi_y^1$$

The carbon (C_2) molecule

(i) We give the electronic configuration of carbon atom



(ii) Choice of the orbital basis {2s, 2px, 2py, 2pz}.

(iii) We note that there are no electron doublets in the np orbitals of the outermost shell of the atom C. Hence, the diagram used is the CI type.

(iv) The electrons are placed in the molecular levels starting with the lower energy levels, respecting the Pauli exclusion principle and Hund's rule.

(v) We calculate the bond index I = (6-2)/2 = 2.

(vi) The bond index is different to zero and the molecule may exist.

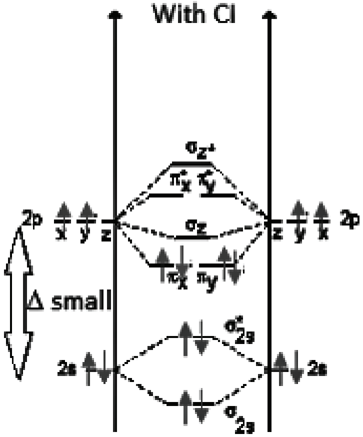


Figure VII-26: MO correlation diagram for the C_2 molecule.

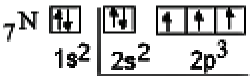
(vii) The molecule is diamagnetic since all electrons in the outermost shell are paired.

(viii) Its electronic configuration is

$$C_2 \ : \sigma_{2s}^2 \sigma_{2s}^{*2} \pi_x^2 \pi_y^2$$

The Nitrogen (N_2) molecule

(i) The electronic structure of nitrogen atom



(ii) Choice of the orbital basis $\{2s, 2p_x, 2p_y, 2p_z\}$.

(iii) There is a p orbital concerned in the fundamental state. The diagram that must be used is the CI type because there are unpaired electrons in the 2p orbitals.

(iv) The diagram is drawn and the electrons are placed respecting the rules stated above (**Fig. VII-26**).

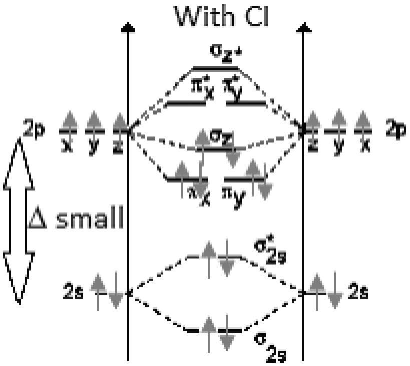


Figure VII-27: MO correlation diagram for the N_2 molecule.

We limit ourselves to the outermost shell. The basis is therefore {2s, 2p}. There is an interaction between the 2s and 2p orbitals of each atom.

(v) We calculate the bond index i = (8-4)/2 = 2.

(vi) The molecule can exist.

(vii) The molecule is paramagnetic since it retains unpaired electrons in the outermost shell.

(viii) Its electronic configuration is

$$N_2 \ : \sigma_{2s}^2 \sigma_{2s}^{*2} \sigma_z^2 \pi_x^2 \pi_y^2$$

The Oxygen (O_2) molecule

(i) The electronic structure of the oxygen atom

(ii) Choice of the orbital basis {2s, $2p_x$, $2p_y$, $2p_z$}.

(iii) There is a p orbital concerned in the fundamental state. The diagram that must be used is the a priori type because there are one doublet in the 2p orbitals.

(iv) The diagram is drawn and the electrons are placed respecting the rules stated above.

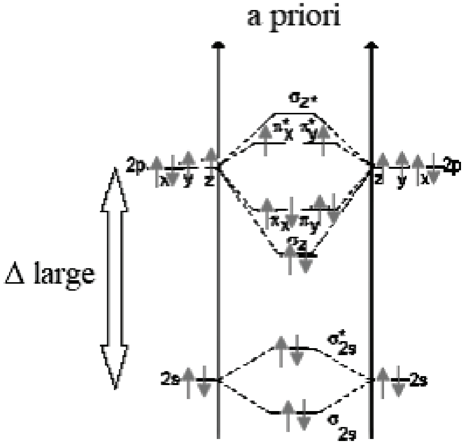


Figure VII-28: MO correlation diagram for the O_2 molecule.

We limit ourselves to the peripheral shell. The basis is therefore {2s, 2p}. There is an interaction between the 2s and 2p orbitals of each atom.

(v) We calculate the bond index I = (8-4)/2 = 2.

(vi) The molecule can exist.

(vii) The molecule is paramagnetic since it retains unpaired electrons in the outermost shell.

(viii) Its electronic configuration is

$$O_2\ :\sigma_{2s}^2\sigma_{2s}^{*2}\sigma_z^2\pi_x^2\pi_y^2\pi_x^{*1}\pi_y^{*1}$$

We leave it to the reader to discover the molecular diagrams of difluorine and dineon.

It should be noted that we find the same evolution with the molecules resulting from the elements of the third period of the periodic table.

6. Molecular orbitals and physical properties of diatomic molecules

By presenting a few examples, we shall see how the evolution of the properties of diatomic molecules can be understood using the theory of molecular orbitals.

Consider the oxygen molecule O_2: we can ionize it and create positive ions like O_2^+ and negative ions like O_2^-. Let us build the molecular orbital diagrams of these entities.

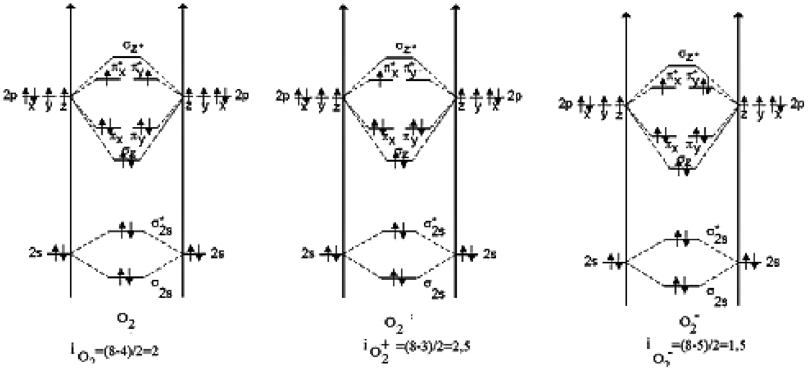


Figure VII-29: MO correlation diagram for O_2, O_2^+, and O_2^- molecules.

As can be seen, we have

$$\mathrm{i}_{O_2^-} < \mathrm{i}_{O_2} < \mathrm{i}_{O_2^+}$$

The higher the bond index, the higher the dissociation energy, the higher the vibration frequency, and the shorter the interatomic distance at equilibrium. We can conclude that

$$\mathrm{De}_{O_2^-} < \mathrm{De}_{O_2} < \mathrm{De}_{O_2^+}$$

$$\mathrm{Re}_{O_2^-} > \mathrm{Re}_{O_2} > \mathrm{Re}_{O_2^+}$$

$$\bar{\nu}_{e\,O_2^-} < \bar{\nu}_{e\,O_2} < \bar{\nu}_{e\,O_2^+}$$

which gives the following evolutions when we plot the potential curves

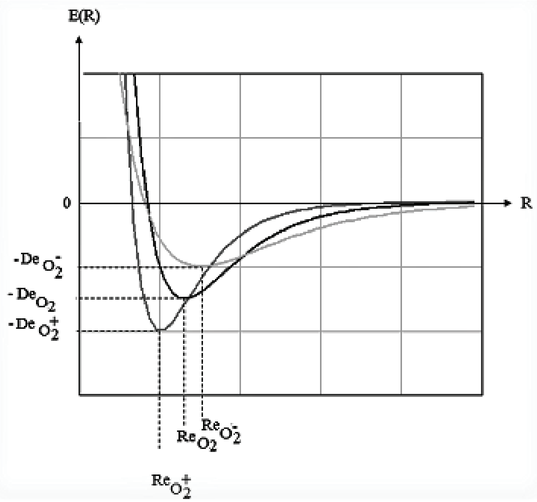


Figure VII-30: Potential curves for O_2 , O_2^+, and O_2^- molecules.

It should be noted that the concavity is less and less marked when we pass from the molecule with the strongest force constant (i.e. the vibration wavenumber) to the weakest.

This has been confirmed experimentally[11], as can been seen in **Table VII-9**.

Table VII-9. Experimental data for O_2 , O_2^+, and O_2^- molecules

	D_e $(e.V)$	R_e $(\mathring{A})$	$\bar{v}_e$ (cm^{-1})
O_2	5.08	1,207	1580
O_2^+	6,48	1.123	1905
O_2^-	4,09	1.350	1090

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[11] K. P. Huber and G. Herzberg, "Molecular Spectra and Molecular Structure. IV Constants of Diatomic Molecules", Van Nostrand Teinhold Company, New York, 1979, p.490-507.

7. MOs and heteronuclear diatomic molecules

When the molecules are made up of different atoms, the energies of the interacting atomic orbitals are no longer the same.

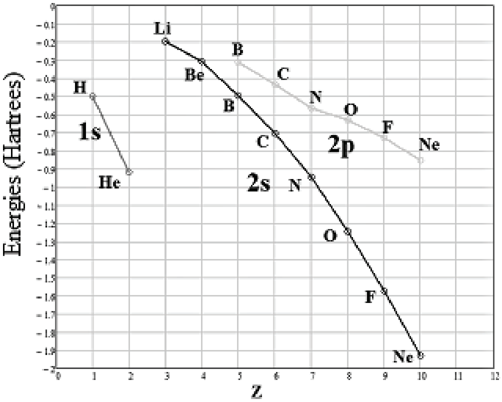
An asymmetry appears due to the different electronegativities of each atom. The more electronegative an atom, the more marked the negative energy of its orbitals.

In some cases, this can lead to interferences between atomic orbitals of the same symmetry, which can end up being fairly similar energetically and allow significant interference. **Table VII-10** gives the energies of the first atomic orbitals versus the atomic number Z calculated by Clementi[12] in 1965. (These data are given in tables in the paper in the references[13].)

E. Clementi

Table VII-10 can be used to position the atomic orbitals that are interfering on an energy scale. We have previously seen the case of interference between orbitals of different energies.

Table VII-10: Calculated atomic orbital energies



Let us see how the theoretical data allow the calculation of a quantity such as the dipole moment, which characterizes the difference in electronic distribution in a chemical bond between two atoms of different

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[12] Enrico Clementi (born 1931). Italian chemist and a pioneer in computational techniques for quantum chemistry and molecular dynamics.

[13] E. Clementi, IBM Journal of Research and Development, 9 (1965) 2. Basic Data Tables for Chemistry, O. Kahn and M-F. Koenig, Hermann, Paris, 1972.

electronegativities.In section VII-2-5c (*vide supra*), we showed how calculate a dipole moment using molecular orbital theory. Let us apply this procedure to the calculation of the dipole moments of some molecules.

The LiH molecule

Let us start by placing the energies of the orbitals concerned. The lithium 1s orbital is too low to interfere with the hydrogen 1s orbital. Interference takes place between the 2s orbital of lithium and the 1s orbital of hydrogen, which are of the same symmetry, to form the molecular orbitals σ_s and σ^*_s.

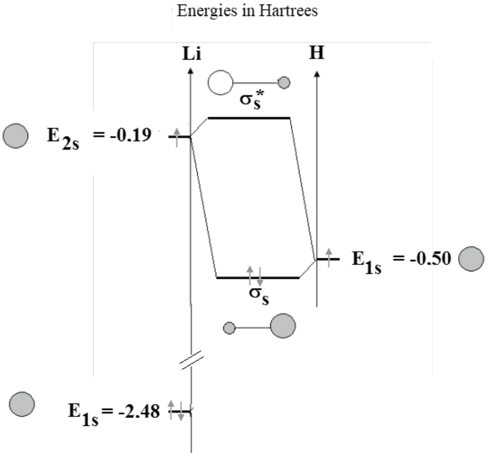


Figure VII-31: Energy position of orbitals in the LiH molecule.

The energies of these molecular orbitals are, respectively, -0.1963 Hartree and -0.50 Hartree. The interaction energy E_{12} between these atomic orbitals is approximately -0.12 Hartree at a distance R_e of 1.60 A. Thus, we can deduce approximately

$$\langle E\rangle_\sigma \simeq E_{1s} + \Delta E \quad \text{and} \quad \langle E\rangle_{\sigma^*} = E_{2s} - \Delta E$$

with

$$\Delta E = \frac{(E_{12})^2}{(E_{22} - E_{11})}$$

then

$$\Delta E = \frac{(E_{12})^2}{(E_{22} - E_{11})} = \frac{(0.12)^2}{-0.50 + 0.19} = -0.047\ \mathit{hartree}$$

and we have

$$\langle E\rangle_{\sigma} = E_{2s} + \Delta E = -0.5 - 0.047 = -0.547\ \textit{hartree}$$
$$\langle E\rangle_{\sigma^*} = -0.1963 + 0.047 = -0.1493\ \textit{hartree}$$

We can calculate the coefficients of the molecular orbitals

$$\left(\frac{C_1}{C_2}\right)^2_{\sigma} = \frac{\langle E\rangle_{\sigma} - E_{2s}}{\langle E\rangle_{\sigma} - E_{1s}}$$

or

$$\left(\frac{C_1}{C_2}\right)^2_{\sigma} = \frac{-0.547 + 0.500}{-0.547 + 0.1963} = 0.135$$

so that

$$C^2_{1_\sigma} = 0.135 C^2_{2_\sigma}$$

Taking into account that the molecular orbitals must be normalized, that is to say, if we neglect the overlap integral, then we must have

$$C^2_{1_\sigma} + C^2_{2_\sigma} = 1$$
$$0.135\ C^2_{2_\sigma} + C^2_{2_\sigma} = 1 \text{ so that } 1.135\ C^2_{2_\sigma} = 1$$

and finally we get

$$C^2_{2_\sigma} = \frac{1}{1.135} = 0.881 \quad \text{and } C^2_{1_\sigma} = 1 - 0.881 = 0.119$$

We can thus calculate the dipole moment of LiH using the results obtained in section VII-2-5c

$$\delta Q =^{-} e\left(1 - 2(C^2_{2_\sigma})^2\right)$$

For LiH, if we consider a distance at equilibrium of Re = 1.60 A, for the dipole moment we find

$$\|\vec{\mu}\| = 1.595 \times 10^{-10} \times 1.6 * 10^{-19} \times (2 * 0.881 - 1) = 1.944624 \times 10^{-29} C.m$$

or, in Debye

$$\|\vec{\mu}\| = \frac{1.944624 \times 10^{-29}}{0.33 \times 10^{-29}} C.m = 5.89\, D$$

The experimental value is 5.88D.

The HF molecule

Another example In the calculation of a dipole moment is the HF molecule. In this case, the situation is reversed—it is the hydrogen atom that has the least negative energy because it is less electronegative than fluorine.

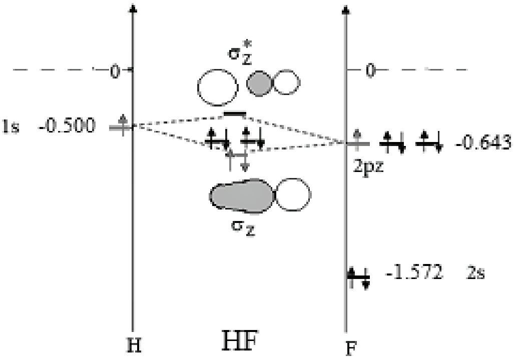


Figure VII-32: Energy position of orbitals in the HF molecule.

However, the imbalance is less strong than in the previous case, as can be seen in **Fig. VII-32**.

These are the 1s orbitals of hydrogen and $2p_z$ of fluorine, which, being of similar symmetry and relatively close energies, will interfere. The dipole moment is directed this time from fluorine to hydrogen and will be of lower value than that found in the case of LiH because the difference between the atomic orbitals that interfere is smaller. As such, we find by calculation that $\|\mu\| = 1.83$ D.

8. Other heteronuclear diatomic molecules

Even if the predictive character is not as complete as in the case of homonuclear diatomic molecules, the same phenomena occur and it seems that we can classify three types of diagrams—with the addition of a *medium CI diagram* to the two already mentioned: a priori and "strong" CI diagrams.

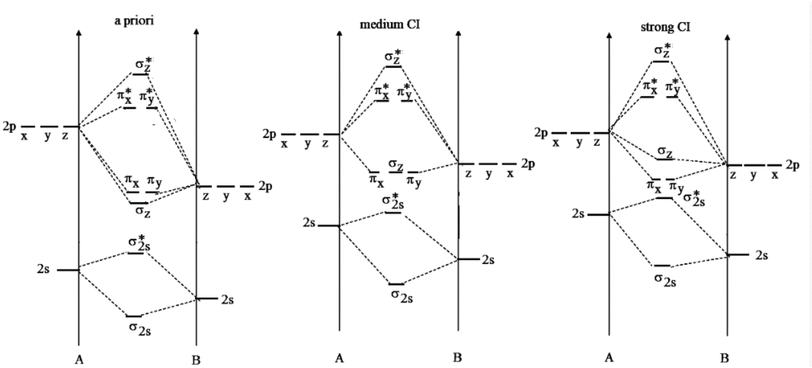


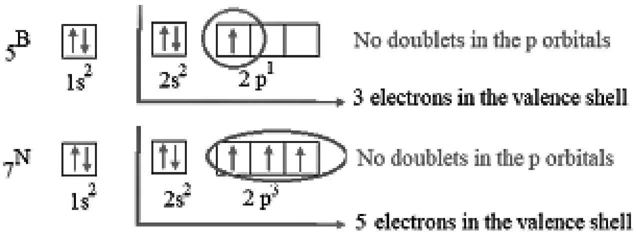
Figure VII-33: Different Types of OM diagrams in heteronuclear diatomic molecules.

The strong configuration interaction reverses the levels σ_z and π with respect to the a priori diagram. An interaction of medium configuration raises the level σ_z to the same level as that of π.

Choosing which of these three diagrams to use will of course depend on the electronic structure of the atoms in terms of interference. In these diagrams, atom B being more electronegative, its atomic will have orbitals with more negative energy than those of atom A.

The BN molecule

The BN molecule is an 8-electron valence system in which nitrogen N is more electronegative than its neighbour, boron (B), being located to its left in the periodic table. We can see their electronic configurations on the right



Boron, like nitrogen, has no doublets in its p orbitals. The repulsion between the p layer and the s layer is reduced and the energy difference is relatively small between these orbitals. As such, we should expect to have a configuration interaction diagram, although we might hesitate over whether to choose a medium or a strong CI type diagram. Experience shows that the BN molecule is paramagnetic and therefore carries unpaired electrons on its valence shell. Let us look at the two hypotheses in **Fig. VII-34**.

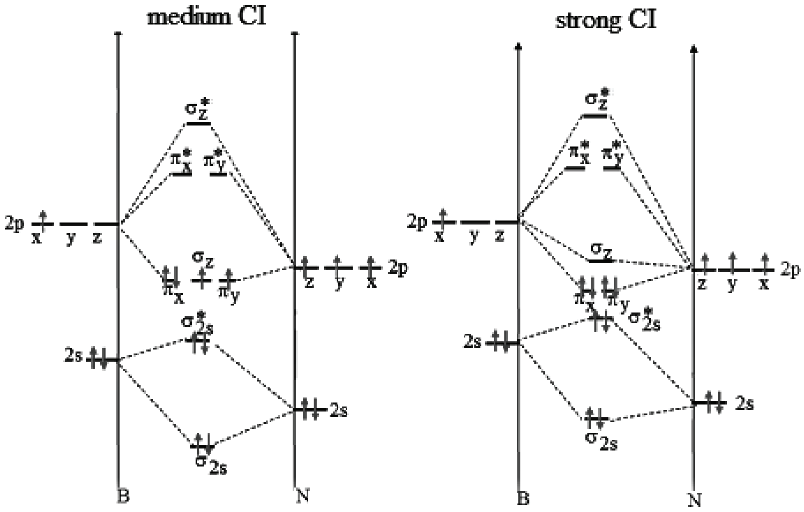


Figure VII-34: hypothesis for BN diagram.

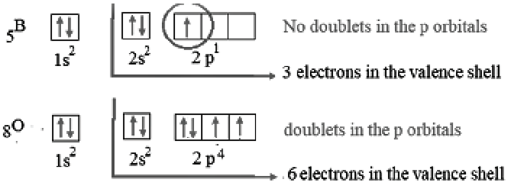
In the strong CI hypothesis, the energy difference between σ_{2s} and σ_z remains large enough for the electrons of shell p to be distributed only in the shells π by virtue of the Pauli construction principle. In the medium CI hypothesis, the increase in σ_z is not sufficient to pass over the molecular orbitals π. Hund's rule therefore applies in the filling of these three levels whose energy is the same. As such, the diagram on the left accounts for the fact that BN is paramagnetic. The electronic structure of the BN molecule is therefore

$$BN : \sigma_{2s}^{2} \sigma_{2s}^{*2} (\pi_x \pi_y \sigma_z)^4$$

The bond index of this molecule is: $i_{BN} = (6-2)/2 = 2$

The BO, CN, and CO⁺ molecules

These entities have 9 valence electrons. Let us look at the BO molecule, the electronic structures of which are shown on the right.



The diagram is a CI type because the repulsions between the electronic shells of the atomic orbitals remain weak.

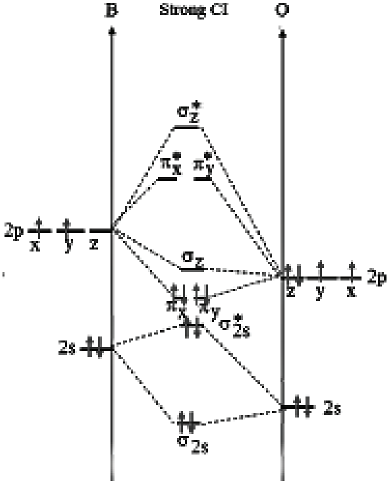


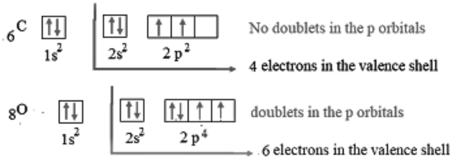
Figure VII-35: BO diagram.

The bond index is $i_{BO} = (7-2)/2 = 2.5$

Thus, we can predict that BO is diamagnetic.

The CO, NO⁺, and CN⁻ molecules

These have 10 valence electrons. Consider for instance the CO molecule.



The electronic structure of the outermost shell of C and O are given on the right. Here, we have an a priori type diagram

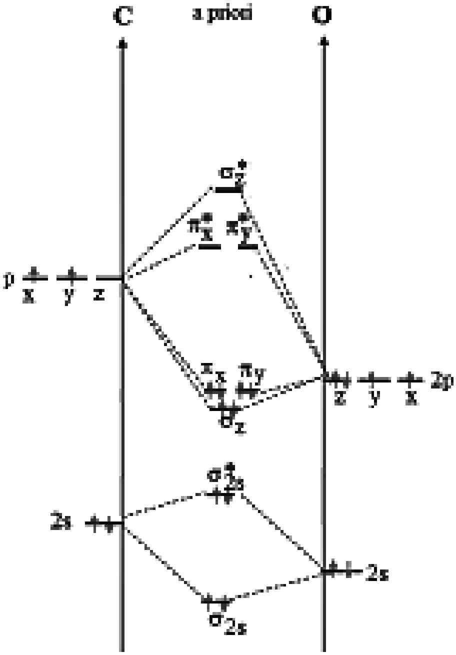


Figure VII-36: CO diagram.

The electronic structure of CO is

$$CO : \sigma_{2s}^{2}\sigma_{2s}^{*2}\sigma_{z}^{2}\pi_{x}^{2}\pi_{y}^{2}$$

and the bond index is: $i_{CO} = (8-2)/2 = 3$ and the CO molecule is diamagnetic.

9. Properties of diatomic molecules in light of the fundamental principles of physics

The theory of molecular orbitals allows us to make a number of predictions about the physical properties of homonuclear diatomic molecules.

The external action of fields on molecules (electric, magnetic, and mechanical fields etc.) modify the distance between the nuclei of the molecule, generating the phenomenon of vibration. A common image of the chemical bond is to compare it to a spring connecting two masses, as shown in **Fig. VII-37**.

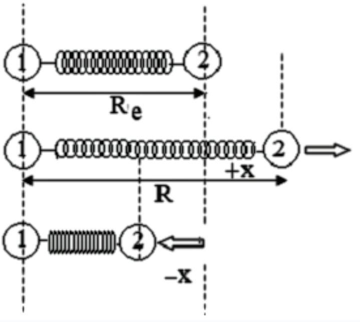


Figure VII-37: A chemical bond is analogous to a spring.

We can reduce the vibration movement to that of a single mass, called the reduced mass μ, the value of which is

$$\mu = \frac{m_1 m_2}{m_1 + m_2}$$

where m_1 and m_2 are the masses of atoms 1 and 2, respectively, undergoing elongation +x or compression -x with respect to length at resting R_e, so that

$$|x| = |R - R_e|$$

Thus, the mass m is subjected to a restoring force, the modulus of which is

$$F = -k_e x$$

where k_e is the force constant of the spring. This restoring force generates potential V(x)

$$V(x) = \frac{1}{2} k_e x^2$$

which characterizes the potential energy of the spring when it deviates from its equilibrium position. If we express the distance as a function of R, we obtain

$$V(R) = \frac{1}{2} k_e (R - R_e)^2$$

If we draw this potential as a function of the internuclear distance R, we obtain the curve with a thin line in the figure below. The quadratic potential is sufficient to describe the potential energy of the molecule when the internuclear distance R does not deviate too much from the equilibrium distance R_e.

In fact, this potential does not describe the reality of the chemical bond because when R becomes greater than the equilibrium distance, a deformation of the chemical bond occurs similar to a spring that has been over-stretched.

Ph. Morse

This phenomenon is called *anharmonicity*: the movement of the nuclei is no longer harmonic, but is said to be anharmonic.

Anharmonicity prevents the bond from returning to a reversible situation. The anharmonic potential of the bond is named the Morse curve[14] after the physicist who proposed an empirical formula describing, in a more realistic way, the potential of diatomic molecules

$$V_{Morse}(R) = D_e(1 - \exp(-\beta(R - R_e))^2 - D_e \qquad \text{(VII-22)}$$

---

[14] Phillip Morse (1903-1985). American physicist.

where D_e is the dissociation energy of the molecule, that is to say the energy that must be supplied to the molecule so that its nuclei deviate from each other at infinity, and β is a constant[15] characteristic of the molecule that depends on the quantities measured by spectroscopy.

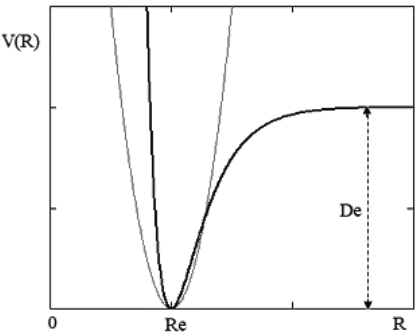


Figure VII-38: Harmonic (thin line) and anharmonic (thick line) potential curves.

This curve is shown (thick line) in **Fig. VII-38**, along with the quadratic potential in order to bring out its characteristics.The quadratic potential $V_Q(R)$ depends on the force constant k_e. It is the second derivative of this potential at the equilibrium internuclear distance R_e

$$k_e = \left[\frac{d^2 V_Q(R)}{dR^2} \right]_{R=R_e}$$

By analogy, we can calculate the force constant for the Morse curve

$$k_e^M = \left[\frac{d^2 V_M(R)}{dR^2} \right]_{R=R_e}$$

Thus, we find

$$k_e^M = 2\beta^2 D_e$$

---

[15] This parameter depends on the dissociation energy, the force constant, and therefore the wavenumber of the vibration of the molecule in the ground state. All the values of these parameters can be found in G. Herzberg *Molecular Spectra and Molecular Structure. I. Spectra of Diatomic Molecules*. Van Nostrand, New York, 1950.

then

$$\beta = \sqrt{\frac{k_e^M}{2D_e}}$$

given that the wavenumber ν_e of the bond vibration in the ground state is

$$\bar{\nu}_e = \frac{1}{2\pi c}\sqrt{\frac{k_e^M}{\mu}}$$

where μ is the reduced mass of the molecule, the force constant is

$$k_e^M = \bar{\nu}_e^2 4\pi^2 c^2 \mu$$

and so we find that

$$\beta = \bar{\nu}_e \pi c \sqrt{\frac{2\mu}{D_e}}$$

We can thus reconstruct the potential curves of many diatomic molecules without having to determine them experimentally. It therefore appears from this study of the properties of diatomic molecules that a diatomic molecule can be defined by:

- Its internuclear distance R_e (Å) at equilibrium.
- Its force constant k_e (N.m), which is related to the wavenumber ν_e (cm^{-1}) of the vibration of the molecule in the ground state.
- Its dissociation energy D_0(eV).

We may use the general formula to calculate β in Å^{-1} using μ in Dalton, ν_e in cm^{-1}, and D_e in eV.

$$\beta = 1.3609 \times 10^{-3} \times \bar{\nu}_e \sqrt{\frac{\mu}{D_e}}$$

For example, taking the example of dihydrogen[16], we have

$$\bar{\nu}_e = 4395 cm^{-1} \; ; \mu = 0.504 \, Dalton \; ; \; D_0 = 4.476 \, e.V \; ; \quad R_e = 0.742 Å$$

D_0 is the bond dissociation energy, which may be experimentally found. To obtain the theoretical dissociation energy D_e, we have to take into account what is called the "zero-point-energy", i.e. the residual energy due to quantum fluctuations

Or
$$D_e = D_0 + \frac{1}{2} hc\bar{\nu}_e$$

$$D_e(e.V) = D_0 + 6.199 \times 10^{-5} \times \bar{\nu}_e(cm^{-1})$$

so that, for the H_2 molecule, we have

$$D_e = 4.748 \; e.V \quad \text{and} \quad \beta = 1.949 \, Å^{-1}$$

10.Qualitative prediction of the evolution of the properties of diatomic molecules

Let us see how the application of fundamental principles makes it possible to make such predictions. Key among these principles are the theory of molecular orbitals and the virial theorem.

a. The virial theorem

The theory of molecular orbitals (MO) makes it possible to calculate the bond index, which is related, as we saw above, to the physicochemical properties: the internuclear distance at equilibrium R_e; the dissociation energy D_e; and the force constant k_e of the bond.

However, this level of the method is not sufficient to explain the variations observed when moving within the same column of the periodic classification. Indeed, the bond index remains the same as the bond length increases, while the dissociation energy and the force constant decrease, as can be seen in **Table VII-11**.

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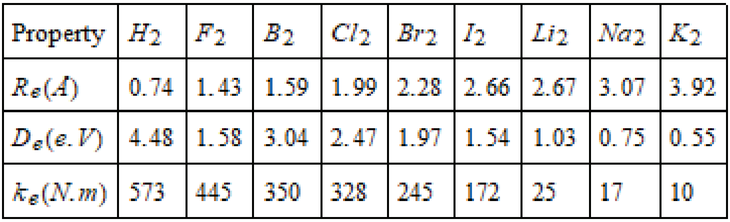
[16] Data from G. Herzberg, 2nd ed. "Molecular spectra and molecular structure, spectra of diatomic molecules", Van Nostrand Reinhold, 1950, p. 531.

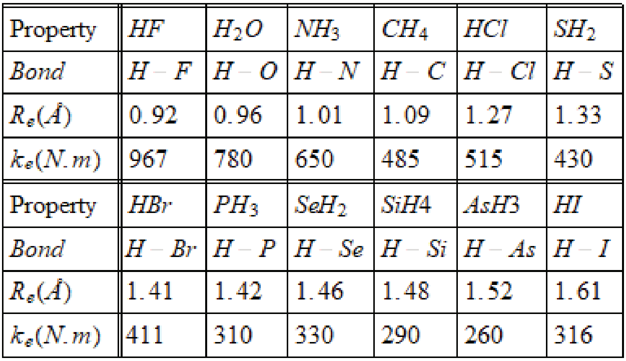
Table VII-11: Physicochemical properties of some diatomic molecules



Property	H_2	F_2	B_2	Cl_2	Br_2	I_2	Li_2	Na_2	K_2
$R_e(\AA)$	0.74	1.43	1.59	1.99	2.28	2.66	2.67	3.07	3.92
$D_e(e.V)$	4.48	1.58	3.04	2.47	1.97	1.54	1.03	0.75	0.55
$k_e(N.m)$	573	445	350	328	245	172	25	17	10

If we consider a given bond, the same observation can be made from **Table VII-12** for bonds in polyatomic molecules[17].

Table VII-12: Physicochemical properties of some bonds in some polyatomic molecules



Property	HF	H_2O	NH_3	CH_4	HCl	SH_2
Bond	$H-F$	$H-O$	$H-N$	$H-C$	$H-Cl$	$H-S$
$R_e(\AA)$	0.92	0.96	1.01	1.09	1.27	1.33
$k_e(N.m)$	967	780	650	485	515	430
Property	HBr	PH_3	SeH_2	$SiH4$	$AsH3$	HI
Bond	$H-Br$	$H-P$	$H-Se$	$H-Si$	$H-As$	$H-I$
$R_e(\AA)$	1.41	1.42	1.46	1.48	1.52	1.61
$k_e(N.m)$	411	310	330	290	260	316

We can explain this evolution using the virial theorem, as was first done several years ago[18].

---

[17] In the case of polyatomic molecules, the force constants are calculated within the framework of the valence force approximation (see E. Wilson, J. Decius, P. Cross, McGraw Hill, New York, 1955, p. 175).

[18] See our paper: P. Blaise, A. Krallafa, O. Henri-Rousseau "Constantes de force et énergie de dissociation des molécules diatomiques" (Force constant and energy of dissociation of diatomic molecules), Actualité Chimique, sept. 1979, p. 53.

Use of the virial theorem

The virial theorem relates the average kinetic energy <T> to the average of the virial forces

$$\left\langle \sum_i \vec{q}_i \vec{F}_i \right\rangle$$

where $\vec{q}_i$ stands for the coordinates of the particle i and $\vec{F}_i$ stands for the forces acting on it

$$\langle T \rangle = -\frac{1}{2}\left\langle \sum_i \vec{q}_i \vec{F}_i \right\rangle \tag{VII-23}$$

The virial theorem is particularly recognized by chemists because of its use in the case of gases. For an atom, the virial of the forces is equivalent to the potential energy

$$\langle V \rangle = \left\langle \sum_i \vec{q}_i \vec{F}_i \right\rangle$$

and so we can write

$$\langle T \rangle = -\frac{1}{2}\langle V \rangle \tag{VII-24}$$

Let us examine the link between diatomic molecules and the virial theorem. Consider a diatomic molecule. If we wish to keep the two nuclei motionless at a distance different from the internuclear distance equilibrium R_e, the nuclei must be subject to a force that is opposite to the restoring force. However, this restoring force is derived from the potential V. Indeed, within the framework of the Born-Oppenheimer approximation, which considers the nuclei immobile with respect to the movement of the electrons, it is possible to obtain a relation between the potential energy V and the internuclear distance R. If R is greater or lesser than the equilibrium distance R_e corresponding to the minimum of the curve, then a force appears that acts on the nuclei to bring them back to their equilibrium position (see **Fig. VII-38**).

$$F = -\frac{dU}{dR}$$

Under these conditions, two types of forces appear, the so-called *Coulomb internal force* and an *external force* that is opposed to the restoring force. The virial of the internal forces is

$$\left\langle \sum_i \vec{q}_i \vec{F}_i \right\rangle_{internal} = \langle V \rangle$$

while the virial of the external forces is

$$\left\langle \sum_i \vec{q}_i \vec{F}_i \right\rangle_{external} = +R\frac{dU}{dR}$$

so that the total virial of the forces is therefore

$$\left\langle \sum_i \vec{q}_i \vec{F}_i \right\rangle_{total} = \left\langle \sum_i \vec{q}_i \vec{F}_i \right\rangle_{internal} + \left\langle \sum_i \vec{q}_i \vec{F}_i \right\rangle_{external}$$

or

$$\left\langle \sum_i \vec{q}_i \vec{F}_i \right\rangle_{total} = \langle V \rangle + R\frac{dU}{dR} \tag{VII-25}$$

From Eq. (VII-24), we have

$$\left\langle \sum_i \vec{q}_i \vec{F}_i \right\rangle_{total} = -2\langle T \rangle$$

then, Eq. (VII-25) becomes

$$2\langle T \rangle = \langle V \rangle + R\frac{dU}{dR}$$

and

$$2\langle T \rangle + \langle V \rangle + R\frac{dU}{dR} = 0 \tag{VII-26}$$

Since

$$U = \langle T\rangle + \langle V\rangle$$

we may write

$$\langle T\rangle + \langle T\rangle + \langle V\rangle + R\frac{dU}{dR} = 0 \quad \text{and} \quad \langle T\rangle + U + R\frac{dU}{dR} = 0$$

then

$$\langle T\rangle = -U - R\frac{dU}{dR}$$

and since

$$\langle V\rangle = U - \langle T\rangle$$

we have

$$\langle V\rangle = 2U + R\frac{dU}{dR}$$

The function U is the total energy and we can use, as an expression of U, the Morse curve given by Eq. (VII-22), so that

$$U(R) = D_e((1 - \exp(-\beta(R - R_e)))^2 - D_e$$

Then, the mean kinetic energy can be obtained using the virial theorem, so that

$$\frac{dU}{dR} = \frac{d\left(D_e \times (1 - \exp(-\beta \times (R - R_e))^2 - D_e\right)}{dR} = -2\beta D_e e^{-\beta(R-R_e)}(e^{-\beta(R-R_e)} - 1)$$

which leads to the expressions

$$\langle T\rangle = D_e e^{-\beta(R-R_e)}[e^{-\beta(R-R_e)}(2\beta R - 1) - 2(\beta R - 1)]$$
$$\langle V\rangle = 2D_e e^{-\beta(R-R_e)}[e^{-\beta(R-R_e)}(1 - \beta R) + (\beta R - 2)]$$

Fig. VII-39 presents the evolution versus the internuclear distance of the total energy U, of the mean electronic kinetic energy <T>, and of the mean potential energy <V>.

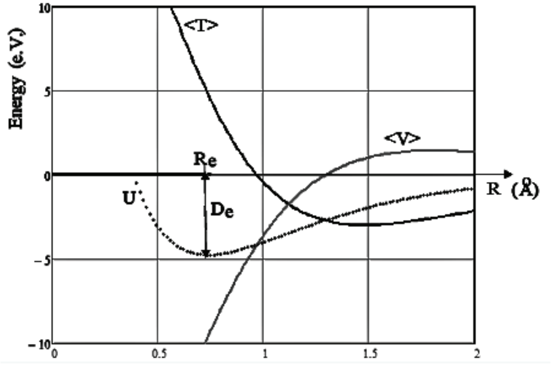


Figure VII-39: Evolution of the kinetic, potential, and total energies for a diatomic molecule according to the virial theorem.

For the equilibrium distance R_e, Eq. (VII-26) becomes

$$2\langle T\rangle + \langle V\rangle = 0$$

so that

$$\langle V\rangle = -2\langle T\rangle$$

and given that we have

$$\langle T\rangle - 2\langle T\rangle = U \ \text{i.e.} \ \ \langle T\rangle = -U$$

If we take the energy level of free atoms as zero, U is equivalent to the dissociation energy $-D_e$ and we may write

$$D_e \simeq \langle T\rangle$$

We are interested in the relation between the mean kinetic energy and the force constant. Starting from the expressions of <T> and <V> above we found

$$\langle T\rangle = -U - R\frac{dU}{dR}$$
$$\langle V\rangle = 2U + R\frac{dU}{dR}$$

We may perform a first derivation with respect to R of these expressions

$$\frac{d\langle T\rangle}{dR} = -\frac{dU}{dR} - \frac{dU}{dR} - R\frac{d^2U}{dR^2} \text{ so that } \frac{d\langle T\rangle}{dR} = -2\frac{dU}{dR} - R\frac{d^2U}{dR^2} \qquad \text{(VII-27)}$$

and

$$\frac{d\langle V\rangle}{dR} = 2\frac{dU}{dR} + \frac{dU}{dR} + R\frac{d^2U}{dR^2} \quad \text{so that} \quad \frac{d\langle V\rangle}{dR} = 3\frac{dU}{dR} + R\frac{d^2U}{dR^2} \qquad \text{(VII-28)}$$

For the equilibrium distances, theses equations become

$$\left(\frac{d\langle T\rangle}{dR}\right)_{R_e} = -R_e\left(\frac{d^2U}{dR^2}\right)_{R_e}$$
$$\left(\frac{d\langle V\rangle}{dR}\right)_{R_e} = R_e\left(\frac{d^2U}{dR^2}\right)_{R_e}$$

Recall that the definition of the force constant is

$$k_e = \left(\frac{d^2U}{dR^2}\right)_{R_e}$$

It is then possible to obtain a simple relation between the force constant k_{e} and the derivative of the mean kinetic energy for R = R_e. Then

$$R_e k_e = -\left(\frac{d\langle T\rangle}{dR}\right)_{R_e} \qquad \text{(VII-29)}$$

For a minimum, as is the case for mean kinetic energy, we have

$$\left(\frac{d^2U}{dR^2}\right)_{R_e} > 0$$

The derivative of <T> must be negative, while that of <V> must be positive. It follows that near the equilibrium distance, as R increases, <T> decreases while <V> increases. This leads to consideration of the equilibrium distance as a result of a compromise between kinetic energy, which tends to repel the nuclei, and a potential energy, which tends to attract them towards each other.

Recall that there exists an approximate relation between the mean kinetic energy <T> and the equilibrium distance R_e. This relation was seen when we studied the model of the potential well. Mean kinetic energy comes directly from the wave properties of particles, i.e. from the Louis de Broglie relation

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

where λ is the wavelength of the wave associated with a particle; h is the Planck constant; and p is the momentum of the particle. When the wavelength of a particle is of the order of magnitude of the size of the space in which it is moving, a quantized expression for the kinetic energy appears, such as

$$\langle T\rangle \propto \frac{h^2}{8mR^2}n^2$$

where m is the mass of the particle; R is the internuclear distance; and n is an integer number called a quantum number, which quantizes the expression of the energies. Using the virial theorem, we find that

$$D_e \propto \langle T\rangle$$

so that

$$\boxed{D_e \propto \frac{h^2 n^2}{8mR_e^2} = \frac{cst \times n^2}{R_e^2}}$$

where cst = $h^2/(8m)$.

Consider the force constant. Then, given Eq. (VII-29), we may write

$$R_e k_e = -\left(\frac{d\langle T\rangle}{dR}\right)_{R_e}$$

with

$$R_e k_e = -\left(\frac{d\langle T\rangle}{dR}\right)_{R_e} \propto \frac{d}{dt}\left(\frac{h^2}{8mR^2}n^2\right)$$

so that

$$k_e = -\frac{1}{R_e}\left(\frac{d\langle T\rangle}{dR}\right)_{R_e} \propto -\frac{1}{R_e}\frac{d}{dR}\left(\frac{h^2}{8mR^2}n^2\right)$$

The derivative of <T> with respect to R is

$$\frac{d}{dR}\left(\frac{h^2}{8mR^2}n^2\right) = -\frac{h^2 n^2}{4m}\frac{1}{R^3}$$

For R = R_e, we have

$$k_e \propto +\frac{h^2 n^2}{4m}\frac{1}{R_e^4}$$

and

$$k_e \propto \frac{cst'}{R_e^4}n^2 \quad \text{with}\, cst' = \frac{h^2}{4m} = 2cst$$

so that

$$\frac{k_e}{De} = \frac{cst}{cst}\frac{1}{R_e^2} \propto \frac{2}{R_e^2}$$

and

$$\boxed{k_e \propto \frac{2De}{R_e^2}}$$

We have the qualitative evolution of D_e and k_e with respect to the equilibrium distance R_e, which allows us to understand, except in a few cases, the experimental evolutions described in the tables. We shall come back to this problem later.

b. Obtaining the parameters of the chemical bond

Here, we present a very simplified model of the H_2^+ molecular ion. We resume here the qualitative approach to a model of the stability of the H_2^+ molecular ion that we published several years ago[19].

H_2^+ is formed by two protons and one electron. **Fig. VII-40** gives a 1-D representation of this ion and we can see the molecular hydrogen ion as a potential well.

Since the probability density of the electron in the potential well is at its maximum at the center of the well in the ground state, we shall suppose that a negative charge is at the center of the space defined by the segment connecting the two protons.

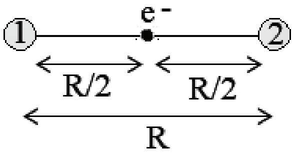


Figure VII-40: 1-D atom coordinates.

In these conditions, the kinetic energy T(n,R) of the electron is of the form obtained for the particle in a box model we studied above

$$T(n,R) = \frac{h^2}{8mR^2}n^2$$

while the potential energy V(R) is the sum of the Coulombian electron-proton attractions and of the proton-proton repulsion

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[19] P. Blaise, Olivier Henri-Rousseau, and P. Mialhe, “Modeling of the molecular ion H_2^+ using only the Coulomb and de Broglie relations: a unified approach of the orders of magnitude of the physical parameters of diatomic molecules” (French), J. Chim. Phys, 91, 1994, p. 1347-1385.

$$V(R) = -K\frac{e^2}{\frac{R}{2}} \times 2 + K\frac{e^2}{R}$$

so that

$$V(R) = -K\frac{e^2}{R} \times 4 + K\frac{e^2}{R} \quad \text{and} \quad V(R) = -K\frac{e^2}{R} \times 3$$

The total energy will be

$$E(n,R) = \frac{h^2}{8mR^2}n^2 - K\frac{e^2}{R} \times 3$$

Putting

$$A_T(n) = \frac{h^2}{8m}n^2 \quad \text{and} \quad A_V = -Ke^2 \times 3 \tag{VII-30}$$

then

$$E(n,R) = \frac{A_T(n)}{R^2} - \frac{A_V}{R} \tag{VII-31}$$

Deriving this equation, we get

$$\frac{d}{dR}E(n,R) = -2\frac{A_T(n)}{R^3} + \frac{A_V}{R^2}$$

and for the equilibrium distance R_e, we have

$$\left(\frac{d}{dR}E(n,R)\right)_{R=R_e} = -2\frac{A_T(n)}{R_e^3} + \frac{A_V}{R_e^2} = 0$$

so that

$$2\frac{A_T(n)}{R_e^3} = \frac{A_V}{R_e^2}$$

and then

$$\boxed{R_e = 2\frac{A_T(n)}{A_V}} \qquad \text{(VII-32)}$$

The energy for R = R_e is thus

$$E(n) = \frac{A_T(n)}{R_e^2} - \frac{A_V}{R_e}$$

$$\boxed{E(n) = -\frac{A_V^2}{4A_T(n)}}$$

Now, let us evaluate R_e and E(n). We have the following values for the fundamental constants

$$h = 6.6260755 \times 10^{-34}\ \mathrm{J\ s}$$

$$e = 1.60217733 \times 10^{-19}\ \mathrm{C}$$

$$K = 8.98755 \times 10^{9} SI$$

$$m = 9.1093897 \times 10^{-31}\ \mathrm{kg}$$

Introducing these values in the expressions of A_T(n) and A_V gives

$$A_T(n) = 6.024673164 \times 10^{-38} \times n^2 \times J\,m^{-2}$$

$$A_V = 6.92123729 \times 10^{-28} J\,m^{-1}$$

so that, for the ground state n = 1 we have

$$R_e = 1.741 \times 10^{-10} m = 1.741\,\mathring{A}$$

and for the energy of the ground state we have

$$E = -1.988 \times 10^{-18} J = -12.407\, e.V$$

To obtain the dissociation energy, we must subtract the energy of the hydrogen atom obtained in the spirit of this simplification. Let us imagine a 1-D atom with the electron is moving on a diameter. If r is the maximum extension of the electron displacement, the system is a potential well of width 2r as shown in **Fig. VII-41**.

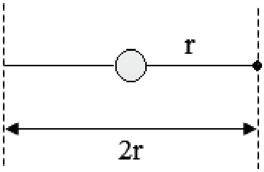

Figure VII-41: 1-D atom.

Of course, the exact position of the electron cannot be known because of the uncertainty principle.

The kinetic energy of the electron would be that of a particle in a potential well, i.e.

$$T = \frac{h^2}{8m(2r)^2} n^2$$

while the potential energy would be

$$V = -K\frac{e^2}{r}$$

where K is the Coulomb constant. Thus, the total energy of the 1-D atom is

$$E_{at}(n,r) = \frac{h^2}{8m(2r)^2} n^2 - K\frac{e^2}{r}$$

As above, we put

$$a_T(n) = \frac{h^2}{32m} n^2 \quad \text{and} \quad a_V = Ke^2 \qquad \text{(VII-33)}$$

so that

$$\boxed{E_{at} = \frac{a_T^2}{r^2} - \frac{a_V}{r}} \qquad \text{(VII-34)}$$

This energy is at a minimum when

$$\left(\frac{dE_{at}}{dr}\right)_{r=r_e} = 0$$

$$2\frac{a_T^2}{r_e^3} + \frac{a_V}{r_e^2} = 0 \quad \text{so that: } r_e = \frac{2a_T}{a_V}$$

leading to the energy minimum

$$E_{\min} = -\frac{a_V^2}{4a_T(n)}$$

Using the constants

$$h = 6.6260755 \times 10^{-34} \text{ J s}$$
$$e = 1.60217733 \times 10^{-19} \text{ C}$$
$$K = 8.98755 \times 10^{9} SI$$
$$m = 9.1093897 \times 10^{-31} \text{ kg}$$

so that

$$a_T = 1.506 \times 10^{-38} n^2 \quad \text{and} \quad a_V = 2.307 \times 10^{-28}$$

The energy of the ground state of the 1-D hydrogen atom is

$$E_{\min} = -8.834 \times 10^{-19} J \quad \text{or, in e.V.} \quad E_{\min} = -5.514 e.V$$

and the dissociation energy D_e of the 1-D hydrogen molecular ion would be

$$D_e = -(E_{H2+} - E_H) = -(-12.407 + 5.514) = 6.893 e.V$$

We can find the experimental values concerning H_2^+ in the book by Herzberg, i.e. $R_e = 1.06$ Å and $D_e = 2.64$ eV. The results of the 1-D hydrogen molecular ion calculations are Re = 1.741 Å and De = 6.89 eV, which are of the same order of magnitude.

c. Introduction of fine structure constant and Compton wavelength in the expression of the equilibrium distance R_e

In physics, the *fine structure constant* is the dimensionless coupling constant associated with the electromagnetic interaction. The constant is so designated for historical reasons with reference to the fine structure and was proposed by the German physicist A. Sommerfeld (1868-1951) in 1916.

Its conventional symbol is α and it has no dimension

$$\alpha = \frac{e^2}{4\pi\varepsilon_0 \hbar c}$$

where e is the elementary charge; ε_0 is the permittivity of the free space; $\hbar$ is the reduced Planck constant; and c is the light velocity. Using the constant values, we find

$$\alpha = 7.297\,347 \times 10^{-3}$$

The inverse of which is

$$\frac{1}{\alpha} = 137.04$$

This constant appears in a lot of expressions in physics.

The Compton wavelength[20]

When a primary photon hits a free particle, a secondary photon is emitted whose wavelength is higher than that of the primary photon; this is the *Compton effect*. The difference in wavelength between the primary photon and the emitted photon is proportional to a constant value known as the Compton wavelength, see the example of an electron in **Fig. VII-42**.

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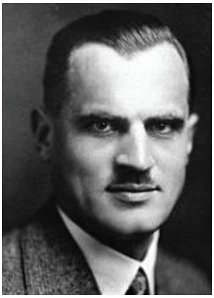
[20] Arthur Compton (1892-1962). American physicist who won the Nobel Prize in Physics in 1927 for his 1923 discovery of the Compton effect.



A. Compton

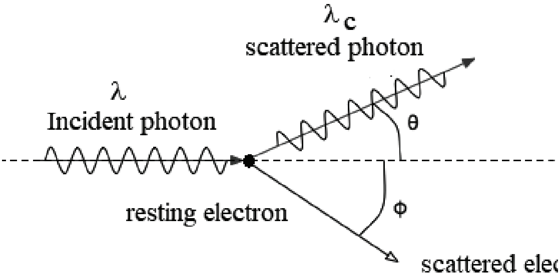


Figure VII-42: The Compton effect.

The Compton wavelength is

$$\lambda_C = \frac{h}{mc} \tag{VII-35}$$

where h is the Planck constant; m is the electron resting mass; and c is the speed of light.

Consider the expression of the equilibrium distance R_e given above in the case of 1-D H_2^+ molecular ion

$$A_T = \frac{h^2}{8m} \quad \text{or} \quad A_T = \frac{h}{m}\frac{h}{8}$$

Using the expression of the Compton wavelength, we have

$$A_T = \lambda_C \frac{hc}{8} \quad \text{and} \quad A_V = Ke^2 \times 3$$

The proportionality constant K may be expressed in term of the fine structure constant

$$K = \frac{1}{4\pi\varepsilon_0} = \alpha\frac{\hbar c}{e^2}$$

and the constant A_V may be written

$$A_V = \alpha\hbar c \times 3$$

The equilibrium distance R_e is then

$$R_e = \frac{2A_T}{A_V} = \frac{\pi}{6}\frac{\lambda_C}{\alpha} \quad \text{(VII-36)}$$

Neglecting the constant term we obtain the qualitative relation using the Compton wavelength and the fine structure constant

$$\boxed{R_e \backsimeq \frac{\lambda_C}{\alpha}} \quad \text{(VII-37)}$$

d. Expression of the rotation energy of the molecule

We can imagine H_2^+ as a rigid rotator of length R_e, being the equilibrium distance, while r_1 and r_2 are the distance from the nuclei to the center of mass of the system, as shown in **Fig. VII-43**.

Using the expression of the equilibrium distance R_e, we are able to determine the order of magnitude of the energy of rotation of the molecule E_{rot} and, consequently, that of the frequency of rotation ν_{rot} of the molecular ion.

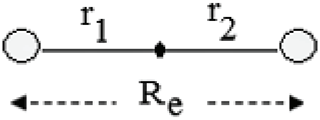


Figure VII-43: The rigid rotator.

This can be done simply by writing the classical expression for rotational energy as a function of the moment of inertia I of the molecule and its rotational pulsation ω_{rot}

$$E_{rot} = \frac{1}{2}I\omega_{rot}^2 \quad \text{(VII-38)}$$

The quantum treatment of the rotation energy leads to the expression

$$E_{rot} = \frac{\hbar^2}{2I}J(J+1) \quad \text{(VII-39)}$$

where J is the rotation quantum number and can take the values 0, 1, 2, 3...

We can imagine a simplified treatment based on the fundamental Bohr hypothesis of the quantization of angular momentum, which may lead us to an analogous expression. First, recall that pulsation ω_{rot} is related to the angular momentum and to the moment of inertia by the expression

$$\omega_{rot} = \frac{L}{I}$$

Now, we introduce the Bohr hypothesis concerning the quantization of angular momentum

$$L = n\hbar$$

where h is the Planck constant and n is an integer representing quantization. The expression of ω_{rot} becomes

$$\omega_{rot} = n\frac{\hbar}{I} \tag{VII-40}$$

By introducing Eq. (VII-40) into Eq. (VII-38), we get

$$E_{rot} = \frac{\hbar^2}{2I}n^2 \tag{VII-41}$$

This expression looks like the exact one (VII-39), except that n^2 replaces J(J+1), which quantizes the rotational energy.

Let us express the moment of inertia of the rigid rotator as

$$I = \sum_i M_i r_i^2$$

that is

$$I = M_1 r_1^2 + M_2 r_2^2$$

where M_i is the mass of the nucleus i and r_i is the distance of the electron to the nucleus i. Since $M_1 = M_2 = M$ and $r_1 = r_2 = R_e/2$, we have

$$I = \frac{M}{2}R_e^2 \tag{VII-42}$$

By introducing Eq. (VII-42) into Eq. (VII-41) we get

$$E_{rot} = \frac{n^2\hbar^2}{MR_e^2}$$

and the rotational frequency

$$\omega_{rot} = n\frac{\hbar}{I}$$

becomes

$$\omega_{rot} = 2\frac{\hbar}{MR_e^2}n$$

or, since $\hbar = h/2\pi$

$$\omega_{rot} = \frac{h}{\pi MR_e^2}n$$

There is a relation between the pulsation ω_{rot} and the frequency ν_{rot}, so we may write

$$\omega_{rot} = 2\pi\nu_{rot}$$

and

$$\nu_{rot} = \frac{2h}{MR_e^2}n \tag{VII-43}$$

Let us introduce the approximate expression (VII-37) of R_e in Eq. (VII-43). In doing so, we obtain an approximate relation for which λ_C is the Compton wavelength

$$\nu_{rot} \backsimeq \frac{2h\alpha^2}{M(\lambda_C)^2}n$$

Since we have

$$\lambda_C = \frac{h}{mc}$$

with m being the electron mass and c the speed of the light, the rotational frequency becomes

$$\nu_{rot} \backsimeq \frac{2c\alpha^2}{\lambda_C}\frac{m}{M}n$$

Since

$$\frac{c}{\lambda_C} = \nu_C$$

the rotational frequency may be approximately written as

$$\nu_{rot} \backsimeq \nu_C\alpha^2\frac{m}{M}n$$

For the ground state, we have n = 1

$$\nu_{rot} \backsimeq \nu_C\alpha^2\frac{m}{M}$$

Replacing the constants by their respective values, we get the approximate value for the rotational frequency

$$\nu_{rot} \backsimeq 3.58 \times 10^{12} Hz$$

This value may be compared to the experimental one of 1.83×10^{12}Hz, highlighting that the qualitative approach remains in an experimental order of magnitude.

We can express the rotational energy of the ground state as

$$E_{rot}^{(1)} = h\nu_C\alpha^2\frac{m}{M}$$

so that

$$E_{rot}^{(1)} = 2.37 \times 10^{-21} J \quad \text{or in e.V.} \; E_{rot}^{(1)} = 1.5 \times 10^{-2} e.V$$

e. Expression of the vibration energy of the molecule

Let us consider **Fig. VII-37**, which represents the extension or compression of the spring formed by the chemical bond, for which

$$x = R_e - R$$

Consider a space of width x in which the H_2^+ molecular ion of reduced mass μ is moving. If we consider this mass as a quantum particle, its kinetic energy will be quantized and of the type of a potential well of width x.

$$T = \frac{h^2}{8\mu x^2} n^2 \tag{VII-44}$$

Its potential energy will be that of a spring, i.e.

$$V = \frac{1}{2} k_e x^2 \tag{VII-45}$$

where k_e is the force constant of the spring. The total energy will thus be

$$E_{Tot} = T + V = \frac{h^2}{8\mu x^2} n^2 + \frac{1}{2} k_e x^2 \tag{VII-46}$$

Now let us simplify as

$$A = \frac{h^2}{8\mu} n^2 \quad \text{and} \quad B = \frac{1}{2} k_e$$

Eq. (VII-46) thus becomes

$$E_{Tot} = \frac{A}{x^2} + Bx^2$$

Let us derive this expression as

$$\frac{d}{dt} E_{Tot} = \frac{-2A}{x^3} + 2Bx$$

The minimum energy is required so that

$$\left(\frac{d}{dt}E_{Tot}\right)_{x=x_e} = 0$$

i.e.

$$\frac{-2A}{x_e^3} + 2Bx_e = 0$$

or

$$\frac{2A}{x_e^3} = 2Bx_e \text{ so that } \frac{A}{B} = x_e^4$$

and

$$x_e^2 = \sqrt{\frac{A}{B}}$$

Transposing this expression into that for the energy, we get

$$E_{vib} = \frac{A}{\sqrt{\frac{A}{B}}} + B\sqrt{\frac{A}{B}}$$

that is

$$E_{vib} = \sqrt{AB} + \sqrt{AB} = 2\sqrt{AB}$$

Replacing A and B by their expressions, we obtain

$$x_e^2 = \frac{1}{2}h\sqrt{\frac{1}{\mu k_e}}n$$

and

$$E_{vib} = \frac{1}{2}hn\sqrt{\frac{k_e}{\mu}}$$

since the vibrational angular frequency ω_e is

$$\omega_e = \sqrt{\frac{k_e}{\mu}}$$

and the energy takes the form

$$E_{vib} = \frac{1}{2} nh\omega_e$$

Since the angular frequency is related to the frequency by

$$\omega_e = 2\pi\nu_e$$

we get the vibrational energy

$$E_{vib} = \pi nh\nu_e \tag{VII-47}$$

where n is the vibrational quantum number. This expression may be compared to that obtained in the case of the full treatment of the quantum oscillator

$$E_{vib} = h\nu_e\left(v + \frac{1}{2}\right)$$

We find that the approximate expression leads to equidistant energy levels as in the quantum harmonic oscillator, but the energy $h\nu_e$ is multiplied by the factor π and for the quantum number the approximate model starts from n = 1, whereas in the exact model it is v = 0.

We still need to find the value of the vibrational frequency ν_e in the ground state. Let us recall the simplified model of H_2^+. The expression (VII-31) of the energy is

$$E(n,R) = \frac{A_T(n)}{R^2} - \frac{A_V}{R}$$

with $A_T(n)$ and A_V given respectively by

$$A_T(n) = \frac{h^2}{8m} n^2 \quad \text{and} \quad A_V = Ke^2 \times 3$$

Consider now the bottom of the potential well of the ground state n = 1 obtained from the graph of the energy (VII-31) versus the internuclear distance R. For distances near the minimum, the potential energy is that of a harmonic oscillator. In this approximation, the force constant may be obtained as the second derivative of the energy at its minimum.

Then

$$\frac{d^2}{dR^2}E(1,R) = \frac{d^2}{dR^2}\left(\frac{A_T(1)}{R^2} - \frac{A_V}{R}\right) = \left(\frac{6A_T(1)}{R^4} - \frac{2A_V}{R^3}\right)$$

and the force constant is

$$k_e = \left(\frac{6A_T(1)}{R_e^4} - \frac{2A_V}{R_e^3}\right)$$

Replacing the constants in this expression gives

$$k_e = \left(\frac{6\frac{h^2}{8m}}{R_e^4} - \frac{2Ke^2 \times 3}{R_e^3}\right)$$

i.e.

$$k_e = \frac{3h^2 1}{4m}\frac{1}{R_e^4} - \frac{6Ke^2}{R_e^3}$$

Using the expression (VII-32) of R_e we find

$$R_e = 2\frac{A_T(1)}{A_V}$$

Thus, we get

$$k_e = \left(\frac{6A_T(1)}{\left(2\frac{A_T(1)}{A_V}\right)^4} - \frac{2A_V}{\left(2\frac{A_T(1)}{A_V}\right)^3} \right)$$

which leads to

$$\boxed{k_e = \frac{A_V^4}{8(A_T(1))^3}} \qquad \text{(VII-48)}$$

Taking the values obtained above

$$A_T(n) = 6.025 \times 10^{-38} n^2 J m^{-2}$$
$$A_V = 6.921 \times 10^{-28} J m^{-1}$$

for the force constant, we get

$$k_e = 131.173\, J m^{-2}$$

For the vibrational frequency of the ground state ν_e, we have

$$\nu_e = \frac{1}{2\pi}\sqrt{\frac{k_e}{\mu}} = \frac{1}{2\pi}\sqrt{\frac{2k_e}{M}}$$

where M is the proton mass. Then we obtain

$$\nu_e = \frac{1}{2\pi}\sqrt{\frac{131.173 \times 2}{1.673 \times 10^{-27}}} = 6.303 \times 10^{13} Hz$$

i.e. in cm^{-1}

$$\nu_e = 2102 cm^{-1}$$

This result is close to the experimental value for the ground state of H_2^+, which is 2,321 cm^{-1}.

According to Eq. (VII-47), the vibrational energy will then be

$$E_{vib} = 1.312 \times 10^{-19} n \ J \quad \text{and} \quad \text{in e.V.} E_{vib} = 0.819 n \ e.V$$

and the experimental expression is

$$E_{vib} = 0.286\left(v + \frac{1}{2}\right) e.V$$

Now, let us express the vibrational frequency in terms of fundamental constants as undertaken previously for the rotational energy. Recall that for the A_T and A_V constants, we have the expressions

$$A_T = \lambda_C \frac{hc}{8} \quad \text{and} \quad A_V = Ke^2 \times 3$$

with

$$K = \frac{1}{4\pi\varepsilon_0} = \alpha \frac{\hbar c}{e^2} = \alpha \frac{hc}{2\pi e^2}$$

so that, for the force constant k_e, we have

$$k_e = \frac{\left(\alpha \frac{h \times c}{2\pi e^2} e^2 \times 3\right)^4}{8\left(\lambda_C \frac{hc}{8}\right)^3}$$

which, for the force constant, leads to

$$k_e = \frac{324}{\pi^4} \frac{hc\alpha^4}{\lambda_C^3}$$

and for the vibrational angular frequency ν_{vib}, we have

$$\nu_{vib} = 9\frac{\sqrt{2}}{\pi^3} \alpha^2 \nu_C \sqrt{\frac{m}{M}}$$

If we are interested in the order of magnitude, we have

$$\nu_{vib} \backsimeq \alpha^2 \nu_C \sqrt{\frac{m}{M}}$$

This result may be compared to that concerning the rotational vibration energy

$$\nu_{rot} \backsimeq \alpha^2 \nu_C \frac{m}{M}$$

Then, we have roughly

$$\frac{\nu_{vib}}{\nu_{rot}} = \sqrt{\frac{M}{m}}$$

so that we have

$$\frac{\nu_{vib}}{\nu_{rot}} \backsimeq 40$$

f. Expression of the dissociation energy

In the same spirit, we can express the dissociation energy in terms of fundamental constants.

For the ground state the energy of the H_2^+ molecule and that of the separated atoms, we have found

$$E_{mol} = -\frac{A_V^2}{4A_T(n)}$$

with

$$A_T = \lambda_C \frac{hc}{8} \quad \text{and} \quad A_V = Ke^2 \times 3$$

and for the separated atom we have

$$E_{at} = -\frac{a_V^2}{4a_T}$$

with

$$a_T = \lambda_C \frac{hc}{32} \text{ and } a_V = Ke^2$$

By definition, the dissociation energy is

$$D_e = -(E_{mol} - E_{at})$$

so that

$$D_e = -\left(-\frac{A_V^2}{4A_T(n)} + \frac{a_V^2}{4a_T}\right)$$

and

$$D_e = -\left(-\frac{(Ke^2 \times 3)^2}{4\lambda_C \frac{hc}{8}} + \frac{(Ke^2)^2}{4\lambda_C \frac{hc}{32}}\right)$$

i.e.

$$D_e = -\left(-\frac{\left(\alpha \frac{hc}{2\pi} \times 3\right)^2}{4\lambda \frac{hc}{8}} + \frac{\left(\alpha \frac{hc}{2\pi}\right)^2}{4\lambda \frac{hc}{32}}\right)$$

and finally

$$D_e = \frac{5}{2\pi^2} \alpha^2 mc^2$$

This result may be compared to that concerning the rotational energy

$$h\nu_{rot} \backsimeq \alpha^2 \nu_C \frac{m}{M}$$

with

$$\nu_C = \frac{c}{\lambda_C} = \frac{mc^2}{h}$$

then

$$E_{rot} = h\nu_{rot} \backsimeq \alpha^2 mc^2 \frac{m}{M}$$

Hence, the ratio of these energies is

$$\frac{D_e}{E_{rot}} \backsim \frac{M}{m} = 2000$$

which is in the experimental order of magnitude.

If we now compare the dissociation energy D_e with the vibrational energy ν_{vib}

$$\nu_{vib} \backsimeq \alpha^2 \nu_C \sqrt{\frac{m}{M}}$$

we obtain

$$\frac{D_e}{E_{vib}} \backsim \sqrt{\frac{M}{m}} = 45$$

which is also in the experimental order of magnitude.

g. Extension to polyelectronic diatomic molecules

When the 1-D model is extended to other diatomic molecules, the kinetic and potential energies of the system may be given, respectively

$$T = \frac{A_T^*}{R^2} \quad \text{and} \quad V = \frac{A_V^*}{R}$$

where the parameters A_T*and A_V* are of same nature as that evoked above in eqs. (VII-30), which take into account the fact that there are several electrons. Thus, we have

$$A_T^* = \frac{h^2}{8m} \times n_{eff} \quad \text{and} \quad A_V^* = Ke^2 Z_{eff}$$

where n_{eff} is the number of valence electrons implied in the bonding process and Z_{eff} is the effective nuclear charge of the nuclei.

Let us now consider two homonuclear diatomic molecules, I and II, in which elements of the same valence are involved. In these conditions, the number n_{eff} of valence electrons is the same for the two molecules. The consequence is that the two molecules I and II have the same A_T* parameter, so that

$$A^*_{T_I} = A^*_{T_{II}} = A^*_T$$

On the contrary, the A_V* parameters have no reason to be the same

$$A^*_{V_I} \neq A^*_{V_{II}}$$

This allows us to compare the force constants k_{eI} and k_{eII} of the two bonds. Using Eq. (VII-48), we have

$$k_{e_I} = \frac{A^{*4}_{V_I}}{8(A^*_T)^3} \quad \text{and} \quad k_{e_{II}} = \frac{A^{*4}_{V_{II}}}{8(A^*_T)^3}$$

The ratio of these force constants gives

$$\frac{k_{e_I}}{k_{e_{II}}} = \frac{A^{*4}_{V_I}}{A^{*4}_{V_{II}}}$$

The equilibrium distances for the both molecules are given by Eq. (VII-37)

$$R_{e_I} = \frac{2A^*_T}{A^*_{V_I}} \quad \text{and} \quad R_{e_{II}} = \frac{2A^*_T}{A^*_{V_{II}}}$$

and their ratio is

$$\frac{R_{e_I}}{R_{e_{II}}} = \frac{A^*_{V_{II}}}{A^*_{V_I}} \tag{VII-49}$$

Then, we may write

$$\frac{k_{e_I}}{k_{e_{II}}} = \left(\frac{R_{e_{II}}}{R_{e_I}}\right)^4$$

This is a well-established result[21]. Let us undertake a comparison of the dissociation energy of homonuclear diatomic molecules, the atoms of which belong to the same column of the periodic table and have the same bond index. The dissociation energy is given by the approximate relation

$$D_e \backsim \frac{A_V^2}{4A_T}$$

As such, we may write

$$D_{e_I} \backsim \frac{A_{V_I}^{*2}}{4A_T^*} \quad \text{and} \quad D_{e_{II}} \backsim \frac{A_{V_{II}}^{*2}}{4A_T^*}$$

Since all these molecules will have the same A_T* parameter, we may write

$$\frac{D_{e_I}}{D_{e_{II}}} \backsim \frac{A_{V_I}^{*2}}{A_{V_{II}}^{*2}}$$

Given Eq. (VII-49) above, we get

$$\frac{D_{e_I}}{D_{e_{II}}} \backsim \left(\frac{R_{e_I}}{R_{e_{II}}}\right)^2$$

This is also a well-established result[21].

VII-III. Theories Dealing with Molecular Geometry

In this section, we shall address the theories dealing with molecular geometry. In the first step, we examine the VSEPR method, which is used to predict the geometry of molecules with a central atom by means of electrostatic considerations. The predictions made by this method are used, in a second step, to undertake a quantum description using the concept of the hybridization of atomic orbitals in order to construct the orbitals and discover their probability densities in the direction of the bonds. In the third step, we shall apply the theory of molecular orbitals to obtain a description

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[21] see for instance R. Parr, R. Simons, and R. Borkman, J. Chem. Phys, 50, 1969, p. 58.

of localized MOs for several polyatomic molecules. Finally, in order to describe a system, such as the transition metal complexes, we shall use the hybridization theory and obtain information on the magnetic properties of these compounds.

1. The VSEPR method (Valence Shell Electronic Pair Repulsions)

This method deals with molecules having a central atom A surrounded by a certain number of peripheral atoms X, i.e. the ligands, and is down to the work of Gillespie[22] and Nylhom[23].


R. Gillespie


Sir R. Nylhom

a. An electrostatic model

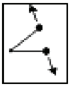
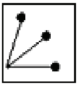
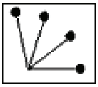
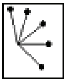
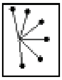
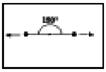
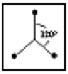
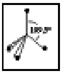
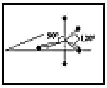
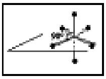
Table VII-13 shows the equilibrium configurations of point charges—configurations that minimize the repulsions between these charges kept at the same distance from a point in space.

---

[22] Ronald Gillespie (born 1924). Canadian chemist known for his work on molecular geometry.

[23] Sir Ronald Sydney Nyholm (1917-1971). Australian chemist. Known for his work on molecular geometry. He is one of the two creators of the VSEPR theory.

Table VII-13: The electrostatic model

	2 charges	3 charges	4 charges	5 charges	6 charges
initial position					
At equilibrium					

The molecules we study here will have one of the geometries presented above, depending on the number of charges that can be counted around the central atom A.

Central atom A

Provides the molecule with its outermost electronic structure. The outermost electrons are distributed on the surface of a sphere centered on the A nucleus, called the *valence sphere*.

Ligand X

They will give their unpaired electrons to the valence sphere.

The outermost electrons of atom A and the unpaired electrons of atoms X will group into doublets, which constitute the charges. These charges on the surface of the valence sphere repel each other until an adequate equilibrium structure is obtained, as given in **Table VII-13**.

Each ligand X collects as many doublets as it has supplied unpaired electrons:

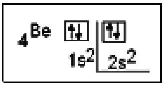
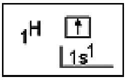
- we then define the number of charges (charge = doublet or grouping of doublets);
- we draw the geometry in space corresponding to the number of charges found according to **Table VII-13**;
- we place the free doublets;
- the ligands are placed in the remaining positions;
- and we define the type of molecule.

A bonding doublet takes up less space than a free doublet. As a result, the free doublets exert a pressure on the bond doublets and will tend to close the bond angles. We can therefore predict certain deformations of the molecule.

b. Examples

The BeH_2 molecule

We have the central atom Be and the outermost shell of Be is 2s AO, containing 2 electrons.

Central atom: beryllium Be		2 electrons on the outermost shell
Ligands:2 hydrogen atoms H		1 unpaired electrons ×2

Total $4e^-$ on the valence shell gives 2 doublets.

As such, each ligand collects as many doublets as it has supplied unpaired electrons, i.e. 1 doublet per H atom. There are therefore 2 charges on the valence sphere, which repel each other until the equilibrium position of 2 charges of the electrostatic model is obtained.

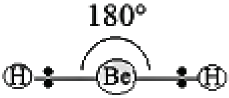


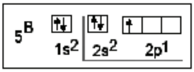
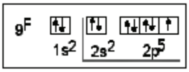
Figure VII-44: Geometry of BeH_2.

In naming this type of molecule, we call the central atom A, the peripheral atoms X_n, and the free doublets E_n.

Hence, BeH_2 is of the AX_2 type.

The BF_3 molecule

Central atom: boron; ligands : fluorines.

Central atom: Boron B		3 electrons in the outermost shell
Ligands:3 Fluorine atoms F		1 unpaired electron in the outermost shell ×3

The 3 fluorine atoms will therefore supply 3 electrons to the valence sphere.

In total, we have 6 electrons which are grouped into 3 doublets.

Each ligand F collects as many doublets as it has supplied unpaired electrons. There are therefore 3 charges on the valence sphere, which are distributed at the corners of an equilateral triangle.

$$6\text{ electrons} \Rightarrow 3\text{ doublets} \left\{ \begin{array}{l} \text{F gets 1doublet} \Rightarrow \text{1charge} \\ \text{F gets 1doublet} \Rightarrow \text{1charge} \\ \text{F gets 1doublet} \Rightarrow \text{1charge} \end{array} \right\} \text{3 charges system}$$

As such, the molecule is of the AX_3 type.

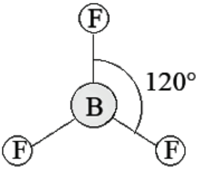
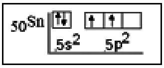
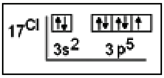


Figure VII-45: Geometry of BF_3.

The $SnCl_2$ molecule

Central atom: tin Sn		4 electrons in the outermost shell
Ligands:2 chlorine atoms Cl		1 electron in the outermost shell×2

Tin (Sn) belongs to the carbon family and therefore has 4 outermost electrons, while chlorine is a halogen and therefore has 1 outermost unpaired electron.

In total, there are 6 electrons on the valence sphere, i.e. 3 doublets

$$6 \text{ electrons} \Rightarrow 3 \text{ doublets} \left\{ \begin{array}{c} \text{Cl gets 1doublet} \Rightarrow \text{1charge} \\ \text{Cl gets 1doublet} \Rightarrow \text{1charge} \\ \text{Free doublet} \Rightarrow \text{1charge} \end{array} \right\} \text{3 charges system}$$

It may be noted that the free doublet occupies a greater volume than a bond doublet, exerting a certain pressure on the two SnCl bonds. Hence the angle between these bonds is less than 120°. This has been confirmed with the experimental value of 95° for this angle.

The molecule is thus of the AX_2E type.

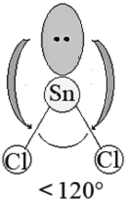
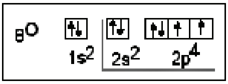
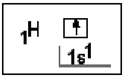


Figure VII-46: $SnCl_2$ geometry.

The H_2O molecule

Central atom: oxygen O	 $_8O$ $1s^2$ $2s^2$ $2p^4$	6 electrons on the outermost shell
Ligands:3 hydrogen atoms H	 $_1H$ $1s^1$	1 unpaired outermost electron ×2

Total 8 electrons on the valence sphere, i.e. 4 doublets.

$$8 \text{ electrons} \Rightarrow 4 \text{ doublets} \left\{ \begin{array}{c} \text{H gets 1doublet} \Rightarrow \text{1charge} \\ \text{H gets 1doublet} \Rightarrow \text{1charge} \\ \text{Free doublet} \Rightarrow \text{1charge} \\ \text{Free doublet} \Rightarrow \text{1charge} \end{array} \right\} \text{4 charges system}$$

This results in a bi-pyramidal arrangement of the atoms with a triangular base (or hexahedron). The free doublets put pressure on the bond doublets so that the angle FClF is less than 90°. This predicted angle has been confirmed experimentally (87.5°).

The molecule is of the AX_3E_2 type.

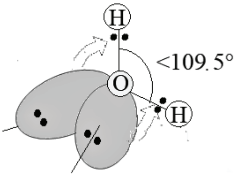
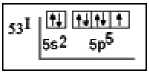
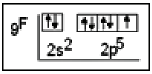


Figure VII-47: H2O geometry.

The IF_5 molecule

The central atom is iodine, which is a halogen and therefore supplies 7 electrons to the valence sphere, while the ligands are fluorines, which are halogens; each of them supplies 1 unpaired electron, i.e. 5 electrons in total.

Central atom: Iodine I		7 outermost electrons
Ligands:3 fluorine atom F		1 unpaired electron on the outermost shell×5

In total we have 12 electrons, which regroup into 6 doublets on the valence sphere.

$$12\text{ electrons} \Rightarrow 6\text{ doublets}\left\{\begin{array}{c}\text{F gets 1doublet} \Rightarrow 1\text{charge}\\ \text{F gets 1doublet} \Rightarrow 1\text{charge}\\ \text{F gets 1doublet} \Rightarrow 1\text{charge}\\ \text{F gets 1doublet} \Rightarrow 1\text{charge}\\ \text{F gets 1doublet} \Rightarrow 1\text{charge}\\ \text{Free doublet} \Rightarrow 1\text{charge}\end{array}\right\}6\text{charges system}$$

The doublets point in the direction of the vertices of a square-based bipyramidal arrangement (octahedral arrangement). The free doublets put pressure on the IF bonds and close the FIF angles, which are <90°. Experimentation (81.9°) has confirmed this prediction.

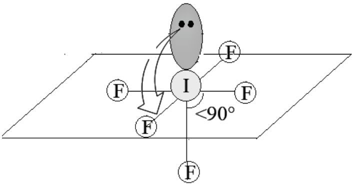


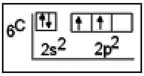
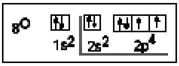
Figure VII-48: IF5 geometry.

The molecule is of the AX_5E type.

c. The case of molecules with multiple bonds

The CO_2 molecule

The central atom is carbon (C) and supplies its 4 outermost electrons to the valence sphere, while the ligands are the two oxygen atoms, which have 2 unpaired electrons each on their outermost shells. The ligands will therefore supply their 4 unpaired electrons to the valence sphere.

Central atom: Carbon C		4 outermost electrons
Ligands:2 oxygen atoms		2 unpaired electrons on the outermost shell ×2

In total, there will be 8 electrons on the valence sphere, which regroup into 4 doublets.

$$8 \text{ electrons} \Rightarrow 4 \text{ doublets} \left\{ \begin{array}{l} \text{O gets 2 doublets} \Rightarrow 1\text{charge} \\ \text{O gets 2 doublets} \Rightarrow 1\text{charge} \end{array} \right\} \text{2 charges system}$$

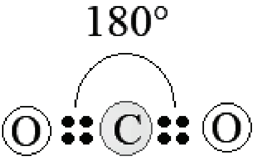


Figure VII-49: CO_2 geometry.

The molecule is linear and of the AX_2 type.

The VSEPR method remains a classic electrostatic method and continues to offer great support to quantum methods, such as the theory of hybridization and the theory of molecular orbitals.

2. The theory of hybridization of atomic orbitals

a. Principles

The theory of hybridization of atomic orbitals is a theory of chemical bonding considered a posteriori. It is thus necessary to know the geometry of the molecule before using this method.

The aim of this method is to adapt the shape of atomic orbitals so that they reflect the directions in which the links are made. This consists of mixing the solution wave functions of the Schrödinger equation.

Polyatomic molecules have a spatial geometry in which a limited number of angles occurs between bonds.

The angles between the bonds that can be noted can be classified into 5 types:

- Angles close to 180° (linear molecules).
- Angles close to 120° (planar molecules and those of equilateral triangle shape).
- Angles close to 109.5° (tetrahedral molecules).
- Angles close to 90° and 120° (bi-pyramid with triangular base).
- Angles close to 90° only (bi-pyramid with square base or octahedron).

The so-called *natural orbitals* are not able to account for the direction of the chemical bonds in these molecules. We must then consider their transformation in order to discover the orbitals that are pointing in the direction of the bonds. This transformation operation is called hybridization. Since it affects the shape of these orbitals, it will therefore modify the analytical expression of the corresponding wave function. It is therefore a mathematical operation, which consists of changing the basis of the atomic orbitals.

Recall that the *basis of the atomic orbitals* is the set of orthogonal wave functions that can describe an atom. This basis can be limited to atomic orbitals occupied only by electrons or extended if other orbitals are included.

In our case, we shall limit ourselves to the orbitals describing the outermost shell of the atoms. Let us consider the outermost shell of an element from the second period of the periodic table.

The *minimum natural basis* of this atom will be the 2s, $2p_x$, $2p_y$, and $2p_z$ orbitals. We represent this basis as

$$\{2s, 2p_x, 2p_y, 2p_z\}$$

Hybridization consists of changing this basis to a new hybrid basis that takes into account the geometry of the molecule. Each hybrid orbital is described as a linear combination of the natural basis orbitals. If φ_k designates an orbital of the natural basis, then we can write

$$t_i = \sum_k C_{ik} \phi_k$$

where t_i is the i^{th} hybrid orbital and C_{ik} is the hybridization coefficients, the weights of the atomic orbital k in the combination constituting the hybrid orbital i.

b. Main types of hybridization

Hybridization sp

The BeH_2 molecule has been shown to be linear through experimental measurements (see **Fig. VII-44**). This geometry suggests that the interactions between beryllium and the hydrogen atoms, i.e. the chemical bonds Be-H, imply the creation of an electronic density between the atoms. This electronic density is therefore concentrated along the internuclear axis. The beryllium atom must therefore be prepared through its atomic orbitals. The beryllium atom is characterized by the atomic orbitals of the outermost shell or valence shell Ψ_{2s}, Ψ_{2pz}, Ψ_{2px}, Ψ_{2py}. We can suggest that these orbitals form a basis as

$$\{\Psi_{2s}, \Psi_{2pz}, \Psi_{2px}, \Psi_{2py}\}$$

If we consider the natural atomic orbitals of beryllium, we can see that they are unsuitable for the description of the molecular geometry. Indeed, the s orbitals have spherical symmetry, while the axial symmetry of the p orbitals points in the direction 90°, as shown in **Fig. VII-50**. Recall the properties of the natural atomic orbitals of the beryllium atom, the energies and shapes of which are given in **Fig. VII-51**.

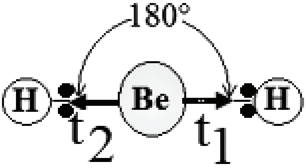


Figure VII-50: Directions of sp hybrids in BeH_2.

One way to make these orbitals conform to molecular symmetry is to undertake *hybridization* of the atomic orbitals. The hybridization of atomic orbitals consists of mixing an s orbital with one or several other orbitals.

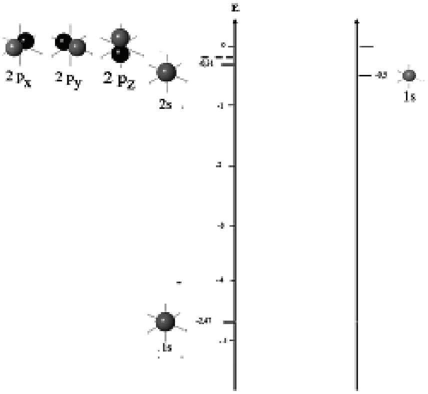


Figure VII-51: Energies and shapes of the natural atomic orbitals of Be and H atoms.

The goal, as in the case of the BeH_2 molecule, is to obtain two hybrids pointing in diametrically opposite directions towards the 1s orbitals of the hydrogen atoms, allowing us to account for the geometry of BeH_2. We can say that beryllium is hybridized into sp. Now, let us see what this hybridization gives. Mathematically, we define a new basis of the hybrid atomic orbitals from the natural atomic orbitals

$$\underbrace{\{\Psi_{2s}, \Psi_{2pz}, \Psi_{2px}, \Psi_{2py}\}}_{\text{Natural basis}} \rightarrow \underbrace{\{t_1, t_2, \Psi_{2px}, \Psi_{2py}\}}_{\text{Hybrid basis}}$$

We then construct the hybrid orbitals as a linear combination of the natural atomic orbitals, so that

$$\begin{aligned} t_1 &= a_1\Psi_{2s} + b_1\Psi_{2pz} \\ t_2 &= a_2\Psi_{2s} + b_2\Psi_{2pz} \end{aligned}$$

where a_i and b_i are the coefficients of the combination expressing the respective “weights” of the atomic orbitals in the hybridization.

Now we apply the properties of these new orbitals.

1. Each orbital must be normalized, i.e.

$$\iiint t_1^2 dv = 1 \quad \text{and} \quad \iiint t_2^2 dv = 1 \tag{VII-50}$$

2. These new orbitals must be orthogonal to each other

$$\iiint t_1 t_2 dv = 0$$

Consequently, for normalization we have

$$\begin{aligned} &\iiint (a_1\Psi_{2s} + b_1\Psi_{2pz})^2 dv = 1 \\ &\iiint (a_2\Psi_{2s} + b_2\Psi_{2pz})^2 dv = 1 \end{aligned} \tag{VII-51}$$

and for orthogonality

$$\iiint(a_1\Psi_{2s}+b_1\Psi_{2pz})(a_2\Psi_{2s}+b_2\Psi_{2pz})dv=0 \tag{VII-52}$$

Developing Eq. (VII-50), we have

$$a_1^2\iiint\Psi_{2s}^2dv+b_1^2\iiint\Psi_{2pz}^2dv+2a_1b_1\iiint\Psi_{2s}\Psi_{2pz}dv=1$$

$$a_2^2\iiint\Psi_{2s}^2dv+b_2^2\iiint\Psi_{2pz}^2dv+2a_2b_2\iiint\Psi_{2s}\Psi_{2pz}dv=1$$

Since Ψ_{2s} and Ψ_{2pz} must be normalized and orthogonal to each other, we obtain

$$a_1a_2\iiint\Psi_{2s}^2dv+b_1b_2\iiint\Psi_{2pz}^2dv+$$
$$a_1b_2\iiint\Psi_{2s}\Psi_{2pz}dv+a_2b_1\iiint\Psi_{2pz}\Psi_{2s}dv=0$$

Thus, we have the following equations

$$a_1^2+b_1^2=1 \tag{VII-53}$$

$$a_2^2+b_2^2=1 \tag{VII-54}$$

$$a_1a_2+b_1b_2=0 \tag{VII-55}$$

Multiplying (VII-53) by (VII-54), we get

$$(a_1^2+b_1^2)(a_2^2+b_2^2)=1$$

so that

$$a_1^2a_2^2+b_1^2a_2^2+a_1^2b_2^2+b_1^2b_2^2=1 \tag{VII-56}$$

From Eq. (VII-55), we have

$$a_1a_2=-b_1b_2$$

and then

$$a_1^2 a_2^2 = b_1^2 b_2^2$$

Eq. (VII-56) becomes successively

$$\begin{aligned} a_1^2 a_2^2 + b_1^2 a_2^2 + a_1^2 b_2^2 + a_1^2 a_2^2 &= 1 \\ a_1^2 a_2^2 + a_1^2 b_2^2 + a_1^2 a_2^2 + b_1^2 a_2^2 &= 1 \\ a_1^2 (a_2^2 + b_2^2) + a_2^2 (a_1^2 + b_1^2) &= 1 \end{aligned}$$

so that, according to (VII-53) and (VII-54)

$$a_1^2 + a_2^2 = 1$$

Likewise, we can show that

$$b_1^2 + b_2^2 = 1 \quad \text{and} \quad a_1 b_1 + a_2 b_2 = 0$$

Matrix writing
Hybrid atomic orbitals can be written in the form

$$\begin{bmatrix} t_1 \\ t_2 \end{bmatrix} = \begin{bmatrix} a_1 & b_1 \\ a_2 & b_2 \end{bmatrix} \begin{bmatrix} \Psi_{2s} \\ \Psi_{2pz} \end{bmatrix}$$

Considering the matrix in this expression, we can note:

- that the sum of the squares of a line is equal to 1

$$a_1^2 + b_1^2 = 1$$

- that the sum of the squares of a column is equal to 1

$$a_1^2 + a_2^2 = 1$$

- that the sum of the products of the matrix elements of a row is zero

$$a_1 a_2 + b_1 b_2 = 0$$

- that the sum of the products of the matrix elements of a column is zero

$$a_1 b_2 + a_2 b_1 = 0$$

Calculation of hybridization coefficients

The sign of the coefficients depends on the geometry of the molecule. Consider the basic atomic orbital $2p_z$.

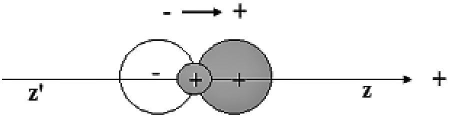


Figure VII-52: Signs of phases in OA 2s and $2p_z$.

Phase + points in the direction of t_1 and the sign in front of $|b_1|$ will be positive. On the contrary, for t_2 the sign will be *negative* because the orbital t_2 points in the direction of the negative z. The contribution of the 2s atomic orbital will always be positive since this orbital has a positive phase regardless of the direction observed. Ultimately, for the matrix coefficients we have

$$\begin{bmatrix} +|a_1| & +|b_1| \\ +|a_2| & -|b_2| \end{bmatrix}$$

If we apply the rules defined above, we have

$$a_1^2 + b_1^2 = 1 \text{ then } b_1^2 = 1 - a_1^2 \text{ and } b_1 = \sqrt{1 - a_1^2}$$
$$a_1^2 + a_2^2 = 1 \text{ then } a_2^2 = 1 - a_1^2 \text{ and } a_2 = \sqrt{1 - a_1^2}$$

which, for the matrix coefficients, gives

$$\begin{bmatrix} +|a_1| & +\sqrt{1-a_1^2} \\ +\sqrt{1-a_1^2} & -|a_1| \end{bmatrix}$$

If we define $|a_1| = a$, the matrix becomes

$$\begin{bmatrix} +a & \sqrt{1-a^2} \\ \sqrt{1-a^2} & -a \end{bmatrix}$$

To find the value of a, we need to apply the rules

$$a_1 b_2 + a_2 b_1 = 0 \quad \text{and} \quad 2a^2 = 1 \quad \text{so that: } a = \frac{\sqrt{2}}{2}$$

and so the matrix becomes

$$\begin{pmatrix} \frac{\sqrt{2}}{2} & \frac{\sqrt{2}}{2} \\ \frac{\sqrt{2}}{2} & -\frac{\sqrt{2}}{2} \end{pmatrix}$$

The shape of the hybrids

We can therefore construct the hybrid atomic orbitals t_1 and t_2

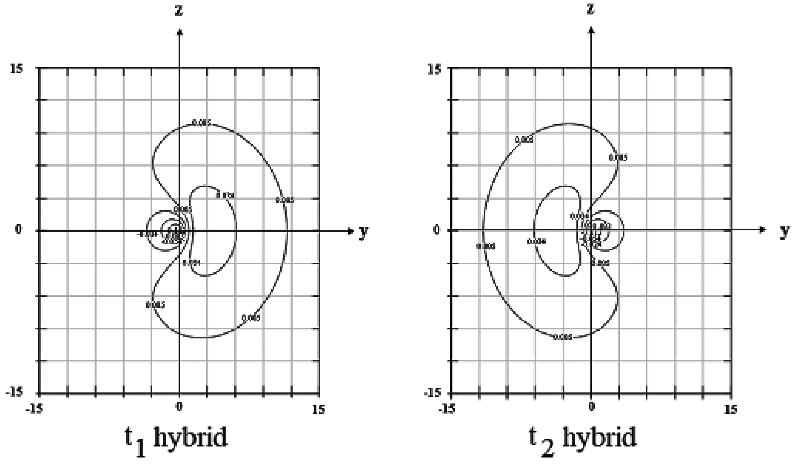
$$t_1 = \frac{\sqrt{2}}{2}\Psi_{2s} + \frac{\sqrt{2}}{2}\Psi_{2pz}$$
$$t_2 = \frac{\sqrt{2}}{2}\Psi_{2s} - \frac{\sqrt{2}}{2}\Psi_{2pz}$$

with

$$\Psi_{2s} = \frac{1}{4\sqrt{2\pi}}(2-r)\exp(-\frac{r}{2})$$

$$\Psi_{2pz} = \frac{1}{4\sqrt{2\pi}}r\cos(\theta)\exp(-\frac{r}{2})$$

The manual construction of the hybrid orbitals uses the same methods as we saw for natural atomic orbitals, namely the representation by angular distribution of the absolute value of the wave function. For practical questions, we use the representation by isoamplitude contours of the orbital t_1 in the plane zOy by changing the variables θ and r by the Cartesian coordinates z and y.



t_1 hybrid

t_2 hybrid

Figure VII-53: sp hybrid isoamplitude contours for beryllium.

To get an idea of the complete representation of these orbitals, we have to vary the angle φ in the xOy plane from 0 to 180° to obtain a 3-D shape of the isoamplitude surfaces.

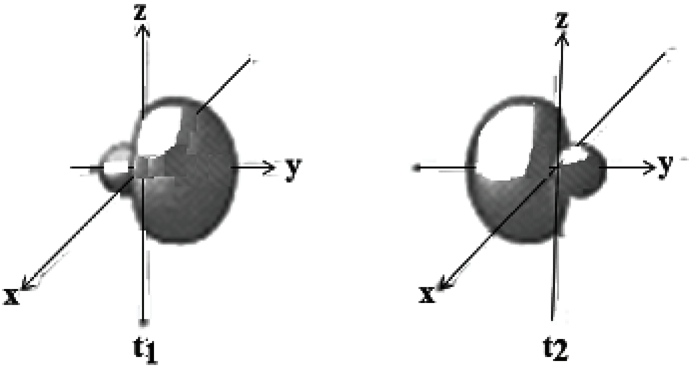


Figure VII-54: isoamplitude surfaces of sp hybrids.

In practice, as in **Fig. VII-55**, we can schematically represent the sp hybrid orbitals t_1 and t_2

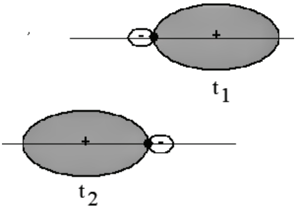


Figure VII-55: Schematic form of sp hybrids.

The large lobe points towards the ligand and the angle between the hybrids is 180°. From an energy point of view, we have the correlation diagram given in **Fig. VII-56**.

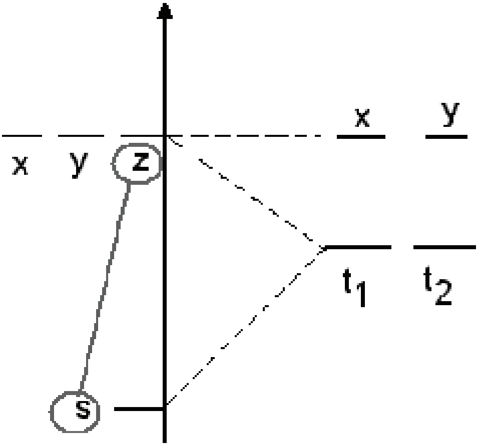


Figure VII-56: sp hybridization diagram.

Hybridization sp^2

This involves the mixing of an orbital s with two orbitals p. The goal is to get three hybrids pointing towards the vertices of an equilateral triangle. This allows us, for example, to account for the geometry of boron hydride (BH_3). It can be said that boron is hybridized into sp^2. Let us see the results of this hybridization.

First, let us recall the basis of the atomic orbitals used

$$\underbrace{\{\Psi_{2s},\Psi_{2pz},\Psi_{2px},\Psi_{2py}\}}_{\text{Natural basis}} \rightarrow \underbrace{\{t_1,t_2,t_{3,}\Psi_{2pz}\}}_{\text{Hybrid basis}}$$

In this case, we have used the atomic orbitals Ψ_{2s}, Ψ_{2px}, and Ψ_{2py} to build the hybrid atomic orbitals sp_2. This gives

$$\begin{aligned} t_1 &= a_1\Psi_{2s} + b_1\Psi_{2px} + c_1\Psi_{2py} \\ t_2 &= a_2\Psi_{2s} + b_2\Psi_{2px} + c_2\Psi_{2py} \\ t_3 &= a_3\Psi_{2s} + b_3\Psi_{2px} + c_3\Psi_{2py} \end{aligned}$$

Matrix writing

$$\begin{pmatrix} t_1 \\ t_2 \\ t_3 \end{pmatrix} = \begin{pmatrix} a_1 & b_1 & c_1 \\ a_2 & b_2 & c_2 \\ a_3 & b_3 & c_3 \end{pmatrix} \times \begin{pmatrix} \Psi_{2s} \\ \Psi_{2px} \\ \Psi_{2py} \end{pmatrix}$$

Definition of the referential

Fig. VII-57 gives the referential used for sp2 hybrids in which the sign of the orientation of the hybrids with respect to the sign of the axes appear.

t_1 confuses itself with the x axis and points to positive x.

t_2 has a positive component in the y direction and is negative in the x direction.

t_3 has a negative component in the y direction and is negative in the x direction.

As such, we have the following equations

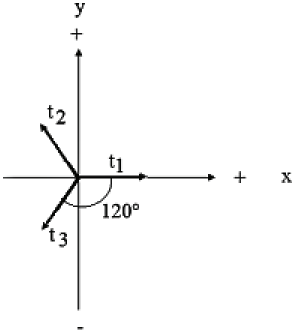


Figure VII-57: Sign convention for sp^2 hybrids.

$$t_1 = |a_1|\Psi_{2s} + |b_1|\Psi_{2px} + 0\Psi_{2py}$$

$$t_2 = |a_2|\Psi_{2s} - |b_2|\Psi_{2px} + |c_2|\Psi_{2py}$$

$$t_3 = |a_3|\Psi_{2s} - |b_3|\Psi_{2px} - |c_3|\Psi_{2py}$$

Besides, given the symmetry we must have

$$|b_2| = |b_3| \text{ and } |c_2| = |c_3|$$

which involves setting $|a_1| = a$ to the transformation matrix

$$\begin{pmatrix} a & |b_1| & 0 \\ a_2 & -|b_2| & |c_2| \\ a_3 & -|b_2| & -|c_2| \end{pmatrix}$$

By applying the rules on the coefficients, we have

$$2|c_2|^2 = 1 \quad \text{so that} \quad |c_2| = \frac{\sqrt{2}}{2}$$

$$a^2 + |b_1|^2 = 1 \quad \text{so that} \; |b_1| = \sqrt{1-a^2}$$

$$|b_1|^2 + 2|b_2|^2 = 1 \text{ so that } 1 - a^2 + 2|b_2|^2 = 1 \text{ then } |b_2| = \frac{a}{\sqrt{2}}$$

$$|a_2|^2 + \frac{a}{2} + \frac{1}{2} = 1 \text{ so that } |a_2| = \sqrt{\frac{1-a^2}{2}}$$

$$|a_3|^2 + \frac{a}{2} + \frac{1}{2} = 1 \text{ so that } |a_3| = \sqrt{\frac{1-a^2}{2}}$$

As such, we have the following transformation matrix

$$\begin{pmatrix} a & \sqrt{1-a^2} & 0 \\ \sqrt{\frac{1-a^2}{2}} & -\frac{a}{\sqrt{2}} & \frac{1}{\sqrt{2}} \\ \sqrt{\frac{1-a^2}{2}} & -\frac{a}{\sqrt{2}} & -\frac{1}{\sqrt{2}} \end{pmatrix}$$

a remains to be determined. To do this, let us introduce the physics in the problem. If we compare the directions of the hybrid atomic orbitals to the vectors, we have

$$t_1 . \vec{t}_3 = \left\| \vec{t}_1 \right\| \left\| \vec{t}_3 \right\| \cos 120°$$

with

$$t_1 \begin{cases} \sqrt{1-a^2} \\ \\ 0 \end{cases} \qquad \text{and} \, \vec{t}_3 \begin{cases} -\frac{a}{\sqrt{2}} \\ \\ -\frac{1}{\sqrt{2}} \end{cases}$$

so that

$$\cos 120° = \frac{\vec{t}_1 . \vec{t}_3}{\left\| \vec{t}_1 \right\| \left\| \vec{t}_3 \right\|}$$

We have vector lengths equal to

$$\left\| \vec{t}_1 \right\| = \sqrt{x_1^2 + y_1^2} \text{ and } \left\| \vec{t}_3 \right\| = \sqrt{x_3^2 + y_3^2}$$

or

$$\left\| \vec{t}_1 \right\| = \sqrt{1 - a^2} \text{ and } \left\| \vec{t}_3 \right\| = \left(\frac{a^2}{2} + \frac{1}{2} \right)$$

Let us express the scalar product of the hybrid vectors

$$\vec{r}_1 \vec{r}_3 = x_1 x_3 + y_1 y_3$$

so that

$$\vec{t}_1 \vec{t}_3 = \sqrt{1 - a^2} \left(-\frac{a}{\sqrt{2}} \right) = -a\sqrt{\frac{1 - a^2}{2}}$$

We can then write

$$\frac{1}{2} = \frac{-a\sqrt{\frac{1 - a^2}{2}}}{\sqrt{1 - a^2}\sqrt{\frac{a^2}{2} + \frac{1}{2}}}$$

or

$$\frac{1}{2} = \frac{-a\sqrt{\frac{1}{2}}}{\sqrt{\frac{a^2 + 1}{2}}} = \frac{-a}{\sqrt{a^2 + 1}}$$

Let us square this expression

$$\frac{a^2}{a^2+1} = \frac{1}{4}$$

We can thus deduce

$$a^2 = \frac{1}{3} \text{ i.e. } a = \frac{1}{\sqrt{3}}$$

so that the equations giving the hybrid orbitals sp² are

$$\begin{pmatrix} t_1 \\ t_2 \\ t_3 \end{pmatrix} = \begin{pmatrix} \sqrt{\frac{1}{3}} & \sqrt{\frac{2}{3}} & 0 \\ \sqrt{\frac{1}{3}} & -\frac{1}{\sqrt{6}} & \frac{1}{\sqrt{2}} \\ \sqrt{\frac{1}{3}} & -\frac{1}{\sqrt{6}} & -\frac{1}{\sqrt{2}} \end{pmatrix} \times \begin{pmatrix} \Psi_{2s} \\ \Psi_{2px} \\ \Psi_{2py} \end{pmatrix}$$

where

$$\Psi_{2s} = \frac{1}{4\sqrt{2\pi}}(r-2)\exp\left(-\frac{r}{2}\right)$$

$$\Psi_{2px} = \frac{1}{4\sqrt{2\pi}} r\sin\theta\cos\phi\exp\left(-\frac{r}{2}\right)$$

$$\Psi_{2py} = \frac{1}{4\sqrt{2\pi}} r\sin\theta\sin\phi\exp\left(-\frac{r}{2}\right)$$

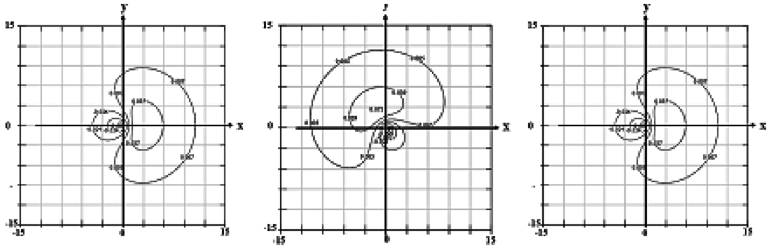
If we use Cartesian coordinates, we obtain

$$\Psi_{2s} = \frac{1}{4\sqrt{2\pi}}\left(\sqrt{x^2+y^2}-2\right)\exp\left(-\frac{\sqrt{x^2+y^2}}{2}\right)$$

$$\Psi_{2px} = \frac{1}{4\sqrt{2\pi}} x\exp\left(-\frac{\sqrt{x^2+y^2}}{2}\right)$$

$$\Psi_{2py} = \frac{1}{4\sqrt{2\pi}} y\exp\left(-\frac{\sqrt{x^2+y^2}}{2}\right)$$

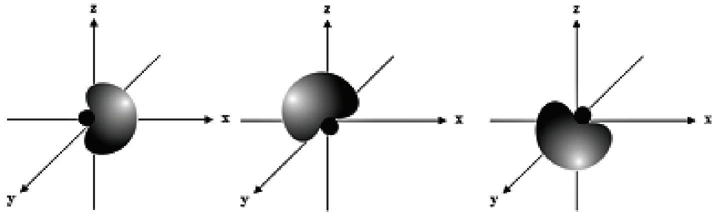
Then, in the xOy plane we can draw the isoamplitude contours of the hybrid atomic orbitals.



t1 t2 t1

Figure VII-58: Isoamplitude contours of sp^2 hybrids.

If we vary the angle ϕ, we obtain volumes contained in the outermost amplitude surface.



t_1 t_2 t_3

Figure VII-59: Isoamplitude surface of sp^2 hybrids.

Energetically speaking, we have the following correlation diagram.

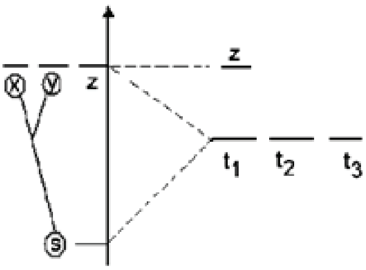


Figure VII-60: Hybridization diagram sp^2.

We can mix an s orbital and 2 p_z orbitals and thus obtain three hybrid orbitals t_1 , t_2, and t_3, the schematic form of which is in the diagram below.

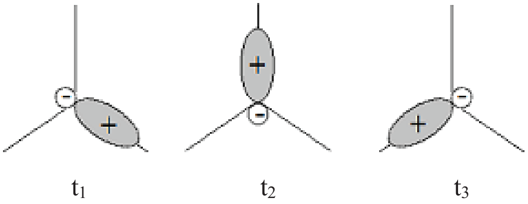


Figure VII-61: Schematic forms of sp² hybrids.
The angle between the hybrids is 120°.

sp³ hybridization

sp³ hybridization consists of mixing an orbital s with three orbitals p. The goal is to obtain 4 hybrids pointing towards the vertices of a cube, as in the CH_4 molecule. This allows us to account for the geometry of CH_4. It can be said that the carbon is hybridized in sp³. There are several ways of designing the referential.

We shall see two types of representation, one with pure sp³ the other close to sp³.

Pure sp³ hybridization molecules

We speak of pure hybridization when hybrids are obtained making an angle of 109° 28′ exactly between them. **Fig. VII-62** gives an example of pure sp³ hybridization. The hybrids point, two by two, towards the opposite corners of a cube. The angle between the hybrids is 109° 28′ exactly. This is a fully symmetric disposition.

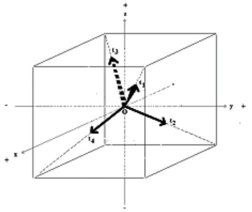


Figure VII-62:
pure sp³ hybrids.

The hybridization equations in this case are

$$\begin{pmatrix} t_1 \\ t_2 \\ t_3 \\ t_4 \end{pmatrix} = \begin{pmatrix} a_1 & b_1 & c_1 & d_1 \\ a_2 & b_2 & c_2 & d_2 \\ a_3 & b_3 & c_3 & d_3 \\ a_4 & b_4 & c_4 & d_4 \end{pmatrix} \begin{pmatrix} \Psi_{2s} \\ \Psi_{2px} \\ \Psi_{2py} \\ \Psi_{2pz} \end{pmatrix}$$

In this kind of hybridization, all the coefficients have the same weight, but the signs are different depending on how the hybrid orbitals point to the positive or negative coordinates.

$$\begin{pmatrix} +|a| & +|b_1| & +|b_1| & +|b_1| \\ +|a| & -|b_1| & +|b_1| & -|b_1| \\ +|a| & -|b_1| & -|b_1| & -|b_1| \\ +|a| & +|b_1| & -|b_1| & -|b_1| \end{pmatrix}$$

By initially distinguishing the 2s and 2p orbitals we get the hybridization matrix on the right. Thus, we have the relation

$$a^2 + 3b_1^2 = 1$$

from which we deduce

$$|b_1| = \sqrt{\frac{1-a^2}{3}}$$

Besides

$$4a^2 = 1 \text{ so that } |a| = \frac{1}{2}$$

then $|b_1|$ to get

$$|b_1| = \sqrt{\frac{1-a^2}{3}} = \sqrt{\frac{1-\frac{1}{4}}{3}} = \frac{1}{2}$$

leading to the hybridization matrix

$$\begin{pmatrix} +\frac{1}{2} & +\frac{1}{2} & +\frac{1}{2} & +\frac{1}{2} \\ +\frac{1}{2} & -\frac{1}{2} & +\frac{1}{2} & -\frac{1}{2} \\ +\frac{1}{2} & -\frac{1}{2} & -\frac{1}{2} & -\frac{1}{2} \\ +\frac{1}{2} & +\frac{1}{2} & -\frac{1}{2} & -\frac{1}{2} \end{pmatrix}$$

Hybridization close to sp^3

The angle between the hybrids can be different to 109° 28′, but it must remain relatively close to this value. This is the case for the hybridization of nitrogen in the ammonia molecule (NH_3), for example.

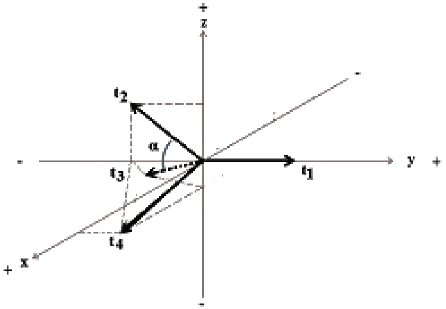


Figure VII-63: Other types of sp^3 hybridization.

For this, we can consider the arrangement given in **Fig. VII-63** of the hybrid orbitals with respect to the Cartesian referential. Thus, we have the following equations

$$\begin{pmatrix} t_1 \\ t_2 \\ t_3 \\ t_4 \end{pmatrix} = \begin{pmatrix} a_1 & b_1 & c_1 & d_1 \\ a_2 & b_2 & c_2 & d_2 \\ a_3 & b_3 & c_3 & d_3 \\ a_4 & b_4 & c_4 & d_4 \end{pmatrix} \times \begin{pmatrix} \Psi_{2s} \\ \Psi_{2px} \\ \Psi_{2py} \\ \Psi_{2pz} \end{pmatrix}$$

Taking into account the symmetry, one can provide a transformation matrix of the type

$$\begin{pmatrix} a & 0 & +|c_1| & 0 \\ +|a_2| & 0 & -|c_2| & +|d_2| \\ +|a_3| & -|b_3| & -|c_3| & -|d_3| \\ +|a_3| & |b_3| & -|c_3| & -|d_3| \end{pmatrix}$$

Using the relation between the coefficients we saw above, we may write

$$a^2 + c_1^2 = 1 \text{ so that } |c_1| = \sqrt{1 - a^2}$$

The matrix takes the form

$$\begin{pmatrix} a & 0 & +\sqrt{1 - a^2} & 0 \\ +|a_2| & 0 & -|c_2| & +|d_2| \\ +|a_3| & -|b_3| & -|c_3| & -|d_3| \\ +|a_3| & |b_3| & -|c_3| & -|d_3| \end{pmatrix}$$

and we can deduce

$$2b_3^2 = 1 \text{ then } |b_3| = \frac{1}{\sqrt{2}}$$

Furthermore, we can see on the graph that $|c_2| = |c_3|$. The three hybrids t_2, t_3, and t_4 are superimposed by a simple rotation around an axis and the contribution of the orbital 2s is therefore the same for these three sp^3.hybrids. So we have

$$\begin{pmatrix} a & 0 & \sqrt{1 - a^2} & 0 \\ +|a_2| & 0 & -|c_2| & +|d_2| \\ +|a_2| & -\frac{1}{\sqrt{2}} & -|c_2| & -|d_3| \\ +|a_2| & \frac{1}{\sqrt{2}} & -|c_2| & -|d_3| \end{pmatrix}$$

We thus deduce

$$3a_2^2 = 1 - a^2 \text{ so that } |a_2| = \sqrt{\frac{1-a^2}{3}}$$

and

$$3c_2^2 + 1 - a^2 = 1 \text{ so that } 3c_2^2 = a^2 \text{ and } |c_2| = \sqrt{\tfrac{a^2}{3}}$$

Then, we have the matrix

$$\begin{pmatrix} a & 0 & \sqrt{1-a^2} & 0 \\ +\sqrt{\frac{1-a^2}{3}} & 0 & -\sqrt{\frac{a^2}{3}} & +|d_2| \\ +\sqrt{\frac{1-a^2}{3}} & -\frac{1}{\sqrt{2}} & -\sqrt{\frac{a^2}{3}} & -|d_3| \\ +\sqrt{\frac{1-a^2}{3}} & \frac{1}{\sqrt{2}} & -\sqrt{\frac{a^2}{3}} & -|d_3| \end{pmatrix}$$

and deduce that

$$d_2^2 = 1 - \frac{a^2}{3} - \frac{1-a^2}{3} \text{ and } |d_2| = \sqrt{\frac{2}{3}}$$

we get the matrix as a function of a

$$\begin{pmatrix} a & 0 & \sqrt{1-a^2} & 0 \\ +\sqrt{\dfrac{1-a^2}{3}} & 0 & -\sqrt{\dfrac{1-a^2}{3}} & +\sqrt{\dfrac{2}{3}} \\ +\sqrt{\dfrac{1-a^2}{3}} & -\dfrac{1}{\sqrt{2}} & -\sqrt{\dfrac{1-a^2}{3}} & -|d_3| \\ +\sqrt{\dfrac{1-a^2}{3}} & \dfrac{1}{\sqrt{2}} & -\sqrt{\dfrac{1-a^2}{3}} & -|d_3| \end{pmatrix}$$

leading us to write

$$2d_3^2 + \tfrac{2}{3} = 1 \quad \text{so that } |d_3| = \sqrt{\frac{1}{6}}$$

and thus the matrix takes the form

$$\begin{pmatrix} a & 0 & \sqrt{1-a^2} & 0 \\ +\sqrt{\dfrac{1-a^2}{3}} & 0 & -\sqrt{\dfrac{1-a^2}{3}} & +\sqrt{\dfrac{2}{3}} \\ +\sqrt{\dfrac{1-a^2}{3}} & -\dfrac{1}{\sqrt{2}} & -\sqrt{\dfrac{1-a^2}{3}} & -\sqrt{\dfrac{1}{6}} \\ +\sqrt{\dfrac{1-a^2}{3}} & \dfrac{1}{\sqrt{2}} & -\sqrt{\dfrac{1-a^2}{3}} & -\sqrt{\dfrac{1}{6}} \end{pmatrix}$$

Now we apply the physical condition of the angle α between the hybrids, t_3 and t_4 for example. For ammonia we have the angle α = 107.3°. This is not the value of 109° 28' of pure sp^3 hybridization, but sp^3 hybridization can be applied to this case.

If we assimilate hybrids to vectors, we can write their scalar product

$$\vec{t}_3 . \vec{t}_4 = \left\| \vec{t}_3 \right\| \left\| \vec{t}_4 \right\| \cos\alpha$$

with the vector components

$$\vec{t}_3 \begin{cases} -\frac{1}{\sqrt{2}} \\ -\sqrt{\frac{1-a^2}{3}} \\ -\sqrt{\frac{1}{6}} \end{cases} \quad \text{and } \vec{t}_4 \begin{cases} \frac{1}{\sqrt{2}} \\ -\sqrt{\frac{1-a^2}{3}} \\ -\sqrt{\frac{1}{6}} \end{cases}$$

We thus have

$$\cos\alpha = \frac{\vec{t}_3 \vec{t}_4}{\left\| \vec{t}_3 \right\| \left\| \vec{t}_4 \right\|}$$

Besides, we have the dot product t_3t_4, which is equal to

$$\vec{t}_3 . \vec{t}_4 = \left(-\frac{1}{\sqrt{2}}\right)\left(\frac{1}{\sqrt{2}}\right) + \left(-\sqrt{\frac{1-a^2}{3}}\right)\left(-\sqrt{\frac{1-a^2}{3}}\right) + \left(-\sqrt{\frac{1}{6}}\right)\left(-\sqrt{\frac{1}{6}}\right)$$

i.e.

$$\vec{t}_3 . \vec{t}_4 = \frac{-a^2}{3}$$

Besides

$$\left\| \vec{t}_3 \right\| = \sqrt{x_2^2 + y_2^2 + z_2^2} \text{ and } \left\| \vec{t}_4 \right\| = \sqrt{x_3^2 + y_3^2 + z_3^2}$$

then

$$\left\| \vec{t}_3 \right\| = \sqrt{\left(-\frac{1}{\sqrt{2}}\right)^2 + \left(-\sqrt{\frac{1-a^2}{3}}\right)^2 + \left(-\sqrt{\frac{1}{6}}\right)^2} \text{ and } \left\| \vec{t}_4 \right\| = \left\| \vec{t}_3 \right\|$$

i.e.

$$\left\| \vec{t}_3 \right\| = \sqrt{1 - \frac{1}{3}a^2} \text{ and } \left\| \vec{t}_4 \right\| = \left\| \vec{t}_3 \right\|$$

We can then write

$$\cos\alpha = \frac{\vec{t}_3 . \vec{t}_4}{\left\| \vec{t}_3 \right\| \left\| \vec{t}_4 \right\|}$$

or

$$\cos\alpha = \frac{\frac{-a^2}{3}}{1 - \frac{1}{3}a^2}$$

so that

$$\cos\alpha = \frac{-a^2}{3 - a^2}$$

and using the physical data

$$\cos(107.5) = \frac{-a^2}{3 - a^2}$$

we obtain

$$a = \sqrt{\frac{0.9}{1.3}} = 0.832$$

Finally, the hybridization matrix close to sp^3 takes the form

$$\begin{pmatrix} 0.832 & 0 & \sqrt{1-(0.832)^2} & 0 \\ +\sqrt{\dfrac{1-(0,.832)^2}{3}} & 0 & -\sqrt{\dfrac{1-(0.832)^2}{3}} & +\sqrt{\dfrac{2}{3}} \\ +\sqrt{\dfrac{1-(0.832)^2}{3}} & -\dfrac{1}{\sqrt{2}} & -\sqrt{\dfrac{1-(0.832)^2}{3}} & -\sqrt{\dfrac{1}{6}} \\ +\sqrt{\dfrac{1-(0.832)^2}{3}} & \dfrac{1}{\sqrt{2}} & -\sqrt{\dfrac{1-(0.832)^2}{3}} & -\sqrt{\dfrac{1}{6}} \end{pmatrix}$$

Numerically, we obtain

$$\begin{pmatrix} 0.832 & 0 & 0.555 & 0 \\ 0.320 & 0 & -0.320 & 0.816 \\ 0.320 & -0.707 & -0.320 & -0.408 \\ 0.320 & 0.707 & -0.320 & -0.408 \end{pmatrix}$$

We deduce the NH_3 hybrid orbitals

$$\begin{pmatrix} t_1 \\ t_2 \\ t_3 \\ t_4 \end{pmatrix} = \begin{pmatrix} 0.832 & 0 & 0.555 & 0 \\ 0.320 & 0 & -0.320 & 0.816 \\ 0.320 & -0.707 & -0.320 & -0.408 \\ 0.320 & 0.707 & -0.320 & -0.408 \end{pmatrix} \begin{pmatrix} \Psi_{2s} \\ \Psi_{2px} \\ \Psi_{2py} \\ \Psi_{2pz} \end{pmatrix}$$

If we draw the isoamplitude contours in the yOz plane, for the hybrid orbitals t_1 and t_2, we obtain the figure below.

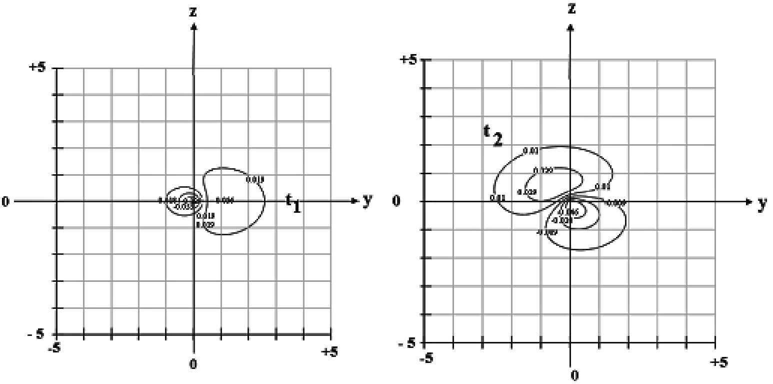


Figure VII-64: sp^3 hybrid amplitude contours t_1 and t_2 for ammonia.

The other hybrid orbitals t_3 and t_4 are deduced by a rotation of $\pi/3$ around the axis y'Oy.

Note that the hybrid pointing to the y axis will be the one that carries the free doublet of nitrogen in NH_3. The other hybrids will point towards the hydrogen atoms.

Energetically speaking, we have the following correlation diagram: we mix an s orbital and 2 p orbitals and obtain three sp^3 hybrid orbitals t_1, t_2, and t_3.

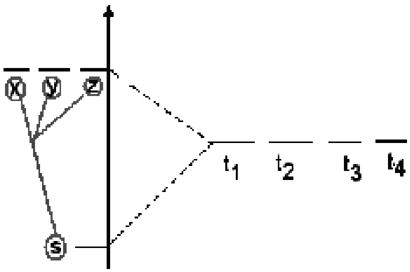


Figure VII-65: sp^3 hybridization.

The shape of the hybrid orbitals is presented schematically in **Fig. VII-66**; the other 3 directions are similar. In the pure sp^3 form, that of CH_4 for example, each hybrid points towards the vertices of a tetrahedron whose central atom is in O. The angle between the hybrids is then 109° 28′.

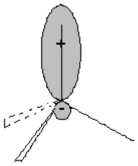


Figure VII-66: Schematic representation of an sp^3 hybrid.

As the number of ligands increases, the d orbitals must become involved. Thus we have sp^3d type hybridizations to account for structures having a bi-pyramidal form with a triangular base (hexahedron), or sp^3d^2 for geometries of bi-pyramidal type with a square base (octahedron). We have previously seen such geometries during our examination of the VSEPR method and the principle of construction remains the same.

sp^3d and dsp^3 hybridizations

These concern molecules with a hexahedron or bi-pyramidal arrangement with a triangular base, such as transition metal complexes.

Here, we use one s atomic orbital, three p orbitals, and one d orbital.

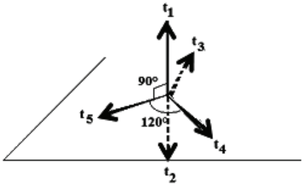
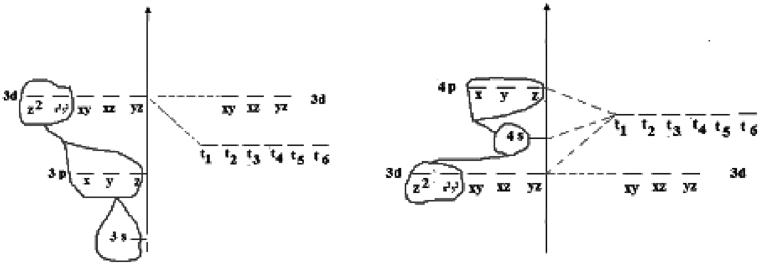


Figure VII-67: Directions of hybrids sp^3d^2 or $d^2 sp^3$.

If the hybridization involves orbitals of the same shell, we then have sp^3d^2 hybridization and pass from the basis 3s, $3p_x$, $3p_y$, $3p_z$, $3d_{z^2}$, $3d_{x^2-y^2}$, $3d_{xy}$, $3d_{xz}$, and $3d_{yz}$, to the new hybrid basis

$$\left\{3s, 3p_x, 3p_y 3p_z, 3d_{z^2}, 3d_{x^2-y^2}\right\} \rightarrow \{t_1, t_2, t_3, t_4, t_5, t_6\}$$

which gives the diagrams in **Fig. VII-68**. On the left of this figure we have the sp^3d^2 hybridization and on the right the $d^2 sp^3$ hybridization.



sp^3d^2

$d^2 sp^3$

Figure VII-68: Hybridization diagrams for sp^3d^2(left) or $d^2 sp^3$(right).

c. Use of hybridization theory to construct molecular orbitals of polyatomic molecules

In this section we shall see how to simply build the molecular orbital diagrams of polyatomic molecules on the basis of hybridized atomic orbitals.

The BeH_2 molecule

We have previously seen that the sp type hybridization of beryllium leads to the hybrid orbitals t_1 and t_2, as shown in **Fig. VII-69**.

Both 2s electrons of beryllium are found in the hybrid orbitals t_1 and t_2 with each pointing in the direction of the ligands so that we have the interactions given in **Fig. VII-70**.

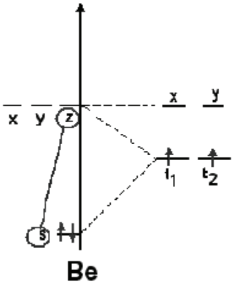


Figure VII-69: sp hybridization of Be.

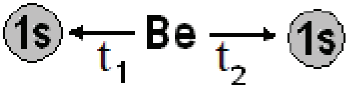


Figure VII-70: Interaction scheme of orbitals in BeH_2.

We can then obtain a correlation diagram (**Fig. VII-71**) for the AOs and MOs of BeH_2. Each hybrid AO thatinterferes with the AO 1s of hydrogen, which is opposite, gives a bonding MO of σ type and an anti-bonding MO of σ* type.

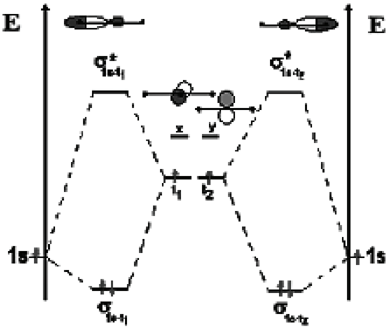


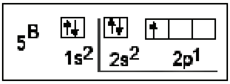
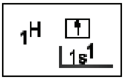
Figure VII-71: MO diagram of the BeH_2 molecule.

We thus have a description in terms of *localized molecular orbitals*. This description is close to the chemist's vision of the chemical bond in Lewis notation, in which the bond is considered to be due to a pair of electrons located between the bonding atoms.

There is another description of the molecular orbitals of BeH_2 that we shall not describe here—the *delocalized molecular orbitals*. This description allows molecular orbitals of the same symmetry to interfere. For example, OM $\sigma_{\text{s-t1}}$ and OM $\sigma_{\text{s-t2}}$ having the same energy and being of the same axial symmetry have the possibility of interfering leading to delocalized molecular orbitals.

The BH_3 molecule

Recall the VSEPR procedure for determining the geometry of this molecule. It consists of counting the number of electrons in the outermost shell of the central atom, boron here, and the number of unpaired electrons brought in by the ligands.

Central atom: Boron *B*		**3 outermost electrons**
Ligands:3 hydrogen atoms *H*		**1 outermost unpaired electron×3**

The 3 hydrogen atoms will therefore supply 3 electrons to the valence sphere.

In total we have 6 electrons, which are grouped into 3 doublets.

$$6\text{ electrons} \Rightarrow 3\text{ doublets} \left\{ \begin{array}{ll} \text{H retrieves a doublet} & \Rightarrow 1\text{ charge} \\ \text{H retrieves a doublet} & \Rightarrow 1\text{ charge} \\ \text{H retrieves a doublet} & \Rightarrow 1\text{ charge} \end{array} \right\} 3\text{ charges system}$$

Each ligand H collects as many doublets as the number of unpaired electrons it has supplied. There are therefore 3 charges on the valence sphere, which are distributed at the corners of an equilateral triangle, as shown in **Fig. VII-72**.

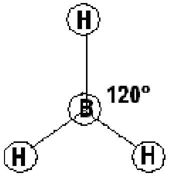


Figure VII-72: geometry of BH_3.

The angle formed by the BH connections is therefore 120°. In order to make the atomic orbitals of boron directional, we need to use

sp^2 hybridization, which will consist of mixing the 2s orbital with the $2p_x$ and $2p_y$ orbitals of boron.This mixing leads to the 3 hybrid orbitals t_1, t_2, and t_3, as shown in **Fig. VII-73**.

The shape of the hybrid orbitals is given in **Fig. VII-59** and the angle between the hybrids is 120°. Thus, we have the following diagram (**Fig. VII-74**) for the BH_3 molecule.

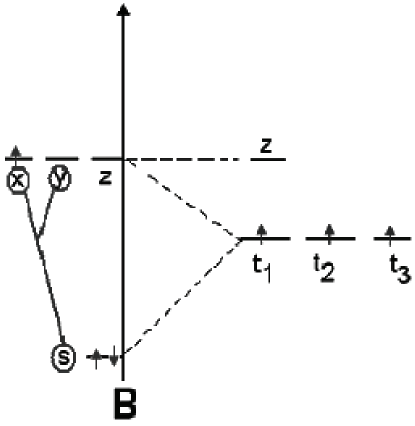


Figure VII-73: sp^2 hybridization for boron.

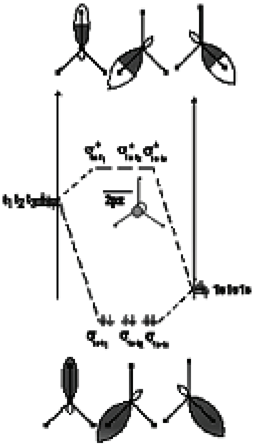


Figure VII-74: Localized MO of BH_3.

The ethylene molecule (C_2H_4)

sp^2 hybridization is also found in molecules of larger size, such as ethylene (C_2H_4).

This molecule is planar and the directions of the CC bond form an angle of 120° with the CH bonds.

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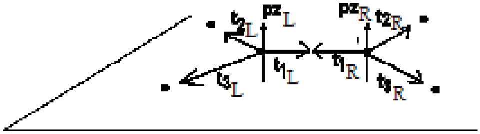


Figure VII-75: Interaction scheme in ethylene. The subscripts L and R mean, respectively, “left” and “right”.

Each carbon being hybridized in sp², we have the interaction scheme given in **Fig. VII-75.** The correlation diagram of orbitals is given in **Fig. VII-76**, knowing that carbon has 4 valence electrons.

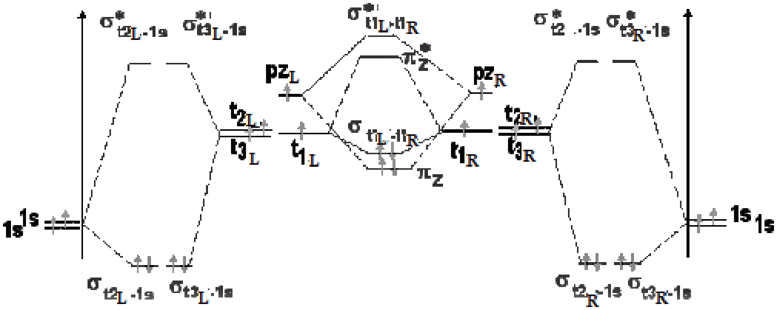


Figure VII-76: Correlation diagram of localized MO in ethylene. The subscripts L and R mean, respectively, “left” and “right”.

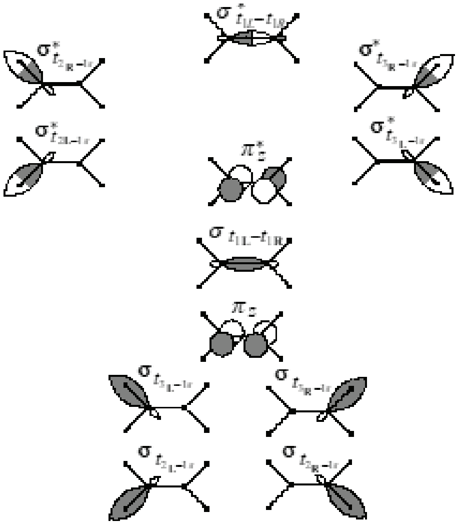


Figure VII-77: Schematic form of localized MOs of ethylene. The subscripts L and R mean, respectively, “left” and “right”.

d. Counting molecular orbitals in a molecule

Finally, we have a method to determine, without drawing the energy diagrams, the different molecular orbitals of a polyatomic molecule. We take as an example the ozone molecule O_3. Looking at the geometry of this molecule, we are able to propose a type of hybridization for oxygen. The ozone molecule is in a folded form and the angle between the O-O bonds is 117°.

Figure VII-78:
Geometry of ozone O_3.

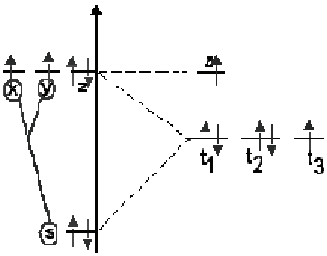


Figure VII-79: sp^2 hybridization for the oxygen atom of ozone.

This angle being close to 120°, one can envisage the sp^2 hybridization of the oxygen atoms, which will consist of mixing the 2s orbital with the $2p_x$ and $2p_y$ orbitals.

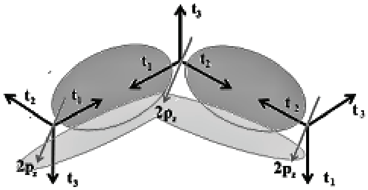
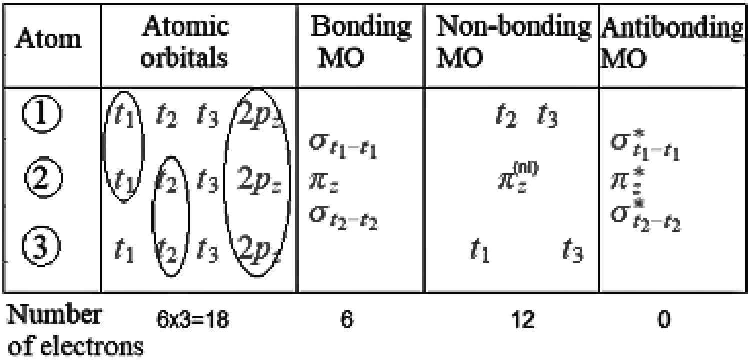


Figure VII-80: Interaction scheme between AOs in ozone.

As such, each oxygen atom carries 3 hybrid atomic orbitals and an OA $2p_z$. We then have the interaction scheme given in **Fig. VII-80**, which will help us identify the molecular orbitals of ozone given in **Table VII-14.**

Table VII-14: Molecular orbitals of ozone



Atom	Atomic orbitals	Bonding MO	Non-bonding MO	Antibonding MO
①	t_1 t_2 t_3 $2p_z$	$\sigma_{t_1-t_1}$	t_2 t_3	$\sigma^*_{t_1-t_1}$
②	t_1 t_2 t_3 $2p_z$	π_z	$\pi_z^{(nl)}$	π^*_z
③	t_1 t_2 t_3 $2p_z$	$\sigma_{t_2-t_2}$	t_1 t_3	$\sigma^*_{t_2-t_2}$
Number of electrons	6x3=18	6	12	0

Knowing that there are 2 electrons per orbital, we have 6 electrons in the bonding MO and 12 in the non-bonding MO. The overall binding index is therefore 6/2 = 3. As an exercise, repeat the same reasoning with the hypothesis of sp hybridization for oxygen. We should also find a bond index of 3. However, in this new configuration, there are electrons in the anti-MO. It may be noted that the anti-bonding effect is more important than the bonding effect, for an equal overall index, in the configuration of which no electron in the anti-bonding MO is preferred.

e. Electronic and magnetic properties of transition metal complexes

In this paragraph we give another illustration of the use of the theory of hybrid orbitals to try to theoretically explain the electronic and magnetic properties of complexes.

The transition metal complexes constitute an important part of compounds where the hybridization theory is used.

Nomenclature of complexes

The rules below were issued by the International Union of Pure and Applied Chemistry (IUPAC).

Formulas

The central atom is indicated in first place, then, in order, the negative, neutral, and positive ligands.

The formula is enclosed in square brackets [].

Names

The central atom is named in last place and the ligands appear in alphabetical order, whatever their charge.

The oxidation number of the central atom is indicated by a Roman numeral to accentuate its formal character: Fe (II) or Fe^{II}.

If the complex is anionic, the name of the central atom has the suffix "-ate".

Example

$$K_3[Fe(CN)_6] = \text{Potassium hexacyanoferrate (III)}$$

Name of ligands

If the ligands are anionic, they have the suffix "o": Cl^- = "chloro"; $S_2O_3^{2-}$ = "thiosulfate"; NO_2 = "nitrito".

If the ligands are molecules or cations, the name is unchanged. Exceptions: H_2O = "aqua"; NH_3 = "ammine"; CO = "carbonyl"; NO = "nitrosyl".

If the ligands are bridging, they are indicated by "µ-", example: Cl^- = "µ-chloro".

Number of ligands

The number of ligands is indicated by the prefixes di-, tri-, tetra-, penta-, hexa-, etc.

If the ligand has a composite name, we use bis-, tris-, tetrakis-, pentakis, hexakis, etc.

Examples

$[Cr(H_2O)_6]Cl_3$:aqua chromium(III) hexachloride

$[Co(NH_3)_4(H_2O)_2]Cl_3$: tetra ammine diaqua cobalt(III) chloride

$Na[AlCl_4]$: sodium tetrachloro aluminate

$[CoCl(NO_2)(NH_3)_4]Cl$: Chloro nitrito cobalt(III) tetra ammine chloride

There are several theories dealing with the properties of complexes.

Valence bond theory

Defined by Linus Pauling, it uses the concept of hybridization. Consider an octahedral metal complex.

The position of the ligands is indicated by numbers. M^+ is the central positive metallic ion as given in **Fig. VII-81**.

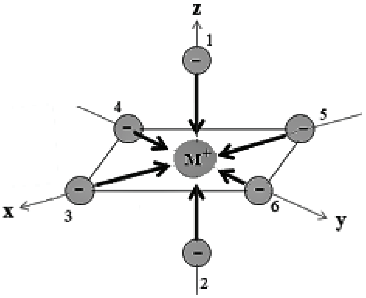


Figure VII-81. Octahedral complex.

If we compare this last figure with the direction of the d atomic orbitals, we note that only the AOs $3dz^2$ and $3dx^2$-y^2 are pointing in the direction of the ligands and consequently will be useful in the construction of hybrid atomic orbitals.

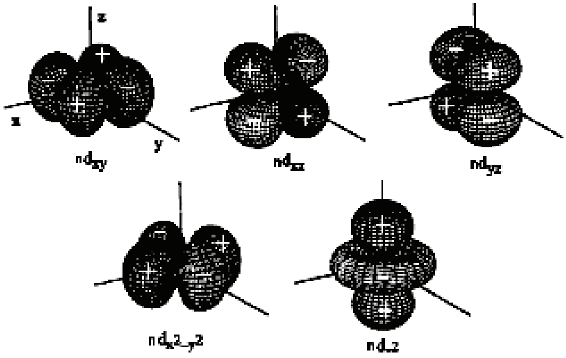


Figure VII-82: 3 atomic orbitals.

We note that only the AOs $3d_{z^2}$ and $3d_{x^2-y^2}$ are pointing in the direction of the ligands and consequently will be useful in the construction of hybrid atomic orbitals.

We can consider two types of octahedral hybridization involving the d orbitals.

The *inner orbital complexes* and the *outer orbital complexes*. These two types correspond to the following hybridizations.

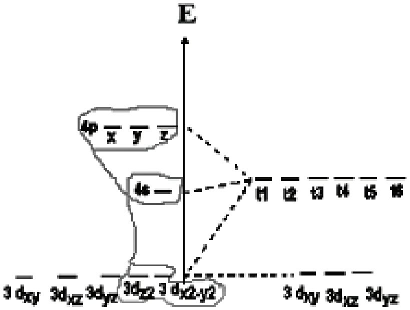


Figure VII-83: d^2sp^3 hybridization diagram.

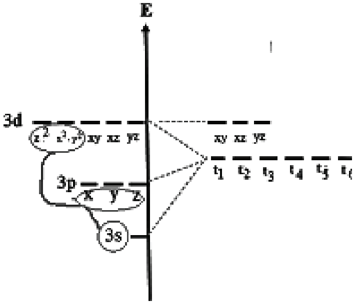


Figure VII-84: sp^3d^2 hybridization diagram.

d^2sp^3 or sp^3d^2 hybridization both lead to the same spatial disposition for the hybrid orbitals, that is, to the octahedral disposition given in **Fig. VII-85**.

Inner orbital complexes

The hybridization is then of the d^2sp^3 type.

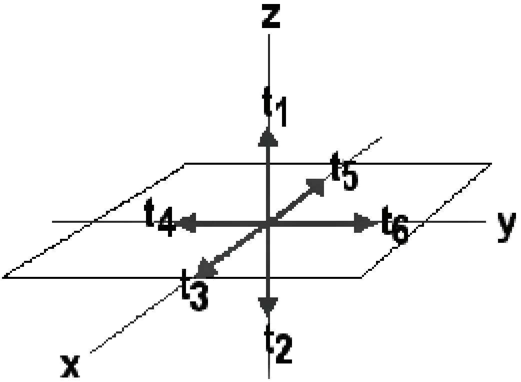


Figure VII-85: Coordination octahedron.

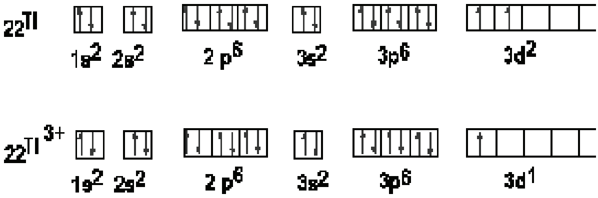
In order to understand this type of hybridization, see **Fig. VII-83**.In this type of hybridization, 2 d orbitals, 1 s orbital, and 3 p orbitals are mixed. The d_{z^2} and $d_{x^2-y^2}$ orbitals belong to the shell n-1 with respect to the outermost shell, and the hybridization is said to be “with the inner orbitals”. These orbitals are chosen from the 5 possible d orbitals because they “point” towards the ligands and therefore have a privileged position in the hybridization process.

The directions taken by the hybrids are obviously those of the ligands, forming the coordination octahedron given in **Fig. VII-85**.

Example: $[Ti(H_2O)_6]^{3+}$ complex

In this complex, water is the ligand. The water molecule binds to the central atom via one of its oxygen doublets, as seen in **Fig. VII-86**.

The electronic structures of Ti and its Ti^{3+} ion are as follows



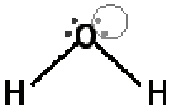
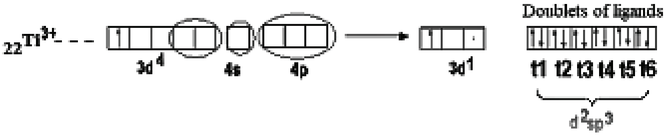


Fig VII-86: Water ligand.

Consider the structure of Ti^{3+}. The d^2sp^3 hybridization will give



where n is the number of unpaired electrons in the d orbitals. In the present case, we have n = 1, which gives a theoretical paramagnetic moment equal to

$$\mu = \mu^\circ\sqrt{1(1+2)} = 1.73\mu^\circ$$

Example: $[Cr(CN)_6]^{3-}$

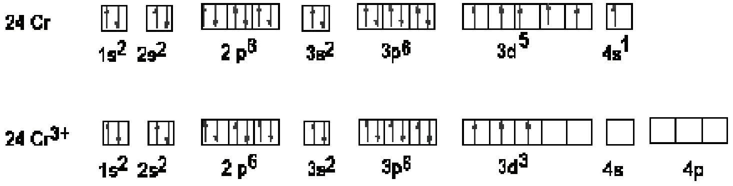
To begin, let us determine the oxidation number of chromium in this ion. If no_{Cr} is the number of oxidation of chromium and no_{CN^-} that of CN^-, then we must have

$$no_{Cr} + 6no_{CN^-} = \text{charge of the ion} = -3$$

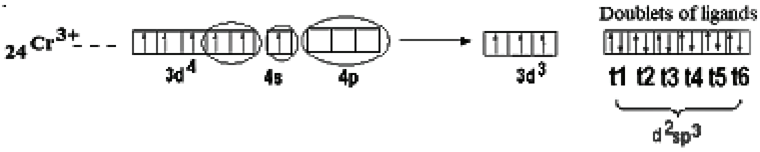
As CN^- carries a negative charge, its oxidation number is -1. Consequently

$$no_{Cr} - 6 = -3 \text{ then } no_{Cr} = +3$$

The chromium in this ion has an oxidation number of +3 and we have the following configurations



d^2sp^3 hybridization gives:



and the doublets of the ligands can then be placed in the hybrid orbitals. Consequently, the number of unpaired electrons in the d orbitals being 3, it follows that the theoretical paramagnetic moment is equal to

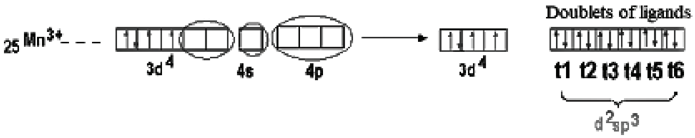
$$\mu = \mu^\circ\sqrt{3(3+2)} = 3.87\mu^\circ$$

Example: $[Mn(CN)_6]K_3$

The experimental paramagnetic moment of the complex $[Mn(CN)_6]K_3$ is equal to 3.18 μ°. Is this value compatible with that of an internal orbital complex? Manganese has the degree of oxidation of +3.

Let us build the electronic structures of Mn

The d^2sp^3 hybridization gives



It has two unpaired electrons in the d AOs and the theoretical paramagnetic moment is therefore

$$\mu = \mu^\circ \sqrt{2(2+2)} = 2.83\mu^\circ$$

This number should be compared to the experimental value 3.18 μ°, which remains within the range of validity. As such, we do have an inner orbital complex.

Outer orbital complexes

Let us now consider the complex $K_3[Mn(Ox)_3],3H_20$ (potassium trioxalato manganate (III)) with an experimental paramagnetic moment equal to 4.81 μ° where Ox represents the ligand oxalate.

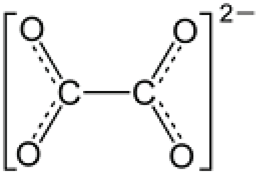


Figure VII-87: Oxalate ligand.

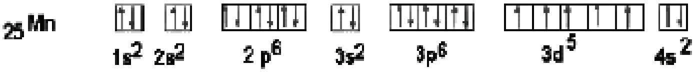
The oxidation number of Ox is -2 and that of K is +1. The oxidation number of Mn is therefore

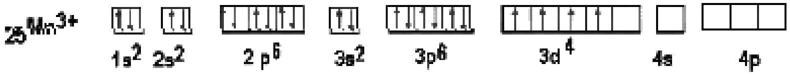
$$no_{Mn} + 3 \times -2 = -3$$

so that

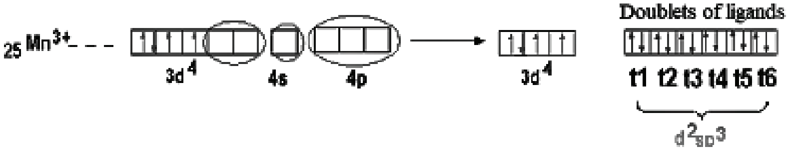
$$no_{Mn} = +3$$

In the first hypothesis, we consider that this complex is described by the model of inner orbitals. Under these conditions, given that Mn has a +3 degree of oxidation, we have





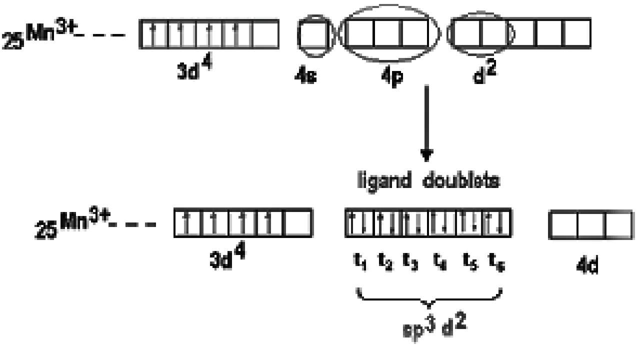
As we saw above, a d²sp³ hybridization would give



With the following theoretical paramagnetic moment

$$\mu = \mu^\circ\sqrt{2(2+2)} = 2.83\mu^\circ$$

This number is very far from the experimental value (4.81 μ°). Therefore we must consider another hypothesis, that of a complex with outer orbitals. In this type of complex, the d orbitals that will be hybridized are outside the outermost shell, hence they are described as an outer orbital complex.



In this type of hybridization, the 4 unpaired electrons remain in their non-hybridized OA d. Consequently, we have

$$\mu = \mu^\circ\sqrt{4(4+2)} = 4.90\mu^\circ$$

which is close to the experimental value.

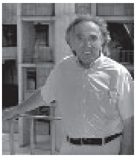
The crystal field theory

Another theory was developed by considering two compounds: manganese (II) oxide (MnO) and copper (I) chloride (CuCl).

Almost at the same time as the previous theory was being developed, the physicists Hans Bethe[24], John Van Vleck[25], and Leslie Orgel[26] proposed another approach called crystal field theory.

H. Bethe

J. van Vleck



L. Orgel

This theory describes the effect of the electric field of surrounding ions on the energy of the valence orbitals of an ion in a crystal. It was developed by considering two compounds: manganese oxide (II) (MnO) and copper chloride (I) (CuCl).

Octahedral crystal field

Consider the manganese ion. Each Mn^{2+} ion is surrounded by 6 O^{2-} ions placed at the points of an octahedron, as shown in **Fig. VII-88**.

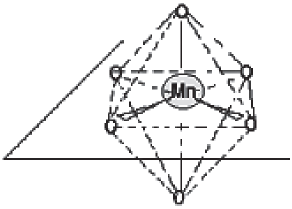


Figure VII-88: Octahedral arrangement in the Mn^{2+} ion.

Now, let us remember the shape of the 3 d atomic orbitals of this central atom.

---

[24] Hans Bethe (1906-2005). American winner of the Nobel Prize in Physics in 1967 for his contribution to the understanding of stellar nucleosynthesis.

[25] John Hasbrouck van Vleck (1899-1980). American physicist known for his fundamental theories on magnetism and the crystal structures of metals. Won the Nobel Prize in Physics in 1977.

[26] Leslie Eleazer Orgel (1927- 2007). British chemist known for his theories on the origin of life.

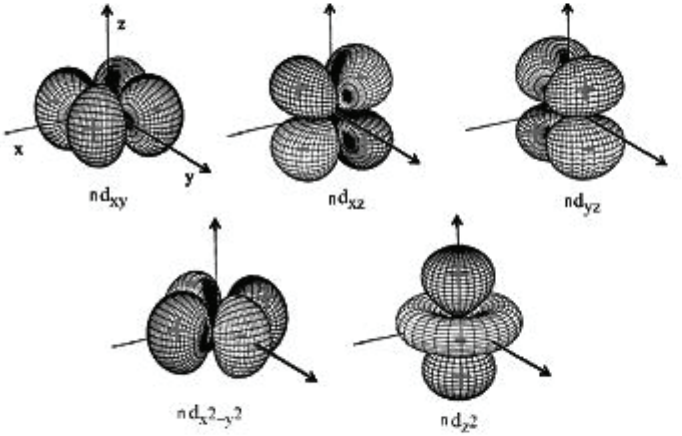


Figure VII-89: The five OA d.

We can see that among these orbitals, 2 are pointing in the direction of the ligands. They will therefore be subject to the action of these ligands more than the other d atomic orbitals.

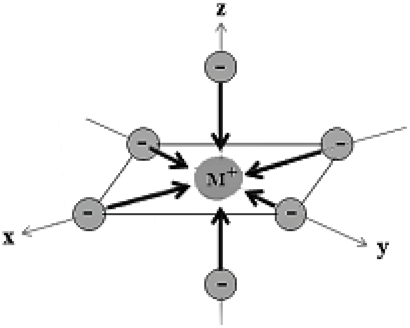


Figure VII-90: Octahedral central atom and ligands.

How do the energies of AOs 4s and 4p of the central ion behave when this ion is enclosed in an Mn0 crystal? The electronic repulsions between the electrons located in these orbitals and those of the six O^{2-} ions will increase their energy. The four p orbitals, while seeing their energy increase, remain energetically degenerate because they all point in the direction of the ligands and are therefore affected in the same way. On the other hand, the repulsions between the electrons of the O^{2-} ions and those of the 3d orbitals of the metal in MnO undergo an energy increase, which differs given their respective situation with respect to the ligands. The five d OAs do not remain degenerate and the two AOs $3d_{z^2}$ and $3d_{x^2\text{-}y^2}$ will be more destabilized than the other d AOs.

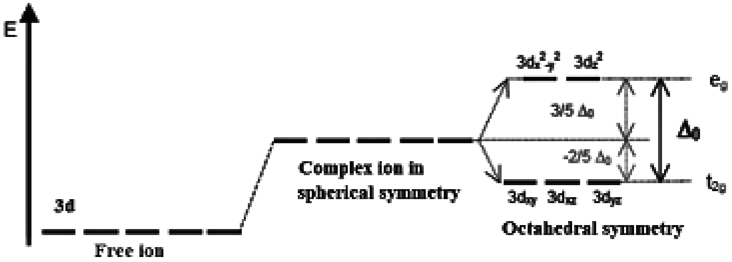


Figure VII-91: Effects of ligands on the energy of OA d of the central ion.

We note the energy e_g of the most destabilized orbitals and that of the least destabilized orbitals t_{2g}. To remember the name of the levels, we make the link between t of t_{2g} and the three levels d_{xy}, d_{yz}, and d_{xz}.

The energy difference between the t_{2g} and e_g orbitals in an octahedral complex is represented by the symbol Δ_0. This burst of energy in previously degenerate orbitals is not random, but depends on the nature of the central metal and the ligands. Thus, for the complex ion $[Ti(H_2O)_6]^{3+}$ we have, for example, $\Delta_0 = 242$ kJ/mol.

Spectrochemical series

The parameter Δ_0 represents the energy difference between the t_{2g} and e_g orbitals, which is the jump that the electrons of the shell d must make to pass to the excited state.

The value of Δ_0 varies depending on the type of ligand. A series of ligands for the same central ion, classified according to their effect on the gap Δ_0, is called a spectrochemical series.

Example: Cr^{3+} ion

Table VII-15 gives the values of the Δ_0 parameter for different ligands of the Cr^{3+} ion.

Table VII-15: Δ_0 parameter for different ligands

Ligand	Cl^-	H_2O	NH_3	CN^-
$\frac{\Delta}{10^6} m^{-1}$	1.36	1.74	2.16	2.63

The link between Δ_0 and the magnetic properties

The magnetic properties can be related to the importance of Δ_0. As an example, let us take the case of the two following complexes $[Fe(CN)_6]^{4-}$ and $[Fe(H_2O)_6]^{2+}$.

First, we calculate the oxidation number of iron in these two complexes.

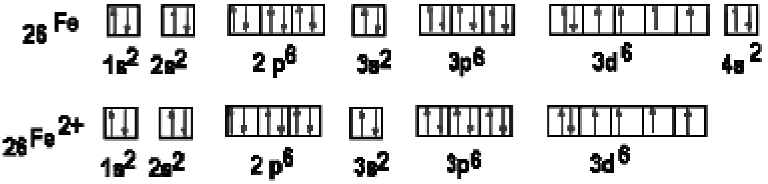
In $[Fe(CN)_6]^{4-}$, the iron is surrounded by six CN^- ions, giving

$$no_{Fe} + 6 \times (-1)) = -4 \quad \text{then} \quad no_{Fe} = +2$$

In $[Fe(H_2O)_6]^{2+}$, the iron is surrounded by six neutral molecules of water H_2O, giving

$$no_{Fe} + 6 \times (0)) = +2 \quad \text{then} \quad no_{Fe} = +2$$

In the two complexes, the electronic configuration of iron is Fe^{2+}.



Now, let us construct the correlation diagram between the d atomic orbitals of the isolated central ion and those of the central ion in the crystal field of ligands.

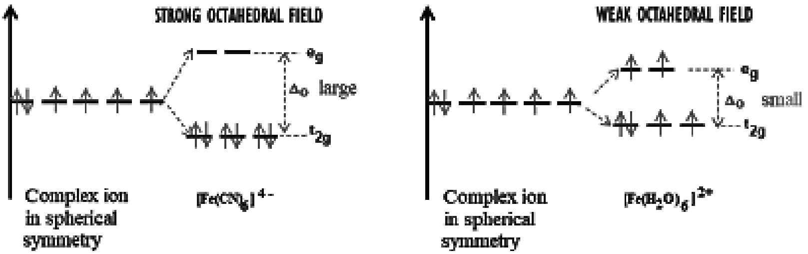


Figure VII-92: Comparison of strong (left) and weak (right) octahedral fields.

In the first case, that of $[Fe(CN)_6]^{4-}$, the crystal field is strong because of the presence of doublets resulting from the CN^- ion. As such, the burst Δ_0 will be large. The six electrons of Fe^{2+} will be arranged in the level t_{2g} because the energy difference in the levels e_g is too large. As a result, there will be no more single electrons in the d orbitals and the paramagnetic moment will therefore be zero.

In the second case, the crystal field will be weak because the doublets of the ligands belong to an H_2O molecule. The difference Δ will be small and the levels t_{2g} and e_g will be energetically close. Hund's rule will therefore apply. We observe a distribution of electrons between these two levels and can therefore observe that the central ion will have four unpaired electrons, which gives this complex a paramagnetic moment that can be evaluated as

$$\mu = \mu^\circ \sqrt{4(4+2)} = 4.9\mu^\circ$$

Indeed, the experiment shows a paramagnetic moment equal to 5 μ°. This method can be extended to other types of complexes.

Tetrahedral field complexes

Now, we consider complexes such as copper chloride. In this complex, 4 Cl^- ions surround the Cu^+ ion, placed at the vertices of a tetrahedron.

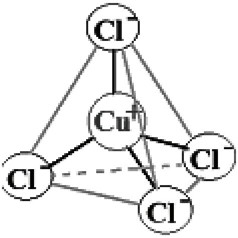


Figure VII-93: Arrangement of ligands in a tetrahedral complex.

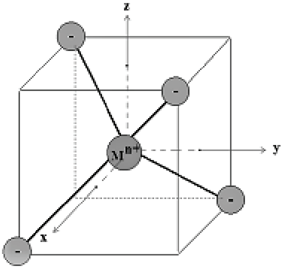


Figure VII-94: orientation of the axes with respect to the ligands.

We can see that, this time, the d_{xy}, d_{xz}, and d_{yz} orbitals point towards the ligands. It is therefore these orbitals that will be most destabilized by the approach.

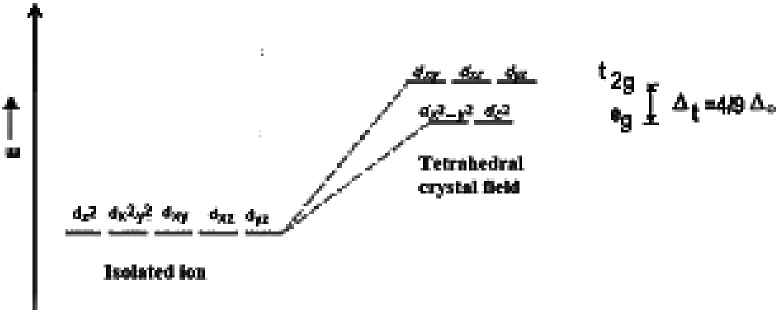


Figure VII-95 : Influence of a tetrahedral field on the d AOs.

Given that, in this type of complex, the number of ligands involved is lower than in the octahedral field, the energy difference Δ_t will be approximately half that of the octahedral field. The levels t_{2g} and e_g will thus be reversed compared to the situation of the octahedral field.

Square planar complexes

The square-planar configuration is mainly encountered for the elements d^8 (Ni^{2+}, Pd^{2-}, and Pt^{2-}). It is obtained from an octahedral complex in which the ligands placed along the z axis are infinitely distant. Thus, the orbitals oriented along the x and y axis are more destabilized than those oriented along the z axis, as shown in **Fig. VII-96**.

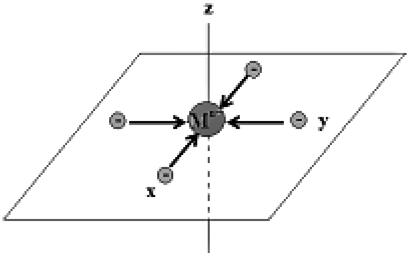


Figure VII-96: Square-planar crystal field.

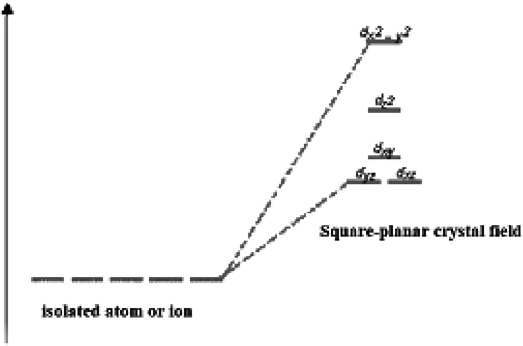


Figure VII-97: Energies of d orbitals in the case of a square-planar crystal field.

This transition from octahedral geometry to square-planar geometry involves a deformation of the octahedron called the Jahn-Teller effect, which is encountered in particular in the ions d^9 (Cu^{2+}) and d^4 (Cr^{2+} and Mn^{3-}), and which causes a new degeneracy removing the d orbitals, thus leading to 4 energy levels.

VII-IV. Extended Systems and the Hückel Lcao Method: Principles

In referring to extended systems we mean molecules or crystals with a large number of atoms. We shall limit our study to that of conjugated polyenes for which quantum processing is relatively easy.

We saw in the examples of the previous chapter that the molecular orbitals of an organic molecule can be classified into two categories: molecular orbitals of σ-type and molecular orbitals of π-type. The π molecular orbitals play a particular role because they are generally placed on the frontier between the occupied molecular orbitals and the vacant molecular orbitals. This is why they are called frontier orbitals and in this position, they play an important role in chemical reactivity. Studying the system formed by these orbitals (π system) gives valuable information, for example on the possibility of atoms being able to receive reagents. Indeed, π electrons are very sensitive to polarization and therefore to disturbances caused by chemical reactions.

This method is called the *linear combination of atomic orbitals* (LCAO) and was developed in the 1930s by Erich Hückel[27].

It applies in particular to molecules with carbon chains having multiple conjugate bonds forming a π system.

E. Hückel

1. The Hamiltonian

The molecular Hamiltonian limited to the π system is written as

$$\mathbf{H}_\pi = \sum_{i=1}^{n_\pi} \mathbf{H}_{eff}(i)$$

where $\mathbf{H}_{\text{eff}}$ (i) is a Hamiltonian that incorporates the repulsion effects of the π electrons statistically, without specifying the manner. Therefore, there is no explicit form of $\mathbf{H}_{\text{eff}}$ (i).

2. Energy of state i

We shall use the Dirac notation discussed in Chapter VI.

Let us consider a stationary state $|\phi_i>$ of the electron centered on an atom constituting the polyene obeying the equation with the eigenvalues

$$\mathbf{H}_{eff}(i)|\varphi_i\rangle = e_i|\varphi_i\rangle$$

where e_i is the energy of the electron i. This is, for example, the energy of an electron in a $2p_z$ orbital.

3. Molecular state

Let us assume by hypothesis that the molecular state $|\Psi>$ is a linear combination of the atomic eigenstates represented by $|\phi_r>$ according to the

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[27] Erich Hückel (1896-1980). German physicist and chemist. He is mainly known for two major contributions: the Debye-Hückel theory on electrolytic solutions and the Hückel method of calculating molecular orbitals by approximation.

principles of the LCAO method that we saw in Chapter VI with the molecular ion hydrogen. Thus

$$|\Psi\rangle = \sum_{r=1}^{n_\pi} C_r|\varphi_r\rangle$$

4. Molecular energy

This molecular state is of course approximate and therefore cannot be claimed to be a solution to the Schrödinger equation. Thus, we are led to define an average value for the energy of the system π so that

$$\langle E\rangle = \frac{\langle\Psi|\mathbf{H}_{eff}\big|\,\Psi\big\rangle}{\langle\Psi|\Psi\rangle}$$

5. Variational method

Let us now apply the variational method to energy by saying that the energy of the system must be minimal compared to the coefficients C_r of the linear combination. That is

$$\begin{cases} \dfrac{\partial\langle E\rangle}{\partial C_1} = 0 \\ \dfrac{\partial\langle E\rangle}{\partial C_2} = 0 \\ \ldots \\ \dfrac{\partial\langle E\rangle}{\partial C_{n_\pi}} = 0 \end{cases}$$

Furthermore, we define the Coulomb integral α by

$$\alpha = \langle\varphi_r|\mathbf{H}_{eff}\big|\,\varphi_r\big\rangle \text{ whatever r may be}$$

and the exchange integral β by

$$\beta_{rs} = \langle\varphi_r|\mathbf{H}_{eff}\big|\,\varphi_s\big\rangle = \beta \text{ for } s = r \pm 1$$

Writing that

$$0 = \langle \varphi_r | \mathbf{H}_{eff} \big| \, \varphi_s \big\rangle \text{ for s} \neq \text{r} \pm 1$$

and the overlap integral S

$$S = \delta_{rs} \qquad \text{(VII-58)}$$

one obtains the following secular equations

$$\begin{cases} C_1(\alpha - \langle E \rangle) + C_2\beta + \ldots \qquad = 0 \\ C_1\beta + C_2(\alpha - \langle E \rangle) + C_3\beta \ldots = 0 \\ \ldots \\ \ldots \quad C_{n_\pi - 1}\beta + C_{n_\pi}(\alpha - \langle E \rangle) = 0 \end{cases}$$

the resolution of which supposes that the secular determinant must be equal to zero

$$\begin{bmatrix} (\alpha - \langle E \rangle) & \beta & 0 & \ldots \\ \beta & (\alpha - \langle E \rangle) & \beta & \ldots \\ \ldots & \ldots & \ldots & \ldots \\ \ldots & 0 & \beta & (\alpha - \langle E \rangle) \end{bmatrix} = 0$$

one then obtains the energies $\langle E \rangle_1$, $\langle E \rangle_2$, ... $\langle E \rangle_{n\pi}$ corresponding to the molecular states

$$\big| \, \Psi \big\rangle_i = \sum C_{ir} \big| \, \varphi_r \big\rangle$$

6. Applications

a. Ethylene

The formula of ethylene is given in **Fig. VII-98**. Each carbon atom has a $2p_z$ AO, which interacts with that of the other atom and gives a π-system.

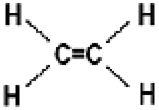


Figure VII-98: Formula of ethylene.

The secular equation of this system are

$$\begin{cases} C_1(\alpha - \langle E \rangle) + C_2\beta = 0 \\ C_1\beta + C_2(\alpha - \langle E \rangle) = 0 \end{cases}$$

and the secular determinant takes the form

$$\begin{bmatrix} (\alpha - \langle E \rangle) & \beta \\ \beta & (\alpha - \langle E \rangle) \end{bmatrix} = 0$$

To simplify the writing, we divide the whole expression by β. The expression thus becomes

$$\begin{bmatrix} \dfrac{(\alpha - \langle E \rangle)}{\beta} & 1 \\ 1 & \dfrac{(\alpha - \langle E \rangle)}{\beta} \end{bmatrix} = 0$$

Now, let us put

$$x = \frac{(\alpha - \langle E \rangle)}{\beta}$$

we obtain

$$\begin{bmatrix} x & 1 \\ 1 & x \end{bmatrix} = 0$$

This determinant has two solutions

$$x = +1 \text{ and } x = -1$$

The coefficients can then be determined from the secular equations

$$C_1(\alpha - \langle E \rangle) + C_2\beta = C_1 x + C_2 = 0$$

For the solution x = -1, we obtain

$$C_1(-1) + C_2 = 0 \quad \text{that is: } C_1 = C_2$$

Taking into account the condition of normalization

$$\langle \Psi | \Psi \rangle = 1$$

we may write

$$C_1^2\langle \varphi_1 | \varphi_1 \rangle + C_2^2\langle \varphi_2 | \varphi_2 \rangle + 2C_1C_2\langle \varphi_1 | \varphi_2 \rangle = 1$$

Taking into account the rule (VII-58) concerning the overlap integral, we have

$$C_1^2 + C_2^2 = 1$$

or, because $C_1 = C_2$, we get

$$2C_1^2 = 1 \quad \text{i.e.} \quad C_1 = \frac{1}{\sqrt{2}}$$

As such, as an expression for the lower energy state, we have

$$|\,\Psi\rangle_1 = \frac{1}{\sqrt{2}}\left(|\,\varphi_1\rangle + |\,\varphi_2\rangle\right)$$

The $2p_z$ orbitals are perpendicular to the plane of the molecule and each is containing 1 electron. These electrons will then be found in the molecular orbital π as shown by the diagram given in **Fig. VII-99**.

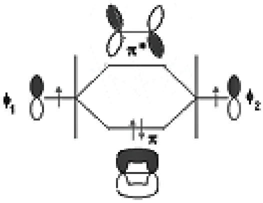


Figure VII-99: Ethylene π MOs.

π charges

By definition, the π-charge carried by a given atom is the sum of the squares of the coefficients of the molecular orbitals corresponding to this atom.

For the <u>ground state</u>, we have the situation described in **Fig. VII-100**.

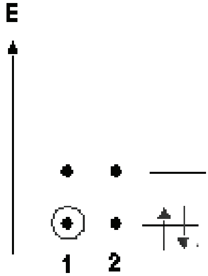


Figure VII-100: Ground state calculation of π-charge.

The charge on atom 1 = charge on atom 2 = 2 electrons x $(1/\sqrt{2})^2$ = **1**

For the <u>first excited state</u>, we have the situation described in **Fig. VII-101**.

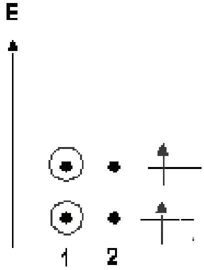


Figure VII-101: excited state calculation of π-charge.

Charge on atom 1 = 1 electron×$(1/\sqrt{2})^2$+1 electron×$(1/\sqrt{2})^2$ = **1**

Charge on atom 2 = 1 electron×$(1/\sqrt{2})^2$+1 electron×$(-1/\sqrt{2})^2$ = **1**

π-bond index

For the bond ij, the sum is extended to the occupied molecular orbitals of the product of the coefficients C_{ki}, C_{kj} of the atoms i and j in the MO k multiplied by the number of electrons of the occupied MO

$$I_{ij} = \sum_k C_{ki} C_{kj} \times 2$$

For the ground state of ethylene, we have

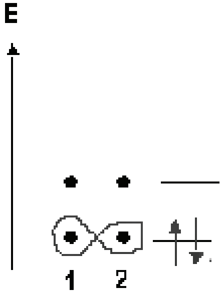


Figure VII-102: Ground state calculation of π-bond index.

$$I_{12} = C_{11} C_{12} \times 2 = \left(\frac{1}{\sqrt{2}}\right)\left(\frac{1}{\sqrt{2}}\right) \times 2 = 1$$

For the 1st excited state of ethylene, we may write

$$I_{12} = C_{11} C_{12} \times 1 + C_{21} C_{22} \times 1 = \left(\frac{1}{\sqrt{2}}\right)\left(\frac{1}{\sqrt{2}}\right) \times 1 + \left(\frac{1}{\sqrt{2}}\right)\left(-\frac{1}{\sqrt{2}}\right) \times 1 = 0$$

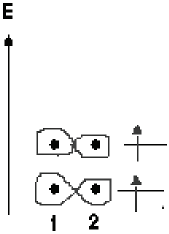


Figure VII-103: 1st excited state calculation of π-bond index.

We can conclude that this molecule dissociates when it is in the 1st excited state.

π transition energy

This is the difference in energy between the ground state and the 1st excited state.

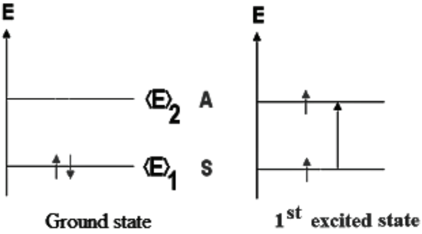


Figure VII-104: π-transition energy for ethylene.

We can see that the energy of the ground state is

$$E_{Fond} = 2 \times \langle E \rangle_1$$

That of the 1st excited state is

$$E_{1ex} = 1 \times \langle E \rangle_1 + 1 \times \langle E \rangle_2$$

The difference in energy between the excited state and the ground state gives us the π-transition energy

$$\Delta E = |E_{1ex} - E_{Fund}| = |1 \times \langle E \rangle_1 + 1 \times \langle E \rangle_2 - 2 \times \langle E \rangle_1|$$

i.e.

$$\Delta E = |E_{1ex} - E_{Fund}| = |\langle E \rangle_2 - \langle E \rangle_1|$$

and

$$\Delta E = |E_{1ex} - E_{Fund}| = |\alpha - \beta - \alpha - \beta| = 2\beta$$

b. Butadiene

Let us continue our study with an examination of butadiene. This molecule presents two configurations: the transoid configuration and the cisoid configuration.

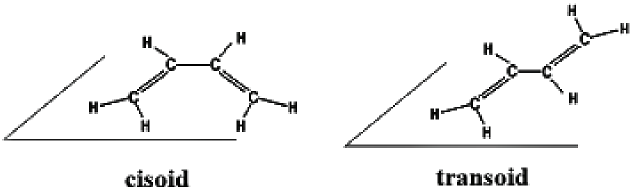
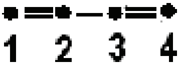


Figure VII-105: Ethylene conformers.

We shall not make a distinction between these two forms and will write polyene in linear form (left) or, more simply, give the atom numbering (right).

$H_2C{=}CH{-}CH{=}CH_2$



There is a relationship between the internuclear distance and the value of the exchange integral. If we consider the exchange integral β of ethylene as a reference, we have for the exchange integrals

$$\beta_{12} = \beta_{34} = \beta \quad \text{and} \quad \beta_{23} = \beta \exp(6.785 - 5.075 \times d_{23})$$

where β_{12} and β_{34} are the exchange integrals between, respectively, atoms 1 and 2 and 3 and 4, whereas d_{23} is the distance between atoms 2 and 3. Then, with d_{23} = 1.47 A, we obtain

$$\beta_{23} = \beta \exp(6.785 - 5.075 \times 1.47) = 0.51\beta$$

Furthermore, the value of the Coulomb integrals and the exchange integrals change with the nature of the atoms involved in the bond. In the following table we give some examples of Coulombic and exchange integral values[28].

Table VII- 16: Coulombic and exchange integrals for various bonds $\alpha_C = \beta_{C=C} = -6.5$ eV

Bond	Coulombic integral	Exchange integral	Bond	Coulombic integral	Exchange integral
Carbon-Carbon	C=C $\alpha_C = \alpha$	Ethylene:β Benzene:0.8β		Nitrated derivatives $\alpha_c = \alpha$ $\alpha_N = \alpha + 1.7\beta$	$\beta_{cN} = 0.6\beta$
Carbon-Oxygen	Carbonyl C=O $\alpha_C = \alpha + 0.2\beta$ $\alpha_O = \alpha + 0.7\beta$	$\beta_{CO} = 1.1\beta$	Carbone-Halogen	Fluoride C-F $\alpha_F = \alpha + 2.7\beta$ Chloride C-Cl	$\beta_{CF} = 0.6\beta$
	Carboxylate, ether, phenol C-O $\alpha_C = \alpha$ $\alpha_O = \alpha + 2\beta$	$\beta_{co} = 0.6\beta$		$\alpha_{Cl} = \alpha + 1.7\beta$ Chloride C-Br $\alpha_{Br} = \alpha + 1.4\beta$	$\beta_{cCl} = 0.6\beta$ $\beta_{cBr} = 0.4\beta$
	Carboxylate O-C=O $\alpha_C = \alpha - 0.7\beta$ $\alpha_O = \alpha - 0.6\beta$	$\beta_{co} = 0.9\beta$	Nitrogen-Oxygen	Group NO_2 $\alpha_N = \alpha + 1.7\beta$ $\alpha_o = \alpha + 0.47\beta$	$\beta_{co} = 0.9\beta$
Carbone-Nitrogen	Pyridine C-N $\alpha_C = \alpha$ $\alpha_N = \alpha + 1.4\beta$ $\alpha_{N_{sp^3}} = \alpha + 1.8\beta$ (aniline)	$\beta_{cN} = 0.6\beta$			

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[28] From A. Julg and O. Julg, Exercices de Chimie Quantique, Dunod, 1967.

Now, let $\beta_{23} = \lambda\beta$. The secular equations become

$$\begin{cases} C_1(\alpha - \langle E \rangle) + C_2\beta = 0 \\ C_1\beta + C_2(\alpha - \langle E \rangle) + C_3\lambda\beta = 0 \\ C_2\lambda\beta + C_3(\alpha - \langle E \rangle) + C_4\beta = 0 \\ C_3\beta + C_4(\alpha - \langle E \rangle) = 0 \end{cases}$$

and the secular determinant is

$$\begin{vmatrix} \alpha - \langle E \rangle & \beta & 0 & 0 \\ \beta & \alpha - \langle E \rangle & \lambda\beta & 0 \\ 0 & \lambda\beta & \alpha - \langle E \rangle & \beta \\ 0 & 0 & \beta & \alpha - \langle E \rangle \end{vmatrix} = 0$$

Dividing the whole expression by β leads to

$$\begin{vmatrix} \dfrac{\alpha - \langle E \rangle}{\beta} & 1 & 0 & 0 \\ 1 & \dfrac{\alpha - \langle E \rangle}{\beta} & \lambda & 0 \\ 0 & \lambda & \dfrac{\alpha - \langle E \rangle}{\beta} & 1 \\ 0 & 0 & 1 & \dfrac{\alpha - \langle E \rangle}{\beta} \end{vmatrix} = 0$$

and by putting

$$x = \frac{\alpha - \langle E \rangle}{\beta}$$

this determinant becomes

$$\begin{vmatrix} x & 1 & 0 & 0 \\ 1 & x & \lambda & 0 \\ 0 & \lambda & x & 1 \\ 0 & 0 & 1 & x \end{vmatrix} = 0$$

To resolve this determinant, we can use the symmetry of the molecule. Consider the cisoid conformer below.

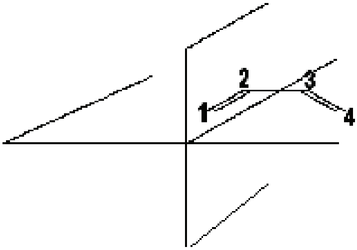

Figure VII-106: Cisoid conformer symmetry.

We consider the median plane of the molecule plane as the plane of symmetry. In relation to this plane, we can consider two types of symmetries:

- symmetrical;
- antisymmetric.

These are the coefficients that will translate the symmetrical or antisymmetric character.

As such, we have

$$\text{Symmetrical solution: } C_1 = C_4 \quad \text{and} \quad C_2 = C_3$$

$$\text{Antisymmetrical solution: } C_1 = -C_4 \quad \text{and} \quad C_2 = -C_3$$

For symmetrical solutions, the secular equations take the form

$$\begin{cases} C_1 x + C_2 = 0 \\ C_1 + C_2 x + C_2 \lambda = 0 \end{cases} \text{so that} \begin{cases} C_1 x + C_2 = 0 \\ C_1 + C_2 (x + \lambda) = 0 \end{cases}$$

Then, the determinant is

$$\begin{vmatrix} x & 1 \\ 1 & x + \lambda \end{vmatrix} = 0 \text{ so that } x(x + \lambda) - 1 = 0$$

i.e.

$$x^2 + \lambda x - 1 = 0$$

This equation admits two solutions

$$x_1 = \frac{-\lambda - \sqrt{\lambda^2 + 4}}{2} = \frac{-0.51 - \sqrt{0.51^2 + 4}}{2} = -1.287$$
$$x_3 = \frac{-\lambda + \sqrt{\lambda^2 + 4}}{2} = \frac{-0.51 + \sqrt{0.51^2 + 4}}{2} = 0.777$$

For antisymmetric solutions, the secular equations take the form

$$\begin{cases} C_1 x + C_2 = 0 \\ C_1 + C_2 x - C_2 \lambda = 0 \end{cases} \quad \text{so that} \begin{cases} C_1 x + C_2 = 0 \\ C_1 + C_2 (x - \lambda) = 0 \end{cases}$$

Then, the determinant is

$$\begin{vmatrix} x & 1 \\ 1 & x - \lambda \end{vmatrix} = 0 \ \text{so that}\ x^2 - \lambda x - 1 = 0$$

This equation admits two solutions

$$x_2 = \frac{-\lambda - \sqrt{\lambda^2 + 4}}{2} = \frac{0.51 - \sqrt{0.51^2 + 4}}{2} = -0.777$$
$$x_4 = \frac{-\lambda + \sqrt{\lambda^2 + 4}}{2} = \frac{-0.51 + \sqrt{0.51^2 + 4}}{2} = 1.287$$

Now, coming back to the energy expressions

$$x_1 = \frac{\alpha - \langle E \rangle_1}{\beta} = -1.287 \Rightarrow \langle E \rangle_1 = \alpha + 1.287\beta$$

$$x_2 = \frac{\alpha - \langle E \rangle_2}{\beta} = -0.777 \Rightarrow \langle E \rangle_2 = \alpha + 0.777\beta$$

$$x_3 = \frac{\alpha - \langle E \rangle_2}{\beta} = 0.777 \Rightarrow \langle E \rangle_3 = \alpha - 0.777\beta$$

$$x_4 = \frac{\alpha - \langle E \rangle_2}{\beta} = 1.287 \Rightarrow \langle E \rangle_4 = \alpha - 1.287\beta$$

These energy levels can be represented with a diagram on which the symmetry of the corresponding molecular orbitals is indicated by S for "symmetric" and A for "antisymmetric".

The corresponding wave functions will be

$$|\Psi_4\rangle = C_1|\varphi_1\rangle - C_2|\varphi_2\rangle + C_2|\varphi_2\rangle - C_1|\varphi_1\rangle$$
$$|\Psi_3\rangle = C_1|\varphi_1\rangle - C_2|\varphi_2\rangle - C_2|\varphi_2\rangle + C_1|\varphi_1\rangle$$
$$|\Psi_2\rangle = C_1|\varphi_1\rangle + C_2|\varphi_2\rangle - C_2|\varphi_2\rangle - C_1|\varphi_1\rangle$$
$$|\Psi_1\rangle = C_1|\varphi_1\rangle + C_2|\varphi_2\rangle + C_2|\varphi_2\rangle + C_1|\varphi_1\rangle$$

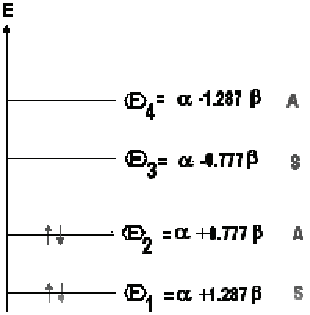

Figure VII-107: Energy levels and symmetries of butadiene π MOs.

Now, let us find the values of the coefficients of these molecular orbitals. For this, we return to the secular equation

$$C_1 x + C_2 = 0 \text{ from which it is deduced } C_1 x = -C_2$$

Then, for the $|\Psi_1>$ state, we shall have

$$C_2 = -C_1(-1.287) = 1.287 C_1$$

In addition, taking into account the normalization condition of the π orbital, one must have

$$C_1^2 + C_2^2 + C_3^2 + C_4^2 = 1$$

hence, taking into account the symmetries of the coefficients, we get

$$2C_1^2 + 2C_2^2 = 1$$

Using the relation obtained above

$$C_2 = 1.287C_1$$

which comes to

$$2C_1^2 + 2(1.287C_1)^2 = 1 \text{ i.e. } 5.3127C_1^2 = 1$$

so that

$$C_1 = \sqrt{\frac{1}{5.3127}} = 0.4339$$

$$C_2 = 1.287C_1 = 1.287 \times 0.4339 = 0.5584$$

Then, the expression of the π-MO wave functions may be found

$$|\Psi_1\rangle = 0.4339|\varphi_1\rangle + 0.5584|\varphi_2\rangle + 0.5584|\varphi_2\rangle + 0.4339|\varphi_1\rangle$$

$$|\Psi_2\rangle = 0.5584|\varphi_1\rangle + 0.4339|\varphi_2\rangle - 0.4339|\varphi_2\rangle - 0.5584|\varphi_1\rangle$$

$$|\Psi_3\rangle = 0.5584|\varphi_1\rangle - 0.4339|\varphi_2\rangle - 0.4339|\varphi_2\rangle + 0.5584|\varphi_1\rangle$$

$$|\Psi_4\rangle = 0.5584|\varphi_1\rangle - 0.4339|\varphi_2\rangle + 0.4339|\varphi_2\rangle - 0.5584|\varphi_1\rangle$$

If we represent the size of the coefficients by the larger or smaller size of the atomic orbitals $2p_z$, we obtain **Fig. VII-108**.

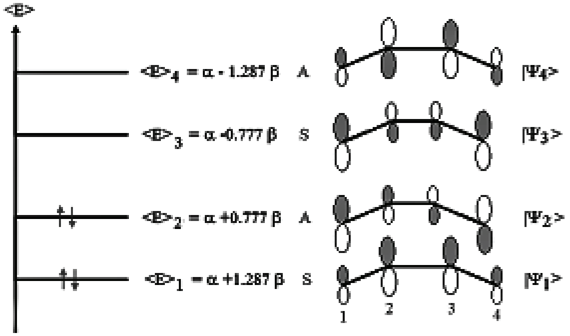

Figure VII-108: Energies and coefficients in the π MOs of butadiene.

Let us find the *π-bond index* or *π-bond order* in the ground state.

The ground state corresponds to the following configuration in which the two doublets π are found in MOs Ψ₁ and Ψ₂. Taking into account the definition of the π-bond index, we have

$$I_{ij} = \sum_k C_{ki} C_{kj} \times 2$$

Then, for the 12 bond of butadiene, we shall have

$$I_{12} = (C_{11}C_{12} + C_{21}C_{22}) \times 2 \; electrons$$

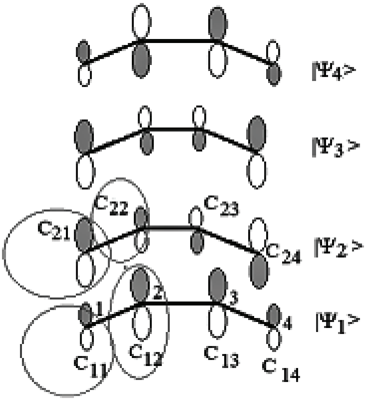

Figure VII-109: Calculation of the bond index π in butadiene.

$$I_{12} = (0.4339 \times 0.5584 + 0.5584 \times 0.4339) \times 2 \; = \mathbf{0,969}$$

Similarly, for the 23 bond

$$I_{23} = (C_{12}C_{13} + C_{22}C_{23}) \times 2 \; electrons$$

$$I_{23} = (0.5584 \times 0.5584 + 0.4339 \times -0.4339) \times 2 \; = \mathbf{0.247}$$

π-charges in the ground state

We can also determine the charges carried by each atom. Thus, we have

$$q_i = 2e \sum_{j-1}^{N_{occ}} (C_{ij})^2$$

where N_{occ} represents the number of occupied MOs. For butadiene, for atoms 1 and 4, we have

$$q_1 = 2\sum_{j=1}^{2}(C_{j1})^2 =$$

$$2 \times \left((C_{11})^2 + (C_{21})^2\right)$$

$$2 \times \left((0,4339)^2 + (0,5584)^2\right) = 1 = q_4$$

Similarly, for atoms 2 and 2

$$q_2 = 2\sum_{j=1}^{2}(C_{j2})^2 =$$

$$2 \times \left((C_{12})^2 + (C_{22})^2\right) =$$

$$2 \times \left((0.5584)^2 + (0.4339)^2\right) = 1 = q_3$$

Transition π-energy

This is the energy that must be supplied to the molecule to move an electron from the highest occupied MO (HOMO) to the lowest unoccupied MO (LUMO). We can see that the energy of the ground state is

$$E_{Ground} = 2 \times (\langle E\rangle_1 + \langle E\rangle_2)$$

and that of the 1st excited state is

$$E_{1ex} = 2 \times \langle E\rangle_1 + 1 \times \langle E\rangle_2 + 1 \times \langle E\rangle_3$$

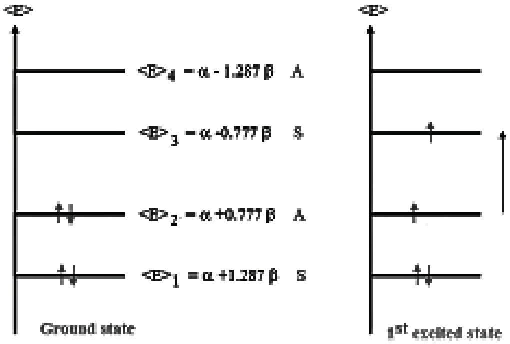

Figure VII-110: Transition energy in butadiene.

The energy difference between the excited state and the ground state gives us the transition π-energy

$$\Delta E = |E_{1ex} - E_{Fond}| = |2 \times \langle E \rangle_1 + 1 \times \langle E \rangle_2 + 1 \times \langle E \rangle_3 - 2 \times (\langle E \rangle_1 + \langle E \rangle_2)|$$

i.e.

$$\Delta E = |E_{1ex} - E_{ground}| = |\langle E \rangle_3 - \langle E \rangle_2|$$

or

$$\Delta E_{But} = |E_{1ex} - E_{Fond}| = |\alpha + 0.777\beta - \alpha + 0.777\beta| = 1.554\beta$$

We can compare this energy to that obtained for ethylene

$$\Delta E_{Eth} = 2\beta$$

The difference in energy is lower for butadiene than for ethylene with a value of 0.46 β. The consequence is that radiation absorbed during transition will have a longer wavelength for butadiene. This is called the *bathochromic effect*.

To evaluate this transition energy and make it coincide with the experimental energy, we must multiply the expression ΔE by an arbitrary factor of 0.54.

As such, the transition energy of butadiene will be

$$\Delta E_{But} = 1.554\beta \times 0.54 = 0.84\beta$$

but β≃-6.5 eV, which gives a transition energy equal to

$$\Delta E_{But} = 1.554 \times 6.5 \times 0.54 = 5.45e.V$$

We can then evaluate the wavelength of the radiation absorbed during this transition

$$\lambda_{But} = \frac{hc}{\Delta E_{But}} = \frac{6,6 \times 10^{-34} \times 3 \times 10^{8}}{5,45 \times 1.6 \times 10^{-19}} = 227nm$$

Experimentation gives a result of λ_{but} (Exp} = 214 nm.

We should note here[29] several intuitive approaches of the coefficients of π OM of linear polyenes, which are compared to the normal vibration modes of a lead string.

VII-V. Tutorial for Chapter VII

T-VII-1. The Lewis method

1) Recall the principles of the Lewis method.

ANSWER

The chemical bond is the realization of a bond between two atoms through the pooling of two electrons. This convention originates with Lewis and remains the basis of descriptions of the chemical bond. Even modern theories of chemical bonding (molecular orbital theory and VSEPR method) use this particular concept of a chemical bond resulting from a shared pair of electrons. The Lewis method is founded on what is known as the Lewis rule.

The atoms acquire the outermost electronic structure of a rare gas by bonding.

2) Where possible, give the Lewis electronic structures of the following molecules using the systematic method. Indicate cases where there is mesomerism.

$CH_4, C_2H_4, SnCl_2, BeCl_2, BF_3, SO_2, SiF_4, NH_4^+, H_3O^+, POF_3, SO_4^{2-}, H_2O, Cl_2O, XeF_4$

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[29] J-M. Capon, P. Blaise, and O. Henri-Rousseau, "Comparison between a classical system with n degrees of freedom: normal modes of vibration of a leaded rope and molecular orbitals of a linear polyene (in French)", l'Actualité Chimique, Sept. 1981, p. 33.
A. Benzaza, P. Blaise, O. Henri-Rousseau, and F. Texier, "Significance and origin of the signs and relative magnitudes of atomic coefficients in π molecular orbitals of unsaturated small molecules common in organic chemistry", Bull. Soc. Chim. Fr, 3-4, 1982. I-138.
B. Boulil, P. Blaise, and O. Henri-Rousseau "An intuitive approach to the relative magnitude of the atomic coefficients in the π molecular orbitals of butadiene", J. Chem. Educ., 58, 1981, p.29-31.

Data: Systematic method

Table VII- T-1: Systematic method

Molecule	Atoms	Electrons	Outermost shell	Bonding	Non bonding	Bonding	Non bonding	Representation
		Lewis rule	electrons	electrons	electrons	doublets	doublets	
		A	B	$C = A - B$	$B - C$	$\frac{C}{2}$	$\frac{B-C}{2}$	

ANSWER

We shall use the systematic method, which counts the binding electrons and the non-binding electrons in the molecule under the Lewis rule. The systematic method is summed up in the tables.

Table VII-T-2: Lewis systematic method for CH_4

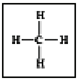
Molecule	Atoms	Electrons	Outermostshell	Bonding	Non bonding	Bonding	Non bonding	Representation
		Lewis rule	electrons	electrons	electrons	doublets	doublets	
		A	B	$C = A - B$	$B - C$	$\frac{C}{2}$	$\frac{B-C}{2}$	
CH_4	$1C$	$1 \times 8 = 8$	$1 \times 4 = 4$					
	$4H$	$4 \times 2 = 8$	$4 \times 1 = 4$					
		$Tot = 16$	$Tot = 8$	$16 - 8 = 8$	$8 - 8 = 0$	$\frac{8}{2} = 4$	0	

Table VII-T-3: Lewis systematic method for C_2H_4

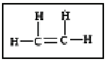
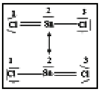
Molecule	Atoms	Electrons	Outermostshell	Bonding	Non bonding	Bonding	Non bonding	Representation
		Lewis rule	electrons	electrons	electrons	doublets	doublets	
		A	B	$C = A - B$	$B - C$	$\frac{C}{2}$	$\frac{B-C}{2}$	
CH_4	$2C$	$2 \times 8 = 16$	$2 \times 4 = 8$					
	$4H$	$4 \times 2 = 8$	$4 \times 1 = 4$					
		$Tot = 24$	$Tot = 12$	$24 - 12 = 12$	12-12=0	$\frac{12}{2} = 6$	0	

Table VII-T-4: Lewis systematic method for SnC_{l2}

Molecule	Atoms	Electrons Lewis rule A	Outermost shell electrons B	Bonding electrons $C = A - B$	Non bonding electrons $B - C$	Bonding doublets $\frac{C}{2}$	Non bonding doublets $\frac{B-C}{2}$	Representation
$SnCl_2$	$1Sn$ $2Cl$	$1 \times 8 = 8$ $2 \times 8 = 16$ $Tot = 24$	$1 \times 4 = 4$ $2 \times 7 = 14$ $Tot = 18$	$24 - 18 = 6$	$18 - 6 = 12$	$\frac{6}{2} = 3$	$\frac{12}{2} = 6$	

The double arrow means that the Lewis structure is intermediate between two limit structures. This characterizes *mesomerism*.

The binding electrons are delocalized on the whole molecule. This suggests that the bonds 12 and 23 are of equal length and intermediate between a single and a double bond (1.42 Å), as shown in **Fig. VII-T1**.

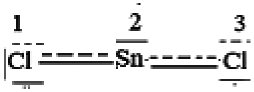


Figure VII-T-1: Resonance form of $SnCl_2$.

The dotted lines signify that the doublets are delocalized.

Table VII-T-5: Lewis systematic method for $BeCl_2$. ($*$) As an exception to the octet rule, beryllium needs only 4 electrons on its outermost shell instead of 8 to verify the Lewis rule

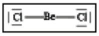
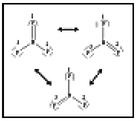
Molecule	Atoms	Electrons Lewis rule A	Outermost shell electrons B	Bonding electrons $C = A - B$	Non bonding electrons $B - C$	Bonding doublets $\frac{C}{2}$	Non bonding doublets $\frac{B-C}{2}$	Representation
$BeCl_2$	$1Be$ $2Cl$	$1 \times 4^{(*)} = 4$ $2 \times 8 = 16$ $Tot = 20$	$1 \times 2 = 2$ $2 \times 7 = 14$ $Tot = 16$	$20 - 16 = 4$	$16 - 4 = 12$	$\frac{4}{2} = 2$	$\frac{12}{2} = 6$	

Table VII-T-6: Lewis systematic method for BF_3

Molecule	Atoms	Electrons Lewis rule	Outermostshell electrons	Bonding electrons	Non bonding electrons	Bonding doublets	Non bonding doublets	Representation
		A	B	$C = A - B$	$B - C$	$\frac{C}{2}$	$\frac{B-C}{2}$	
BF_3	$1B$ $3F$	$1 \times 8 = 8$ $3 \times 8 = 24$ $Tot = 32$	$1 \times 3 = 3$ $3 \times 7 = 21$ $Tot = 24$	$32 - 24 = 8$	$24 - 8 = 16$	$\frac{8}{2} = 4$	$\frac{16}{2} = 8$	

BF_3 is another example of mesomerism. The three BF bonds are undergoing mesomerism. One of their bonding doublets is delocalized on the whole molecule, such as the three BF bonds, which are of equal length and intermediate between a single and a double bond BF, as shown in **Fig. VII-T-2**.

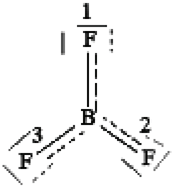
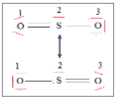


Figure VII-T-2: Resonance form of BF_3.

Table VII-T-7: Lewis systematic method for SO_2

Molecule	Atoms	Electrons Lewis rule A	Outermost shell electrons B	Bonding electrons $C = A - B$	Non bonding electrons $B - C$	Bonding doublets $\frac{C}{2}$	Non bonding doublets $\frac{B-C}{2}$	Representation
SO_2	$1S$ $2O$	$1 \times 8 = 8$ $2 \times 8 = 16$ $Tot = 24$	$1 \times 6 = 6$ $2 \times 6 = 12$ $Tot = 18$	$24 - 18$ $= 6$	$18 - 6$ $= 12$	$\frac{6}{2} = 3$	$\frac{12}{2} = 6$	

Mesomerism is also present here. The two bonds SO are intermediate between a simple and a double bond and are of equal length.

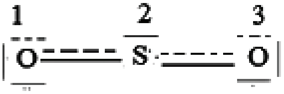


Figure VII-T-3: Resonance form of SO_2.

Table VII-T-8: Lewis systematic method for SiF_4

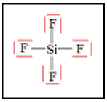
Molecule	Atoms	Electrons Lewis rule A	Outermost shell electrons B	Bonding electrons $C = A - B$	Non bonding electrons $B - C$	Bonding doublets $\frac{C}{2}$	Non bonding doublets $\frac{B-C}{2}$	Representation
SiF_4	$1Si$ $4F$	$1 \times 8 = 8$ $4 \times 8 = 32$ $Tot = 40$	$1 \times 4 = 4$ $4 \times 7 = 28$ $Tot = 32$	$40 - 32$ $= 8$	$32 - 8$ $= 24$	$\frac{8}{2} = 4$	$\frac{24}{2} = 12$	

Table VII-T-9: Lewis systematic method for NH_4^+. (*) we substract an electron for the ion +

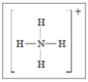
Molecule	Atoms	Electrons	Outermostshell	Bonding	Non bonding	Bonding	Non bonding	Representation
		Lewis rule	electrons	electrons	electrons	doublets	doublets	
		A	B	$C = A - B$	$B - C$	$\frac{C}{2}$	$\frac{B-C}{2}$	
NH_4^+	$1N$	$1 \times 8 = 8$	$1 \times 5 = 5$					
	$4H$	$4 \times 2 = 8$	$4 \times 1 - 1^{(*)} = 3$					
		$Tot = 16$	$Tot = 8$	$16 - 8 = 8$	$8 - 8 = 0$	$\frac{8}{2} = 4$	0	

Table VII-T-10: Lewis systematic method for H_3O^+

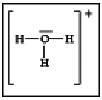
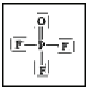
Molecule	Atoms	Electrons	Outermostshell	Bonding	Non bonding	Bonding	Non bonding	Representation
		Lewis rule	electrons	electrons	electrons	doublets	doublets	
		A	B	$C = A - B$	$B - C$	$\frac{C}{2}$	$\frac{B-C}{2}$	
H_3O^+	$1O$	$1 \times 8 = 8$	$1 \times 6 = 6$					
	$3H$	$3 \times 2 = 8$	$3 \times 1 - 1 = 2$					
		$Tot = 14$	$Tot = 8$	$14 - 8 = 6$	$8 - 6 = 2$	$\frac{6}{2} = 3$	$\frac{2}{2} = 1$	

Table VII-T-11: Lewis systematic method for POF_3

Molecule	Atoms	Electrons Lewis rule A	Outermost shell electrons B	Bonding electrons $C = A - B$	Non bonding electrons $B - C$	Bonding doublets $\frac{C}{2}$	Non bonding doublets $\frac{B-C}{2}$	Representation
POF_3	$1P$	$1 \times 10^{(*)} = 10$	$1 \times 5 = 5$					
	$1O$	$1 \times 8 = 8$	$1 \times 6 = 6$					
	$3F$	$3 \times 8 = 24$	$3 \times 7 = 21$					
		$Tot = 42$	$Tot = 32$	$42 - 32 = 10$	$32 - 10 = 22$	$\frac{10}{2} = 5$	$\frac{22}{2} = 11$	

Phosphorus presents *hypervalence*. The Lewis rule states that the number of electrons saturating its outermost shell is 10 and the octet rule is not satisfied.

Table VII-T-12: Lewis systematic method for SO_4^{2-}

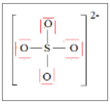
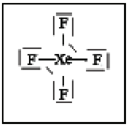
Molecule	Atoms	Electrons Lewis rule A	Outermost shell electrons B	Bonding electrons $C = A - B$	Non bonding electrons $B - C$	Bonding doublets $\frac{C}{2}$	Non bonding doublets $\frac{B-C}{2}$	Representation
SO_4^{2-}	$1S$	$1 \times 8 = 8$	$1 \times 6 = 6$					
	$4O$	$4 \times 8 = 32$	$4 \times 6 + 2 = 26$					
		$Tot = 40$	$Tot = 32$	$40 - 32 = 8$	$32 - 8 = 24$	$\frac{8}{2} = 4$	$\frac{24}{2} = 12$	

Table VII-T-13: Lewis systematic method for XeF_4

Molecule	Atoms	Electrons Lewis rule	Outermost shell electrons	Bonding electrons	Non bonding electrons	Bonding doublets	Non bonding doublets	Representation
		A	B	$C = A - B$	$B - C$	$\frac{C}{2}$	$\frac{B-C}{2}$	
XeF_4	1Xe	$1 \times 12^{(*)} = 12$	$1 \times 8 = 8$					
	4F	$4 \times 8 = 32$	$4 \times 7 = 28$					
		Tot = 44	Tot = 36	$44 - 36 = 8$	$36 - 8 = 28$	$\frac{8}{2} = 4$	$\frac{28}{2} = 14$	

(*) The number of saturating electrons on the outermost shell in the case of xenon is 12. The hypervalence Lewis rule is then 12. This is another exception to the octet rule.

3) Calculate the formal charges of the atoms in the SO_4^{2-} ion.
Data:

$$f_X = Z - \left(\text{core electrons+Non bonded electrons}\right) - \frac{\text{Bonded electrons}}{2}$$

ANSWER

The systematic method applied to SO_4^{2-} gives the results in **Table VII-T-12**.

Using the equation giving the formal charges, we obtain

$$F_S = 16 - (10 + 0) - (8/2) = +2$$

$$F_0 = 16 - (10 + 6) - \frac{2}{2} = -1$$

Note that the sum of the formal charges is

$$Sum = 1 \times F_S + 4 \times F_0 = +2 + 4 \times -1) = -2$$

The sum of the formal charges is equal to the ion charge.

T-VII-2. The theory of molecular orbitals for diatomic molecules

1) Explain why there is a permutation of the levels σ and π in the diagram of the molecular orbitals for the elements of the 2nd period when we move from oxygen to fluorine.

ANSWER

The difference between these diagrams is related to the gap Δ between the energies of the orbitals s and p in the same atom. The gap Δ is significant when there is strong repulsion between the s and p orbitals of the outermost shells of the same atom, which occurs when there are doublets in the p orbitals. The order of the energy levels is that given by the a priori diagram. This term means that this is the natural order of molecular energy levels.

The difference Δ is small when there is little repulsion between the electrons in the outermost shell of the orbitals s and p, that is to say when there are no electron doublets in the p orbitals. We then use the diagram with configuration interaction. These terms mean that, due to their energetic proximity, there is an interaction between the molecular orbitals σ_{2s} and σ_z, which raises the level of orbital σ_z and lowers that of orbital σ_{2s}. Orbital σ_z then passes over the orbitals π_x and π_y. We say that there is permutation of the levels σ and π.

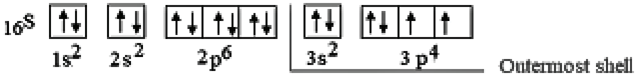
2) Predict the existence and electronic structure of the following diatomic molecules by constructing molecular orbital diagrams:

$_{16}S_2$, $_{15}P_2$, $_{31}Ga_2$, $_{36}Kr_2$.

ANSWER

We must first write the electronic structures of the atoms constituting these molecules.

In the case of $_{16}S_2$, the electronic structure of S is as follows.



If we consider the 3p orbital, we can see that there is an electron doublet and so there will be strong repulsion between this doublet and that present in the 3s orbital, which implies an important gap between the energies of 3s and 3p, allowing an interaction configuration to occur. As such, the order of the natural succession of the energy levels will not be affected and the diagram used will be a priori.

3) Consider the molecule and ions X_2, X_2^-, and X_2^+.

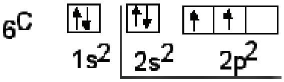
Qualitatively compare the characteristics of each of these entities respectively for the following cases:

X = $_{12}$C; X = $_{14}$N; X = $_{16}$O; X = $_{17}$F

ANSWER

The carbon (C_2) molecule

(i) The electronic configuration of the carbon atom is



(ii) Choice of the orbital basis

{2s, $2p_x$, $2p_y$, $2p_z$}.

(iii) We note that there are no electron doublets in the np orbitals of the outermost shell of the atom C. Hence, the diagram used is of the CI type.

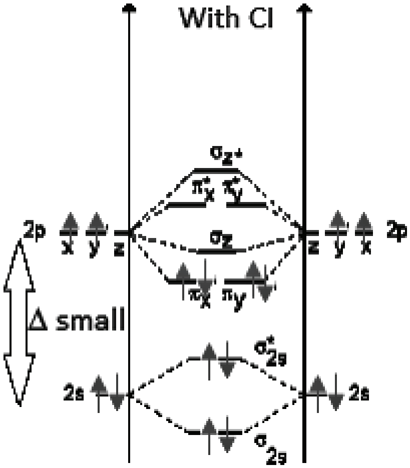


Figure VII-T-4:
MO Correlation diagram for C_2.

(iv) The electrons are placed in the molecular levels starting with the lower energy levels, respecting the Pauli exclusion principle and Hund's rule.

(v) We calculate the bond index

i = (6-2)/2 = 2. (vi) If the bond index is different to zero, then the molecule may exist.

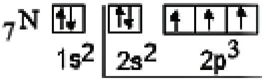
(vii) The molecule is diamagnetic since all electrons in the outermost shell are paired.

(viii) Thus, its electronic configuration is

$$C_2 \ : \sigma_{2s}^2 \sigma_{2s}^{*2} \pi_x^2 \pi_y^2$$

The nitrogen (N_2) molecule

(i) The electronic structure of the nitrogen atom is



(ii) Choice of the orbital basis

{2s, $2p_x$, $2p_y$, $2p_z$}.

(iii) There is a p orbital, which is concerned in the fundamental state. The diagram that must be used is of the CI type because there are unpaired electrons in the 2p orbitals.

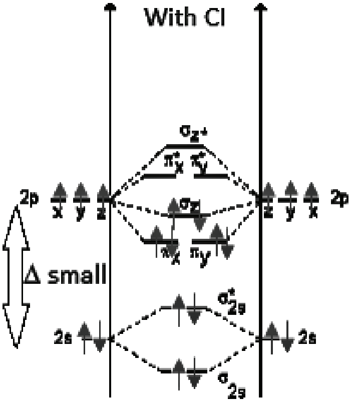


Figure VII-T-5: MO Correlation diagram for N_2.

(iv) The diagram is drawn and the electrons are placed respecting the rules stated above.

We limit ourselves to the outermost shell; the basis is therefore {2s, 2p}. There is an interaction between the 2s and 2p orbitals of each atom. (v) We calculate the bond index i = (8-4)/2=2.

(vi) As such, the molecule can exist.

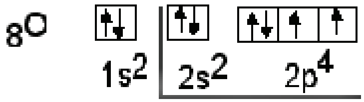
(vii) The molecule is paramagnetic since there are unpaired electrons in the outermost shell.

(viii) Its electronic configuration is

$$N_2\ :\sigma_{2s}^2\sigma_{2s}^{*2}\sigma_z^2\pi_x^2\pi_y^2$$

Oxygen (O_2) molecule

(i) The electronic structure of the oxygen atom is



(ii) Choice of the orbital basis: we limit ourselves to the outermost shell. The basis is therefore

{2s, $2p_x$, $2p_y$, $2p_z$}.

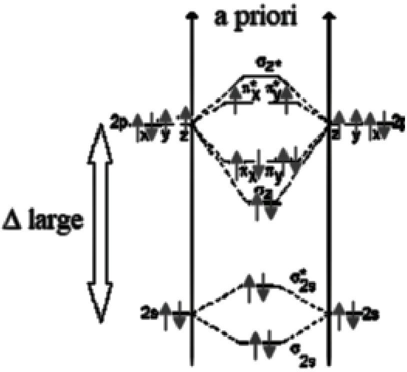


Figure VII-T-6: Correlation diagram for O_2.

(iii) There is a p orbital, which is concerned in the fundamental state. The diagram that must be used is of the a priori type because there is one doublet in the 2p orbitals.

(iv) The diagram is drawn and the electrons are placed respecting the rules stated above. There is an interaction between the 2s and 2p orbitals of each atom.

(v) We calculate the bond index: i = (8-4)/2 = 2.

(vi) As such, the molecule can exist.

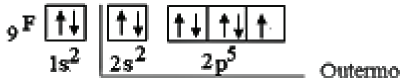
(vii) The molecule is paramagnetic since there are unpaired electrons in the outermost shell.

(viii) Its electronic configuration is

$$O_2\ :\sigma_{2s}^2\sigma_{2s}^{*2}\sigma_z^2\pi_x^2\pi_y^2\pi_x^{*1}\pi_y^{*1}$$

The fluorine (F_2) molecule

(i) The electronic structure of the fluorine atom is



(ii) Choice of the orbital basis

$\{2s, 2p_x, 2p_y, 2p_z\}$.

(iii) There are two paired p orbitals, which are concerned in the fundamental state. The diagram that must be used is of the a priori type because there are doublets in the 2p orbitals. There is an interaction between the 2s and 2p orbitals of each atom.

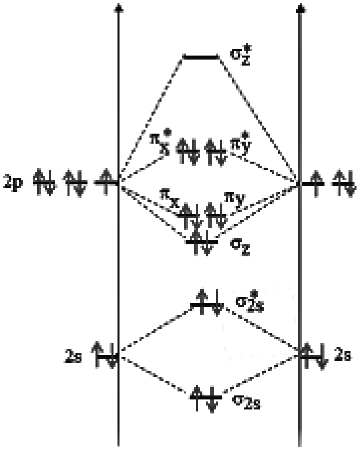


Figure VII-T-7: Correlation diagram for F_2.

(iv) The diagram is drawn and the electrons are placed respecting the rules stated above. (v) We calculate the bond index: i = (8-6)/2=1

(vi) As such, the molecule can exist.

(vii) The molecule is diamagnetic since all the electrons in the outermost shell are paired.

(viii) Its electronic configuration is

$$F_2: \sigma_{2s}^2 \sigma_{2s}^{*2} \sigma_z^2 \pi_x^2 \pi_y^2 \pi_x^{*2} \pi_y^{*2}$$

4) Represent the evolution of a potential curve in the case of a diatomic molecule. What information can we obtain from this curve?

ANSWER

If we consider a diatomic molecule as a system of two masses relied by a spring, it is possible to represent the potential energy of this spring as a function of the distance R between the two nuclei constituting the diatomic molecule.

The length R of the spring may undergo compression or an extension both of which produce an enhancement of the potential energy according to Hooke's law. For a non-deformable spring, the curve obtained is parabolic (in red). The potential is said to be harmonic. In reality, the chemical bond is rather close to a deformable spring and the molecule cannot withstand excessive stretching. The potential is then said to be anharmonic (thick curve).

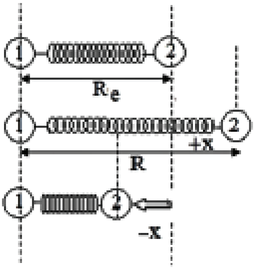


Figure VII-T-8: vibration of a spring.

Looking at this last curve, it is possible to obtain the physical characteristics of the chemical bond: the internuclear equilibrium distance Re, the dissociation energy D_e, and the force constant k_e near the equilibrium distance, which is the second derivative of the potential curve at point $R = R_e$.

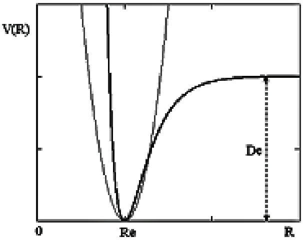
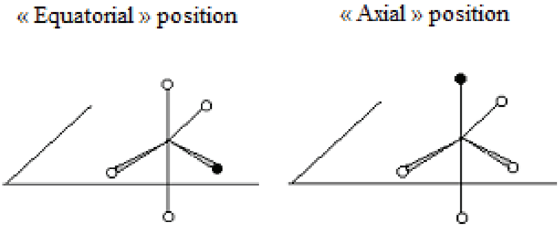


Figure VII-T-9: Potential curves.

T-VII-3. Molecular geometry and the VSEPR method

1) The repulsion energy between 2 identical charges q_i and q_j depends on the distance r_{ij} separating them so that $V_{ij} = Kq_i q_j/r_{ij}$. Calculate the repulsion energy received by a charge (black circle) placed in the situations described by Fig. VII-T9, the distances connecting the peripheral atoms to the central atom being equal to a.



« Equatorial » position

« Axial » position

Figure VII-T-10: Equatorial and axial positions.

ANSWER

Consider the equatorial situation. The "black" atom repulses 2 atoms in the plane making an angle of 120° with respect to it. It also repulses 2 out-of-plane atoms making an angle of 90° to it. We may write the potential energy of the repulsion that the "black" atom is undergoing in the form

$$V_{eq} = 2 \times \frac{e^2}{a\sqrt{3}} + 2\frac{1}{a\sqrt{2}}e^2 = \frac{e^2}{a}\frac{1}{3}\left(3\sqrt{2} + 2\sqrt{3}\right) = 2.57\frac{e^2}{a}$$

Consider the "axial" situation. The "black" atom repulses 3 atoms in the plane and 1 atom in the out-of-plane situation.

$$V_{ax} = 3 \times \frac{e^2}{a\sqrt{2}} + \frac{e^2}{2a} = \frac{e^2}{a}\frac{1}{2}\left(3\sqrt{2} + 1\right) = 2.62\,\frac{e^2}{a}$$

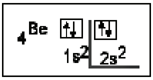
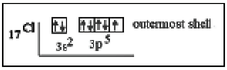
We can see that repulsions with the "black" atom are weaker if it occupies an equatorial situation. This may be an explanation of why free doublets, which, according to the principles of VSEPR, occupy a larger volume than bonding doublets, prefer the equatorial position.

2) Determine the geometries of the following molecules, indicating their type: $BeCl_2$, CS_2, HCN, HNC, BCl_3, H_2CO, $(CO_3)^2$, $SnCl_2$, SO_2, NSF, PCl_5, $(IO_5)^{3-}$, XeO_3F_2, IOF_5, SF_6, XeO_2F_2
Data: $_4Be$, $_{17}Cl$, $_5B$, $_6C$, $_1H$, $_{50}Sn$, $_{16}S$, $_8O$, $_{14}Si$, $_9F$, $_7N$, $_{15}P$, $_{54}Xe$, $_{53}I$, $_{33}As$

ANSWER

Beryllium chloride ($BeCl_2$)

With the central atom Be and the outermost shell of Be has a 2s AO containing 2 electrons.

Central atom: beryllium Be		**2 electrons on the outermost shell= 2**
Ligands:2 chlorine atoms Cl		**1 unpaired electrons ×2 = 2**
		Total: 4 electrons

There is a total of $4e^-$ on the valence shell, which give 2 doublets.

$$4\text{ electrons}\Rightarrow 2\text{ doublets}\left\{\begin{array}{c}\text{Cl gets 1 doublet}\Rightarrow 1\text{charge}\\ \text{Cl gets 1 doublets}\Rightarrow 1\text{charge}\end{array}\right\}2\text{ charges system}$$

Each ligand collects as many doublets as the number of unpaired electrons supplied, i.e. 1 doublet per Cl atom. There are therefore 2 charges on the valence sphere, which repel each other until the equilibrium position of 2 charges of the electrostatic model is reached and we obtain **Fig. VII-T-10**.

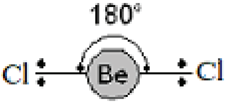
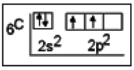
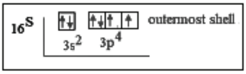


Figure VII-T-11: Geometry of $BeCl_2$.

For this type of molecule we call A the central atom, X_n the peripheral atoms, and E_n the free doublets. Hence, $BeCl_2$ is of the AX_2 type.

Carbon disulfide (CS_2)

The central atom is carbon (C), which supplies its 4 outermost shell electrons to the valence sphere. The ligands are the 2 sulfur atoms. Sulfur has 2 unpaired electrons in its outermost shell and therefore the ligands will supply their 4 unpaired electrons to the valence sphere.

Central atom: Carbon C		4 outermost shell electrons
Ligands:2 sulfur atoms		2 unpaired electrons on the outermost shell ×2
		Total: 8 electrons in the valence shell

In total, there will be 8 electrons on the valence sphere, which regroup into 4 doublets.

$$\text{8 electrons} \Rightarrow \text{4 doublets} \left\{ \begin{array}{l} \text{S gets 2 doublets} \Rightarrow \text{1charge} \\ \\ \text{S gets 2 doublets} \Rightarrow \text{1charge} \end{array} \right\} \text{2 charges system}$$

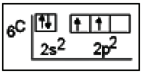
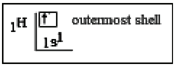
Figure VII-T-12: Geometry of CS_2.

The molecule is linear and of the AX_2 type.

Hydrogen cyanide (HCN)

The central atom is carbon (C) and the ligands are hydrogen (H) and sulfur (S).

$$\text{8 electrons} \Rightarrow \text{4 doublets} \left\{ \begin{array}{l} \text{N gets 3 doublet} \Rightarrow \text{1charge} \\ \text{H gets 1 doublet} \Rightarrow \text{1charge} \end{array} \right\} \text{2 charges system}$$

Central atom: Carbon C		**4 outermost shell electrons=4**
Ligand: Hydrogen atom H		**1 unpaired electrons on the outermost shell ×1 = 1**
Ligand: Nitrogen atom N		**3 unpaired electrons on the outermost shellx1=3**
		Total: 8 electrons in the valence shell

The outermost shell of C is $2s^22p^2$ and contains 4 electrons. H gives 1 unpaired electron and N gives 3 unpaired electrons to the valence shell, giving a total of 8 electrons in 4 doublets.

Each ligand collects as many doublets as the number of unpaired electrons it has supplied, i.e. 1 doublet for H and 2 doublets for C because it has given 2 unpaired electrons. There are therefore 3 charges on the valence sphere that repel each other until the equilibrium position of 2 charges of the electrostatic model is reached and we thus obtain **Fig. VII-T-12**.

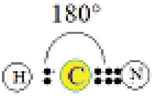
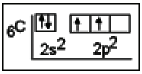


Figure VII-T-13: Geometry of HCN.

For this type of molecule, we call A the central atom, X_n the peripheral atoms, and E_n the free doublets. Hence, HCN is of the AX_2 type.

Hydrogen isocyanide (HNC)

The central atom is nitrogen (N) and the ligands are hydrogen (H) and carbon (C).

Central atom: Nitrogen atom N		**5 electrons on** **the outermost shell= 5**
Ligand atom: Carbon C		**2 unpaired electron of** **the outermost shell electrons=2**
Ligand: Hydrogen atom H		**1 unpaired electrons** **on the outermost shell ×1 = 1**
		Total: 8 electrons **in the valence shell**

The outermost shell of N is $2s^2 2p^3$ and contains 5 electrons. H gives 1 unpaired electron and C gives 2 unpaired electrons to the valence shell, giving a total of 8 electrons in 4 doublets.

Each ligand collects as many doublets as the number of unpaired electrons it has supplied, i.e. 1 doublet for H and 3 doublets for N because it has given 3 unpaired electrons. There are therefore 4 charges on the valence sphere that repel each other until the equilibrium position of 3 charges of the electrostatic model is reached.

$$\text{8 electrons} \Rightarrow \text{4 doublets} \left\{ \begin{array}{c} \text{C gets 2 doublet} \Rightarrow \text{1charge} \\ \text{H gets 1 doublet} \Rightarrow \text{1charge} \\ \text{Free doublet} \Rightarrow \text{1charge} \end{array} \right\} \text{3charges system}$$

The free doublet exerts pressure on the binding doublets, so that the angle between the bonds of NH and NC can be predicted to be less that 120°, as shown in **Fig. VII-T-14**.

The molecule is of the AX_2E type.

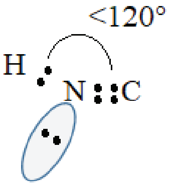
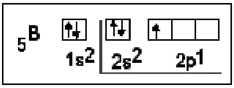


Figure VII-T-14: Geometry of HNC.

Boron trichloride (BCl_3)

Central atom: Boron B		**3 electrons in the outermost shell= 3**
Ligands: 3 Chlorine atoms Cl		**1 unpaired electron in the outermost shell ×3 = 3**
		Total 6 electrons on

Boron has 3 electrons in its outermost shell. The 3 chlorine atoms will therefore supply 3 electrons to the valence sphere. In total, we have 6 electrons grouped into 3 doublets.

$$\text{6 electrons} \Rightarrow \text{3 doublets} \left\{ \begin{array}{l} \text{Cl gets 1doublet} \Rightarrow \text{1charge} \\ \text{Cl gets 1doublet} \Rightarrow \text{1charge} \\ \text{Cl gets 1doublet} \Rightarrow \text{1charge} \end{array} \right\} \text{3 charges system}$$

Each ligand Cl collects as many doublets as it has supplied unpaired electrons. There are therefore 3 charges on the valence sphere, which are distributed at the corners of an equilateral triangle

The molecule is of the AX_3 type and the angle between the BCl bonds is 120°.

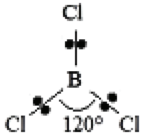
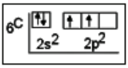
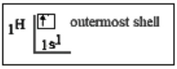
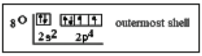


Figure VII-T-15: Geometry of BCl_3.

Methanal (formaldehyde) (H_2CO)

Central atom: Carbon C		**4 electrons in the outermost shell= 4**
Ligands:2 hydrogen atoms H		**1 unpaired electron in the outermost shell ×2 = 2**
Ligand:1 oxygen atom O		**2 unpaired electrons in the outermost shell= 2**
total		**8 electrons on the valence shell**

Carbon has 4 electrons in its outermost shell. The 2 hydrogen atoms will therefore supply 2 electrons to the valence sphere and the oxygen supplies its 2 unpaired electrons

In total, we have 8 electrons grouped into 4 doublets.

$$8\text{ electrons}\Rightarrow 4\text{ doublets}\left\{\begin{array}{c}\text{H gets 1doublet}\Rightarrow\text{1charge}\\ \text{H gets 1doublet}\Rightarrow\text{1charge}\\ \text{O gets 2 doublets}\Rightarrow\text{1charge}\end{array}\right\}\text{3 charges system}$$

Each ligand collects as many doublets as the number of unpaired electrons it has supplied. There are therefore 3 charges on the valence sphere, which are distributed at the corners of an equilateral triangle.

The molecule is of the AX_3 type and the angle between the two CH bonds is less than 120° because of the free doublet repulsion.

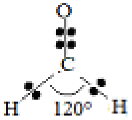
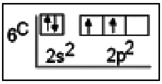


Figure VII-T-16: Geometry of $COCl_2$.

Carbonate ion (CO_3^{2-})

Central atom: Carbon C		4 electrons in the outermostshell= 4
Ligands:3 oxygenatomsO		2 unpaired electrons in the outermostshell x3 = 6
Ion		2 electrons= 2
		total: $4+6+2=12$ electrons

Carbon has 4 electrons in its outermost shell and each of the 3 oxygen atoms will therefore supply 2 electrons, i.e. 6 electrons in total, to the valence sphere. The ion will supply 2 electrons.

In total, we have 12 electrons grouped into 6 doublets.

$$\text{12 electrons} \Rightarrow \text{6 doublets} \left\{ \begin{array}{c} \text{O gets 2doublets} \Rightarrow \text{1charge} \\ \text{O gets 2 doublets} \Rightarrow \text{1charge} \\ \text{O gets 2 doublets} \Rightarrow \text{1charge} \end{array} \right\} \text{3 charges system}$$

Each ligand collects as many doublets as the unpaired electrons it has supplied. There are therefore 3 charges on the valence sphere, which are distributed at the corners of an equilateral triangle.

This molecule is of the AX_3 type and the angle between the two CO bonds is 120°.

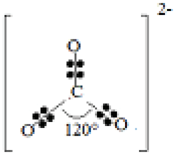
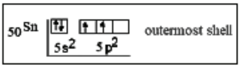
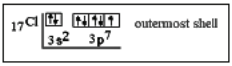


Figure VII-T-17: Geometry of the carbonate ion.

Tin chloride ($SnCl_2$)

Central atom: tin atom Sn		4 electrons in the outermost shell= 4
Ligands:2 Chlorine atoms Cl		1 unpaired electron in the outermost shell ×2 = 2

Tin has 4 electrons in its outermost shell. The 2 chlorine atoms will therefore supply 2 electrons to the valence sphere.

In total, we have 6 electrons grouped into 3 doublets.

$$\text{6 electrons} \Rightarrow \text{3 doublets} \left\{ \begin{array}{c} \text{Cl gets 1doublet} \Rightarrow \text{1charge} \\ \text{Cl gets 1doublet} \Rightarrow \text{1charge} \\ \text{1 free doublet} \Rightarrow \text{1charge} \end{array} \right\} \text{3 charges system}$$

Each ligand Cl collects as many doublets as the number of unpaired electrons it has supplied. There are therefore 3 charges on the valence sphere, which are distributed at the corners of an equilateral triangle.

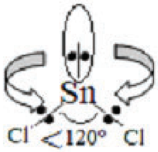
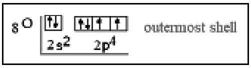
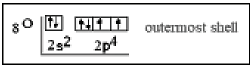


Figure VII-T-18:
Geometry of $SnCl_2$.

The free doublet occupies more space than a binding one and exerts pressure on the two Cl bonds. Thus, the angle ClSnCl will be less than 120°. The type of this molecule is of the AX_2E type

Sulfur dioxide (SO_2)

Central atom: Sulfur atom S		6 electrons in the outermost shell= 6
Ligands:2 oxygen atoms O		2 unpaired electron in the outermost shell ×2 = 4

Central atom: Sulfur atom S		6 electrons in the outermost shell= 6
Ligands:2 oxygen atoms O		2 unpaired electron in the outermost shell ×2 = 4

Sulfur has 6 electrons in its outermost shell. The 2 oxygen atoms will therefore supply 4 unpaired electrons to the valence sphere.

In total, we have 10 electrons grouped into 5 doublets.

$$\text{8 electrons} \Rightarrow \text{4 doublets} \left\{ \begin{array}{c} \text{O gets 2 doublets} \Rightarrow \text{1charge} \\ \text{O gets 2 doublets} \Rightarrow \text{1charge} \\ \text{Free doublet} \Rightarrow \text{1charge} \end{array} \right\} \text{3 charges system}$$

Each ligand O collects as many doublets as the number of unpaired electrons it has supplied. There are therefore 2 charges on the valence sphere, which are distributed at the corners of an equilateral triangle.

The doublets are disposed on the points of an equilateral triangle.

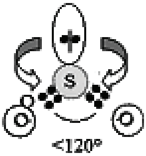
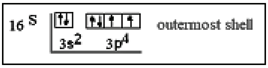


Figure VII-T-19: SO_2 geometry.

However, the free doublet exerts pressure on the two bonds of SO and the angle OSO is less than 120°. Experiments have shown that it is 119.5°. This type of molecule is AX_2E.

Thiazyl fluoride (NSF)

Central atom: Sulfur atom S		**6 electrons in** **the outermost shell= 6**
Ligand:1 Nitrogen atom N		**3 unpaired electron in** **the outermost shell ×1 = 3**
Ligand:1 fluorine atom F		**1 unpaired electron in** **the outermost shell= 1**
		Total=10 electrons **in the valence shell**

Sulfur has 6 electrons in its outermost shell. The nitrogen atom will therefore supply 3 electrons to the valence sphere and the fluorine atom will supply 1 unpaired electron.

In total, we have 10 electrons grouped into 5 doublets.

$$8\text{ electrons}\Rightarrow 4\text{ doublets}\left\{\begin{array}{c}\text{N gets 3 doublets}\Rightarrow\text{1charge}\\ \text{F gets 1doublet}\Rightarrow\text{1charge}\\ \text{Free doublet}\Rightarrow\text{1charge}\end{array}\right\}\text{3 charges system}$$

Each ligand O collects as many doublets as the number of unpaired electrons it has supplied. There are therefore 3 charges on the valence sphere, which are distributed at the corners of an equilateral triangle.

The angle between the bond SN and SF is 116.92°. The molecule is of the AX_2E type.

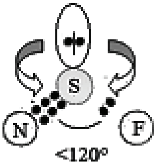


Figure VII-T-20: Geometry of NSF.

Ammonium ion $(NH_4)^+$

Central atom: Nitrogen atom N		**5 electrons in** **the outermost shell** = 5
Ligands:4 hydrogen atoms H		**1 unpaired electron in** **the outermost shell** ×4 = 4
Ion +		**Remove an electron** **in the outermost shell**
		Total=9 − 1 = 8

Nitrogen has 5 electrons in its outermost shell. The 4 hydrogen atoms will therefore supply 4 unpaired electrons to the valence sphere. We must subtract 1 electron for the ion.

In total, we have 8 electrons grouped into 4 doublets.

$$8\text{ electrons}\Rightarrow 4\text{ doublets}\left\{\begin{array}{l}\text{H gets 1doublet}\Rightarrow\text{1charge}\\ \text{H gets 1doublet}\Rightarrow\text{1charge}\\ \text{H gets 1doublet}\Rightarrow\text{1charge}\\ \text{H gets 1doublet}\Rightarrow\text{1charge}\end{array}\right\}\text{4 charges system}$$

Each ligand H collects as many doublets as the unpaired electrons it has supplied. There are therefore 4 charges on the valence sphere, which are distributed at the corners of a tetrahedron.

The molecule is of the AX_4 type.

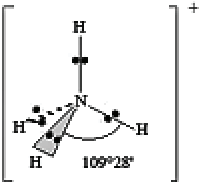
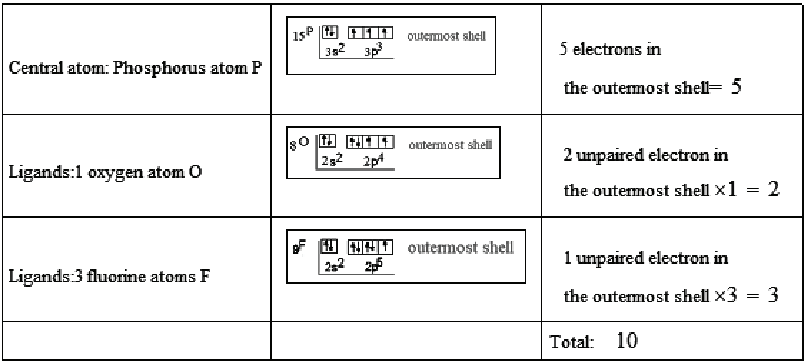


Figure VII-T-21: Geometry of NH_4^+.

Phosphoryl fluoride (POF_3) molecule



Central atom: Phosphorus atom P	$_{15}P$ ⇅ ↑↑↑ $3s^2$ $3p^3$ outermost shell	5 electrons in the outermost shell= 5
Ligands:1 oxygen atom O	$_8O$ ⇅ ⇅↑↑ $2s^2$ $2p^4$ outermost shell	2 unpaired electron in the outermost shell ×1 = 2
Ligands:3 fluorine atoms F	$_9F$ ⇅ ⇅⇅↑ $2s^2$ $2p^5$ outermost shell	1 unpaired electron in the outermost shell ×3 = 3
		Total: 10

Phosphorus has 5 electrons in its outermost shell. Oxygen will therefore supply 2 unpaired electrons to the valence sphere. Fluorine will supply 3 unpaired electrons.

In total, we have 10 electrons grouped into 5 doublets.

$$\text{10 electrons} \Rightarrow \text{5 doublets} \left\langle \begin{array}{c} \text{O gets 2 doublets} \Rightarrow \text{1charge} \\ \text{F gets 1doublet} \Rightarrow \text{1charge} \\ \text{F gets 1doublet} \Rightarrow \text{1charge} \\ \text{F gets 1doublet} \Rightarrow \text{1charge} \end{array} \right\rangle \text{4 charges system}$$

Each ligand H collects as many doublets as the number of unpaired electrons it has supplied. There are therefore 4 charges on the valence sphere, which are distributed at the corners of a tetrahedron.

This molecule is of the AX_4 type.

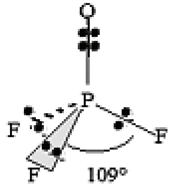
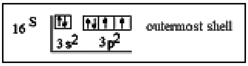
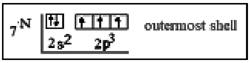


Figure VII-T-22: Geometry of POF_3.

Thiazyl trifluoride (SNF_3) molecule

Central atom: Sulfur atom S		6 electrons in the outermost shell= 6
Ligands:1 nitrogen atom N		3 unpaired electron in the outermost shell ×1 = 3
Ligands:3 fluorine atoms F		1 unpaired electron in the outermost shell ×3 = 3
		Total:12

Sulfur has 6 electrons in its outermost shell. The nitrogen will therefore supply 3 unpaired electrons to the valence sphere and the fluorines will also supply 3 unpaired electrons.

In total, we have 12 electrons grouped into 6 doublets.

$$\text{12 electrons} \Rightarrow \text{6 doublets} \left\{ \begin{array}{c} \text{N gets 3 doublets} \Rightarrow \text{1charge} \\ \text{F gets 1doublet} \Rightarrow \text{1charge} \\ \text{F gets 1doublet} \Rightarrow \text{1charge} \\ \text{F gets 1doublet} \Rightarrow \text{1charge} \end{array} \right\} \text{4 charges system}$$

Each ligand collects as many doublets as the number of unpaired electrons it has supplied. There are therefore 4 charges on the valence sphere, which are distributed at the corners of a tetrahedron

This molecule is of the AX_4 type.

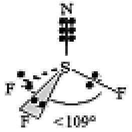
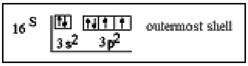
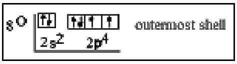


Figure VII-T-23: Geometry of SNF_3.

Thiosulfate ion ($S_2O_3^{2-}$)

Central atom: Sulfur atom S		**6 electrons in the outermost shell= 6**
Ligands:3 oxygen atom		**2 unpaired electron in the outermost shell** $\times 3 = 6$
Ligand: 1 sulfur atom		**2 unpaired electrons in the outermost shell=2**
ion 2-		**Add two electrons to the valence sphere=+2**
		Total:16

Sulfur has 6 electrons in its outermost shell. Oxygen will therefore supply 2×3=6 unpaired electrons to the valence sphere, sulfur will supply 2 unpaired electrons. The ion 2- will supply 2 electrons

In total we have 16 electrons which are grouped into 8 doublets.

$$\textbf{16 electrons}\Rightarrow\textbf{8 doublets}\left\{\begin{array}{l}\textbf{O gets 2 doublets}\Rightarrow\textbf{1charge}\\ \textbf{O gets 2 doublets}\Rightarrow\textbf{1charge}\\ \textbf{O gets 2 doublets}\Rightarrow\textbf{1charge}\\ \textbf{S gets 2 doublets}\Rightarrow\textbf{1charge}\end{array}\right\}\textbf{4 charges system}$$

Each ligand collects as many doublets as the number of unpaired electrons it has supplied. There are therefore 4 charges on the valence sphere, which are distributed at the corners of a tetrahedron.

The molecule is of the AX_4 type.

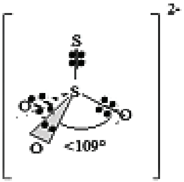
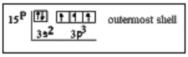
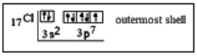


Figure VII-T-24: Geometry of $S_2O_3^{2-}$.

Phosphorus pentachloride (PCl_5)

Central atom: Phosphorus atom P		5 electrons in the outermost shell= 5
Ligands:5 chlorine atom Cl		1 unpaired electron in the outermost shell ×5 = 5
		Total:10

Phosphorus has 5 electrons in its outermost shell and chlorine will therefore supply 1 unpaired electron to the valence sphere.

In total, we have 10 electrons grouped into 5 doublets.

$$10\ \text{electrons} \Rightarrow 5\ \text{doublets} \left\{ \begin{array}{l} \text{Cl gets 1 doublets} \Rightarrow 1\text{charge} \\ \text{Cl gets 1 doublets} \Rightarrow 1\text{charge} \\ \text{Cl gets 1 doublets} \Rightarrow 1\text{charge} \\ \text{Cl gets 1 doublets} \Rightarrow 1\text{charge} \\ \text{Cl gets 1 doublets} \Rightarrow 1\text{charge} \end{array} \right\} 5\ \text{charges system}$$

Each ligand Cl collects as many doublets as the number of unpaired electrons it has supplied. There are therefore 5 charges on the valence sphere, which are distributed at the corners of a hexahedron.

The molecule is of the AX_5 type.

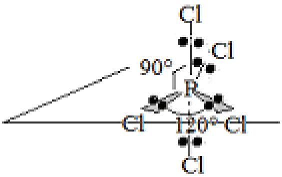


Figure VII-T-25: Geometry of PCl_5.

Ion pentaoxoiodate $(IO_5)^{3-}$

Central atom: Iodine atom I		7 electrons in the outermost shell= 7
Ligand: 5 oxygen atoms O		2 unpaired electron in the outermost shell $\times 5 = 10$
Ion 3-		3 electrons are added to the outermost shell= 3
		Total: 20

Iodine has 7 electrons in its outermost shell and the oxygen atoms will therefore supply 10 unpaired electrons to the valence sphere and the ion will supply 3 electrons.

In total, we have 20 electrons grouped into 10 doublets.

$$20\text{ electrons} \Rightarrow 10\text{ doublets} \left\{ \begin{array}{l} \text{O gets 2 doublets} \Rightarrow 1\text{charge} \\ \text{O gets 2 doublets} \Rightarrow 1\text{charge} \\ \text{O gets 2 doublets} \Rightarrow 1\text{charge} \\ \text{O gets 2 doublets} \Rightarrow 1\text{charge} \\ \text{O gets 2 doublets} \Rightarrow 1\text{charge} \end{array} \right\} 5\text{ charges system}$$

Each ligand collects as many doublets as the number of unpaired electrons it has supplied. They are placed at the vertices of a hexaedron.

The molecular ion is of the AX_5 type.

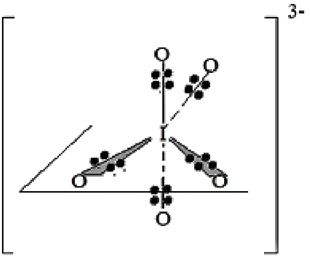
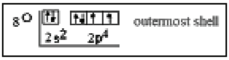


Figure VII-T-26: Geometry of $(IO_5)^{3-}$.

Xenon trioxyfluoride (XeO_3F_2)

Central atom: **Xenon atom Xe**		**8 electrons in the outermost shell= 8**
Ligand: **3 oxygen chlorine atoms O**		**2 unpaired electrons in the outermost shell ×3 = 6**
Ligand:2 **fluorine atoms F**		**1 unpaired electron in the outermost shell×2 = 2**
		Total:16

Xenon has 8 electrons in its outermost shell, the oxygen atoms will therefore supply 6 unpaired electrons to the valence sphere, and the fluorine will supply 2 unpaired electrons.

In total, we have 16 electrons grouped into 8 doublets.

$$\textbf{16 electrons} \Rightarrow \textbf{ 8 doublets} \left\{ \begin{array}{c} \textbf{O gets 2 doublets} \Rightarrow \textbf{1charge} \\ \textbf{O gets 2 doublets} \Rightarrow \textbf{1charge} \\ \textbf{O gets 2 doublets} \Rightarrow \textbf{1charge} \\ \textbf{F gets 1 doublets} \Rightarrow \textbf{1charge} \\ \textbf{F gets 1doublets} \Rightarrow \textbf{1charge} \end{array} \right\} \textbf{5 charges system}$$

Each ligand collects as many doublets as the number of unpaired electrons it has supplied. There are therefore 5 charges on the valence sphere, which are distributed at the corners of a hexahedron.

The molecule is of the AX_5 type.

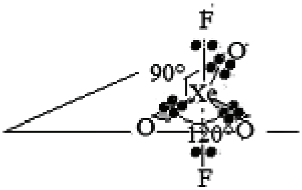
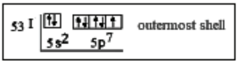
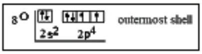
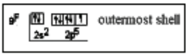


Figure VII-T-27: Geometry of XeO_3F_2.

Iodine oxopentafluoride (IOF_5)

Central atom: Iodine atom I		**7 electrons in** **the outermost shell** $= 7$
Ligand: 1 oxygen chlorine atom O		**2 unpaired electrons** **in the outermost shell** $\times 1 = 2$
Ligand:5 fluorine atoms F		**1 unpaired electron in** **the outermost shell**$\times 5 = 5$
		Total:14

Iodine has 7 electrons in its outermost shell, oxygen will therefore supply 2 unpaired electrons to the valence sphere, and the fluorines will supply 5 unpaired electrons.

In total, we have 14 electrons grouped into 7 doublets.

$$\textbf{14 electrons} \Rightarrow \textbf{7 doublets} \left\{ \begin{array}{l} \textbf{O gets 2 doublets} \Rightarrow \textbf{1charge} \\ \textbf{F gets 1 doublets} \Rightarrow \textbf{1charge} \\ \textbf{F gets 1 doublets} \Rightarrow \textbf{1charge} \\ \textbf{F gets 1 doublets} \Rightarrow \textbf{1charge} \\ \textbf{F gets 1doublets} \Rightarrow \textbf{1charge} \\ \textbf{F gets 1 doublets} \Rightarrow \textbf{1charge} \end{array} \right\} \textbf{6 charges system}$$

Each ligand collects as many doublets as the number of unpaired electrons it has supplied. There are therefore 6 charges on the valence sphere, which are distributed at the corners of an octahedron.

The molecule is of the AX_6 type.

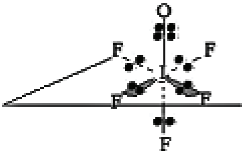
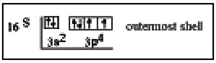


Figure VII-T-28: Geometry of IOF_5.

Sulfur hexafluoride (SF_6)

Central atom: Sulfur atom S		**6 electrons in** **the outermost shell= 6**
Ligand:6 fluorine atoms F		**1 unpaired electron in** **the outermost shell×6 = 6**
		Total:12

Sulfur has 6 electrons in its outermost shell and each fluorine will supply 1 unpaired electron to the valence shell. Each ligand collects as many doublets as the number of unpaired electrons it has supplied.

In total, we have 12 electrons on the valence shell grouped in 6 doublets.

$$\textbf{12electrons} \Rightarrow \textbf{6 doublets} \left\{ \begin{array}{l} \textbf{F gets 1 doublets} \Rightarrow \textbf{1charge} \\ \textbf{F gets 1 doublets} \Rightarrow \textbf{1charge} \\ \textbf{F gets 1 doublets} \Rightarrow \textbf{1charge} \\ \textbf{F gets 1 doublets} \Rightarrow \textbf{1charge} \\ \textbf{F gets 1doublets} \Rightarrow \textbf{1charge} \\ \textbf{F gets 1 doublets} \Rightarrow \textbf{1charge} \end{array} \right\} \textbf{6 charges system}$$

Each ligand collects as many doublets as the number of unpaired electrons it has supplied. There are therefore 6 charges on the valence sphere, which are distributed at the corners of an octahedron.

The molecule is of the AX_6 type.

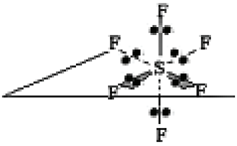
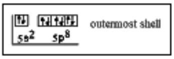
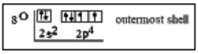
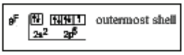


Figure VII-T-29: Geometry of IF_6.

Xenon dioxydifluoride (XeO_3F_2)

Central atom: Xenon atom Xe		**8 electrons in the outermost shell= 8**
Ligand: 3 oxygen chlorine atoms O		**2 unpaired electrons in the outermost shell ×3 = 6**
Ligand:2 fluorine atoms F		**1 unpaired electron in the outermost shell×2 = 2**
		Total:16

Xenon has 8 electrons in its outermost shell, the oxygen atoms will therefore supply 6 unpaired electrons to the valence sphere, and fluorine will supply 2 unpaired electrons.

In total, we have 16 electrons grouped into 8 doublets.

$$\text{16 electrons} \Rightarrow \text{ 8 doublets } \left\{ \begin{array}{c} \text{O gets 2 doublets} \Rightarrow \text{1charge} \\ \text{O gets 2 doublets} \Rightarrow \text{1charge} \\ \text{O gets 2 doublets} \Rightarrow \text{1charge} \\ \text{F gets 1 doublets} \Rightarrow \text{1charge} \\ \text{F gets 1doublets} \Rightarrow \text{1charge} \end{array} \right\} \text{ 5 charges system}$$

Each ligand collects as many doublets as the number of unpaired electrons it has supplied. There are therefore 5 charges on the valence sphere, which are distributed at the corners of a hexahedron.

The molecule is of the AX_5 type.

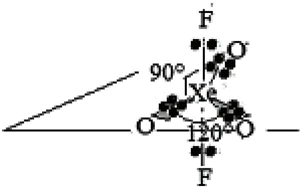
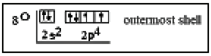


Figure VII-T-30: Geometry of XeO_3F_2.

Tetrafluoro(oxo)xenon ($XeOF_4$)

Central atom: Xenon atom Xe		**8 electrons in** **the outermost shell**= 8
Ligand: 1 oxygen chlorine atom O		**2 unpaired electrons** **in the outermost shell** ×1 = 2
Ligand:4 fluorine atoms F		**1 unpaired electron** **in the outermost shell**×4 = 4
		Total:14

Xenon has 8 electrons in its outermost shell, the oxygen atoms will therefore supply 2 unpaired electrons to the valence sphere, and fluorine will supply 4 unpaired electrons.

$$\textbf{14 electrons} \Rightarrow \textbf{7 doublets} \left\{ \begin{array}{c} \textbf{O gets 2 doublets} \Rightarrow \textbf{1charge} \\ \textbf{F gets 1 doublet} \Rightarrow \textbf{1charge} \\ \textbf{F gets 1 doublet} \Rightarrow \textbf{1charge} \\ \textbf{F gets 1 doublet} \Rightarrow \textbf{1charge} \\ \textbf{F gets 1doublet} \Rightarrow \textbf{1charge} \\ \textbf{Free doublet} \Rightarrow \textbf{1charge} \end{array} \right\} \textbf{6 charges system}$$

In total we have 14 electrons, which are grouped into 8 doublets.

Each ligand collects as many doublets as the number of unpaired electrons it has supplied. Each ligand is place at the vertices of an octahedron. The free doublet occupies a larger volume than the binding doublets and exerts pressure on the Xe-F bonds, making a bond angle OXeF of less than 90°.

The molecule is of the AX_5E type.

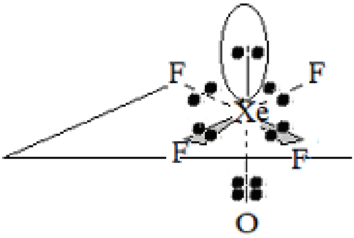


Figure VII-T-31: Geometry of $XeOF_4$.

T-VII-4. Molecular geometry and the hybridization of atomic orbitals

1) Define the concept of hybridization.

ANSWER

The hybridization of atomic orbitals is the mixing of the atomic orbitals of an atom belonging to the same electronic shell in order to form new orbitals, which allow a better qualitative description of the bonds between the atoms.

2) Why is the theory of hybridization described as an *a posteriori* method?

ANSWER

The use of the atomic orbital hybridization method requires prior knowledge of the geometry of the molecule. Hybrid orbitals are defined with respect to the directions of bonds in the molecule and constitute a theoretical basis allowing the use of quantum methods, such as the theory of molecular orbitals.

3) What are sp, sp^2, and sp^3 hybridizations? In which molecules are they involved? Which atoms are often involved?

ANSWER

sp hybridization is the mixing of a ns orbital with a np orbital belonging to the same n shell. It intervenes in linear molecules such as beryllium dihydride (BeH_2), acetylene (C_2H_2), and hydrogen cyanide (HCN), etc.

sp^2 hybridization is the mixing of a ns orbital with two np orbital belonging to the same n shell. It intervenes in boron (B) in plane molecules, such as boron trihydride (BH_3) and in the carbons of ethylene (C_2H_4), etc.

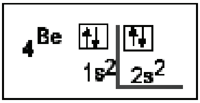
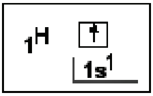
sp^3 hybridization is the mixing of a ns orbital with three np orbital belonging to the same n shell. It intervenes in carbon in tetrahedral molecules such as methane (CH_4), in nitrogen (N) in ammonia (NH_3), or in silicon (Si) in silane (SiH_4).

4) Consider the BeH_2 molecule ($_4Be$, $_1H$).

a) Using the VSEPR method, determine the geometry of this molecule.

ANSWER

In the BeH_2 molecule, the central atom is Be and the outermost shell of Be is a 2s AO containing 2 electrons.

Central atom: beryllium Be		2 electrons on the outermost shell
Ligands:2 hydrogen atoms H		1 unpaired electrons ×2
		Total : 4

There is a total of $4e^-$ on the valence shell, which give 2 doublets.

Each ligand collects as many doublets as the number of unpaired electrons it has supplied, i.e. 1 doublet per atom of H. There are therefore 2 charges on the valence sphere, which repel each other until the equilibrium position of 2 charges of the electrostatic model is reached.

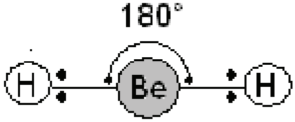


Fig VII-T-32: Geometry of BeH_2.

a) What type of hybridization can we envisage for the beryllium in this molecule? Give their mathematical expression.

ANSWER

In the case of beryllium, we must have two hybrid AOs, t_1 and t_2, pointing in opposite directions, this is sp type hybridization.

$$\{\Psi_{2s}, \Psi_{2pz}, \Psi_{2px}, \Psi_{2py}\} \rightarrow \{t_1, t_2, \Psi_{2px}, \Psi_{2py}\}$$

Natural basis Hybrid basis

We then construct the hybrid orbitals as a linear combination of the natural atomic orbitals, so that

$$t_1 = a_1\Psi_{2s} + b_1\Psi_{2pz}$$
$$t_2 = a_2\Psi_{2s} + b_2\Psi_{2pz}$$

where a_i and b_i are the coefficients of the combination expressing the respective "weights" of the atomic orbitals in the hybridization.

b) Put the above equations into matrix form.

ANSWER

$$\begin{bmatrix} t_1 \\ t_2 \end{bmatrix} = \begin{bmatrix} a_1 & b_1 \\ a_2 & b_2 \end{bmatrix} \begin{bmatrix} \Psi_{2s} \\ \Psi_{2pz} \end{bmatrix}$$

d) Determine the hybridization coefficients knowing that the sum of the squares of the coefficients of a row or of a column of the hybridization matrix is equal to 1 and that the orbitals t_1 and t_2 are orthogonal to each other as well as the atomic orbitals Ψ_{2s} and Ψ_{2pz}.

ANSWER

- The sum of the squares of a line is equal to 1

$$a_1^2 + b_1^2 = 1$$

- The sum of the squares of a column is equal to 1

$$a_1^2 + a_2^2 = 1$$

- The sum of the products of the matrix elements of a row is zero

$$a_1 a_2 + b_1 b_2 = 0$$

- The sum of the products of the matrix elements of a column is zero

$$a_1 b_2 + a_2 b_1 = 0$$

Calculation of hybridization coefficients

The sign of the coefficients depends on the geometry of the molecule. Consider the basic atomic orbital 2pz.

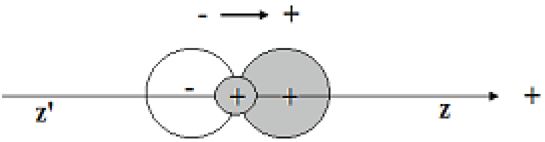


Figure VII-T-33: Signs of phases in AO 2s and 2pz.

Phase + points in the direction of t_1, so the sign in front of $|b_1|$ will be positive. On the contrary, for t_2 the sign will be negative because the orbital t_2 points in the direction of negative z. The contribution of the 2s atomic orbital will always be positive since this orbital has a positive phase regardless of the direction observed. Ultimately, for the matrix coefficients, we will have

$$\begin{bmatrix} +|a_1| & +|b_1| \\ +|a_2| & -|b_2| \end{bmatrix}$$

If we apply the rules defined above, we will have

$$a_1^2 + b_1^2 = 1 \text{ then } b_1^2 = 1 - a_1^2 \text{ and } b_1 = \sqrt{1 - a_1^2}$$
$$a_1^2 + a_2^2 = 1 \text{ then } a_2^2 = 1 - a_1^2 \text{ and } a_2 = \sqrt{1 - a_1^2}$$

which for the matrix coefficients gives

$$\begin{bmatrix} +|a_1| & +\sqrt{1 - a_1^2} \\ +\sqrt{1 - a_1^2} & -|a_1| \end{bmatrix}$$

if we define |a₁| = a, the matrix becomes

$$\begin{bmatrix} +a & \sqrt{1 - a^2} \\ \sqrt{1 - a^2} & -a \end{bmatrix}$$

To find the value of a, we need to apply the rules

$$a_1 b_2 + a_2 b_1 = 0 \quad \text{and} \quad 2a^2 = 1$$

so that

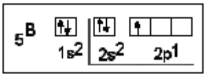
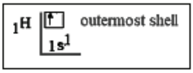
$$a = \frac{\sqrt{2}}{2}$$

and the matrix becomes

$$\begin{bmatrix} \frac{\sqrt{2}}{2} & \frac{\sqrt{2}}{2} \\ \frac{\sqrt{2}}{2} & -\frac{\sqrt{2}}{2} \end{bmatrix}$$

5) Here we consider the BH_3 molecule ($_5B$ and $_1H$). Determine the geometry of the molecule using the VSEPR method and predict the appropriate hybridization for boron. Construct the hybridization matrix and give the analytical expression of the hybrid orbitals.

ANSWER

Central atom: Boron B		3 electrons in the outermost shell
Ligands:3 hydrogen atoms H		1 unpaired electron in the outermost shell ×3

The 3 hydrogen atoms will therefore supply 3 electrons to the valence sphere.

In total, we have 6 electrons grouped into 3 doublets.

$$\text{6 electrons} \Rightarrow \text{3 doublets} \left\{ \begin{array}{l} \text{F gets 1doublet} \Rightarrow \text{1charge} \\ \text{F gets 1doublet} \Rightarrow \text{1charge} \\ \text{F gets 1doublet} \Rightarrow \text{1charge} \end{array} \right\} \text{3 charges system}$$

Each ligand H collects as many doublets as the number of unpaired electrons it has supplied. There are therefore 3 charges on the valence sphere, which are distributed at the corners of an equilateral triangle.

This molecule is of the AX_3 type.

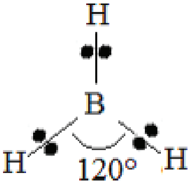


Figure VII-T-34: Geometry of BH_3.

We must get three hybrids pointing towards the summits of an equilateral triangle and thus we can say that the boron has been hybridized into sp^2. Let us examine this hybridization.

First, let us recall the basis of the atomic orbitals used

$$\{\Psi_{2s},\Psi_{2pz},\Psi_{2px},\Psi_{2py}\} \rightarrow \{t_1,t_2,t_3,\Psi_{2pz}\}$$

Natural basis Hybrid basis

In this case, we have used the atomic orbitals Ψ_{2s}, Ψ_{2px}, and Ψ_{2py} to build the hybrid atomic orbitals sp_2. This gives

$$\begin{aligned} t_1 &= a_1\Psi_{2s} + b_1\Psi_{2px} + c_1\Psi_{2py} \\ t_2 &= a_2\Psi_{2s} + b_2\Psi_{2px} + c_2\Psi_{2py} \\ t_3 &= a_3\Psi_{2s} + b_3\Psi_{2px} + c_3\Psi_{2py} \end{aligned}$$

Constructing a matrix form gives

$$\begin{bmatrix} t_1 \\ t_2 \\ t_3 \end{bmatrix} = \begin{bmatrix} a_1 & b_1 & c_1 \\ a_2 & b_2 & c_2 \\ a_3 & b_3 & c_3 \end{bmatrix} \cdot \begin{bmatrix} \Psi_{2s} \\ \Psi_{2px} \\ \Psi_{2py} \end{bmatrix}$$

Definition of the referential

t_1 confuses itself with the x axis and points towards positive x

$$t_1 = |a_1|\Psi_{2s} + |b_1|\Psi_{2px} + 0\Psi_{2p}$$

t_2 has a positive component in the y direction and is negative in the x direction

$$t_2 = |a_2|\Psi_{2s} - |b_2|\Psi_{2px} + |c_2|\Psi$$

t_3 has a negative component in the y direction and is negative in the x direction

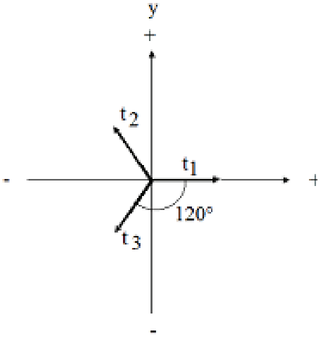


Figure VII-T-35: Referential for BH_3 hybridization.

$$t_3 \;=\; |a_3|\Psi_{2s} - |b_3|\Psi_{2px} - |c_3|\Psi$$

Besides, given the symmetry, one must have

$$|b_2| = |b_3| \text{ and } |c_2| = |c_3|$$

which leads to the transformation matrix by setting |a₁| = a

$$\begin{bmatrix} a & |b_1| & 0 \\ a_2 & -|b_2| & |c_2| \\ a_3 & -|b_2| & -|c_2| \end{bmatrix}$$

By applying the rules on the coefficients we have

$$2|c_2|^2 = 1 \quad \text{so that} \quad |c_2| = \frac{\sqrt{2}}{2}$$

$$a^2 + |b_1|^2 = 1 \;\text{ so that } |b_1| = \sqrt{1 - a^2}$$

$$|b_1|^2 + 2|b_2|^2 = 1 \text{ so that } 1 - a^2 + 2|b_2|^2 = 1 \text{ then } |b_2| = \frac{a}{\sqrt{2}}$$

$$|a_2|^2 + \frac{a}{2} + \frac{1}{2} = 1 \text{ so that } |a_2| = \sqrt{\frac{1 - a^2}{2}}$$

$$|a_3|^2 + \frac{a}{2} + \frac{1}{2} = 1 \text{ so that } |a_3| = \sqrt{\frac{1 - a^2}{2}}$$

and thus we have the following transformation matrix

$$\begin{bmatrix} a & \sqrt{1 - a^2} & 0 \\ \sqrt{\frac{1 - a^2}{2}} & -\frac{a}{\sqrt{2}} & \frac{1}{\sqrt{2}} \\ \sqrt{\frac{1 - a^2}{2}} & -\frac{a}{\sqrt{2}} & -\frac{1}{\sqrt{2}} \end{bmatrix}$$

a remains to be determined. To do this, let us introduce the physics of the problem. If we compare the directions of the hybrid atomic orbitals to the vectors, we have

$$\vec{t}_1 . \vec{t}_3 = \left\| \vec{t}_1 \right\| \left\| \vec{t}_3 \right\| \cos 120°$$

with

$$t_1 \begin{cases} \sqrt{1-a^2} \\ 0 \end{cases} \quad \text{and}\, \vec{t}_3 \begin{cases} -\dfrac{a}{\sqrt{2}} \\ -\dfrac{1}{\sqrt{2}} \end{cases}$$

so that

$$\cos 120° = \frac{\vec{t}_1 . \vec{t}_3}{\left\| \vec{t}_1 \right\| \left\| \vec{t}_3 \right\|}$$

We have vector lengths equal to

$$\left\| \vec{t}_1 \right\| = \sqrt{x_1^2 + y_1^2} \text{ and } \left\| \vec{t}_3 \right\| = \sqrt{x_3^2 + y_3^2} \text{ so that:}$$

$$\left\| \vec{t}_1 \right\| = \sqrt{1-a^2} \text{ and } \left\| \vec{t}_3 \right\| = \left(\frac{a^2}{2} + \frac{1}{2} \right)$$

Let us express the dot product of the hybrid vectors

$$\vec{t}_1 \vec{t}_3 = x_1 x_3 + y_1 y_3$$

so that

$$\vec{t}_1 \vec{t}_3 = \sqrt{1-a^2}\left(-\frac{a}{\sqrt{2}} \right) = -a\sqrt{\frac{1-a^2}{2}}$$

we can then write

$$\frac{1}{2} = \frac{-a\sqrt{\dfrac{1-a^2}{2}}}{\sqrt{1-a^2}\sqrt{\dfrac{a^2}{2}+\dfrac{1}{2}}}$$

or

$$\frac{1}{2} = \frac{-a\sqrt{\dfrac{1}{2}}}{\sqrt{\dfrac{a^2+1}{2}}} = \frac{-a}{\sqrt{a^2+1}}$$

Let us square this expression

$$\frac{a^2}{a^2+1} = \frac{1}{4}$$

and deduce

$$a^2 = \frac{1}{3} \quad \text{i.e.} \quad a = \frac{1}{\sqrt{3}}$$

so that the equations giving the hybrid orbitals sp₂ are

$$\begin{bmatrix} t_1 \\ t_2 \\ t_3 \end{bmatrix} = \begin{bmatrix} \frac{1}{\sqrt{3}} & \sqrt{\frac{2}{3}} & 0 \\ \sqrt{\frac{2}{3}} & -\frac{1}{\sqrt{6}} & \frac{1}{\sqrt{2}} \\ \sqrt{\frac{2}{3}} & -\frac{1}{\sqrt{6}} & -\frac{1}{\sqrt{2}} \end{bmatrix} . \begin{bmatrix} \Psi_{2s} \\ \Psi_{2px} \\ \Psi_{2py} \end{bmatrix}$$

where

$$\Psi_{2s} = \frac{1}{4\sqrt{2\pi}}(r-2)\exp\left(-\frac{r}{2}\right)$$

$$\Psi_{2px} = \frac{1}{4\sqrt{2\pi}} r\sin\theta\cos\phi\exp\left(-\frac{r}{2}\right)$$

$$\Psi_{2py} = \frac{1}{4\sqrt{2\pi}} r\sin\theta\sin\phi\exp\left(-\frac{r}{2}\right)$$

Using Cartesian coordinates, we obtain

$$\Psi_{2s} = \frac{1}{4\sqrt{2\pi}}\left(\sqrt{x^2+y^2}-2\right)\exp\left(-\frac{\sqrt{x^2+y^2}}{2}\right)$$

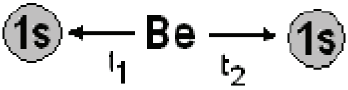
$$\Psi_{2px} = \frac{1}{4\sqrt{2\pi}} x\exp\left(-\frac{\sqrt{x^2+y^2}}{2}\right)$$

$$\Psi_{2py} = \frac{1}{4\sqrt{2\pi}} y\exp\left(-\frac{\sqrt{x^2+y^2}}{2}\right)$$

6) Using the hybridized atomic orbitals of the beryllium atom, construct a diagram of the localized molecular orbitals of the BeH_2 molecule.

We have previously seen that the sp type hybridization of beryllium leads to the hybrid orbitals t_1 and t_2, as shown in **Fig. VII-T-35**.

Both 2s electrons of beryllium are found in the hybrid orbitals t_1 and t_2, which point in the direction of the ligands giving us the following interactions



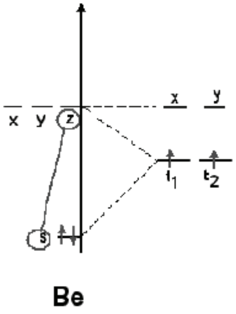


Figure VII-T-36: sp hybridization of Be.

We then obtain the correlation diagram between the AOs and the molecular orbitals of BeH_2. Each hybrid AO that interferes with the 1s AO of hydrogen, which is opposite, gives a bonding MO of σ type and an anti-bonding MO of σ* type.

We thus have a description in terms of *localized molecular orbitals*. This description is close to the chemist's vision of the chemical bond using Lewis notation, where we consider that a bond is due to a pair of electrons located between the bonded atoms.

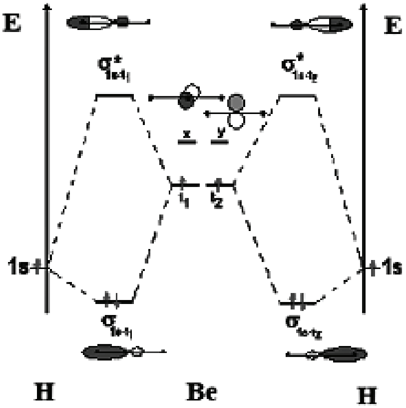


Figure VII-T-37:
MO diagram of the BeH_2 molecule.

T-VII-5. The hybridization of atomic orbitals and transition metal complexes

1) In Fig. VII-T-37, we give a space representation of a complex ion.

a) What possible types of hybridization of cobalt can take place in this ion? What is the name of the polyhedron formed by the nitrogen and oxygen atoms in the cation?

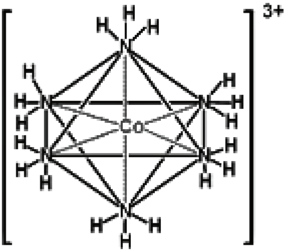


Figure VII-T-38: Complex ion.

ANSWER

Hybridization types: sp^3d^2 or d^2sp^3. The polyhedron is called a *coordination polyhedron*.

b) Give the IUPAC nomenclature of this complex.

ANSWER

In the formula, the central atom is indicated in the first place, followed by, in order, the negative, neutral, and positive ligands; the formula is enclosed within square brackets [ ]. As such, the formula of the compound is

$$[Co(NH3)_4(H_2O)_2]Cl$$

When written in words, the central atom is named in last place and the ligands appear in alphabetical order, regardless of their charge. The degree of oxidation is indicated in parentheses

tetraammine diaqua cobalt (III) chloride

Names of the ligands: H_2O: aqua; NH_3: ammine.

2) Show how the magnetic properties are explained within the framework of the valence bond theory (VB), based on the hybridization of atomic orbitals, and within the framework of the theory of the crystal field, based on the removal of degenerated d orbitals by ligands. Take the example of the complexes $[FeF_6]^{3-}$ and $[Fe(CN)_6]^{3-}$ whose theoretical paramagnetic moments are, respectively, $\mu = 5.90\ \mu°$ and $\mu = 1.73\mu°$, where $\mu°$ is the unit of paramagnetic moment.

ANSWER

Let us start by determining the degree of iron oxidation in these compounds $[FeF_6]^{3-}$

no_{Fe}+6×no_{F}=-3

the fluorine oxidation number is -1. For the Fe in $[FeF_6]^{3-}$, we can deduce that

$$no_{Fe} = +3$$

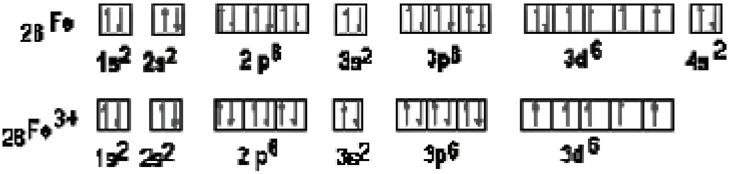
Let us do the same with $[Fe(CN)_6]^{3-}$

$$no_{Fe} + 6 \times no_{CN} = -3$$

However, the oxidation number of the CN group is -1. For the Fe in $[Fe(CN)_6]^{3-}$, we can deduce that

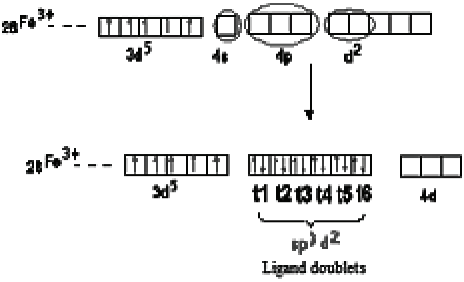
$$no_{Fe} = +3$$

Now, let us give the electronic configuration of iron (III)



Within the framework of the valence bond method, we must consider two types of hybridization depending on whether we are dealing with a complex with external or internal orbitals.

Outer orbital complex

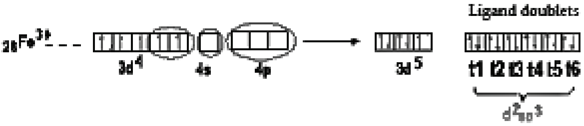


There are 5 unpaired electrons in the unhybridized orbitals, which gives a theoretical paramagnetic moment of

$$\mu = \mu^\circ\sqrt{5(5+2)} = 5.92\mu^\circ$$

Inner orbital complex

Let us examine the hypothesis of a complex with *internal orbitals*



There is only one unpaired electron left and therefore a theoretical paramagnetic moment of

$$\mu = \mu^\circ\sqrt{1(1+2)} = 1.73\mu^\circ$$

Taking into account what we know about the experimental paramagnetic moment, we can see that with $[FeF_6]^{3-}$ we are dealing with a complex with external orbitals, while $[Fe(CN)_6]^{3-}$ is a complex with internal orbitals due to the low value of its paramagnetic moment.

Let us examine the crystal field theory. In this theory, the ligands disturb the energy of the atomic orbitals d and cause their degeneration. The $3dz^2$ and $3dx^2$-y^2 AOs that point in the direction of the ligands more than the other d orbitals are the most disturbed..

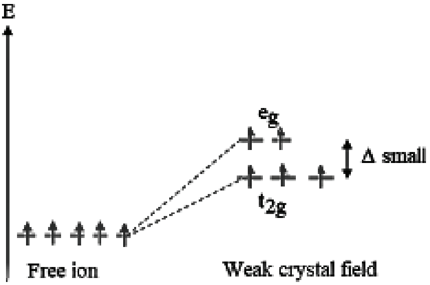


Figure VII-T-39: $Fe(CN)_6^{3-}$: weak octahedral field.

If the disturbance is not too great, we have a weak field complex. As a result, the new orbitals have slightly different energy and allow the application of Hund's rule concerning the distribution of electrons. We therefore have the simplified diagram in **Fig. VII-T-38**

As such, we have 5 unpaired electrons in the orbitals of the outermost shell and thus a large paramagnetic moment, i.e.

$$\mu = \mu^\circ\sqrt{5(5+2)} = 5.92\mu^\circ$$

We find the same result as with the valence bond method.

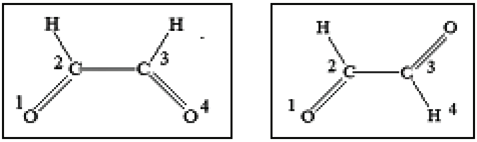
We can also show that in the case of $[Fe(CN)_6]^{3-}$, the burst between the orbitals e_g and t_{2g} is large; the electrons cannot reach the e_g levels and therefore they remain in the t_{2g} orbital with a single electron giving a weak paramagnetic moment.

T-VII-6. Extended systems

Glyoxal or ethanedial. The glyoxal molecule, with the formula O = CH-CH = O, resembles butadiene. It exists in 2 forms, cisoid and transoid, that Hückel's rule cannot distinguish between.

1) Represent the cisoid and transoid forms of ethanedial by numbering the carbon atoms.

ANSWER



transoid form cisoid form

Figure VII-T-40: The two conformers of butadiene.

2) Recall the principles of Hückel's rule.

ANSWER

In a polyatomic molecule, the π molecular orbitals play a large role in reactivity because of their energetic situation with respect to other orbitals, which place them in a border position between occupied molecular orbitals and vacant molecular orbitals. Everything happens as if the π system alone had intervened. To access the π system, using Hückel's rule, we can examine the interaction between 2p atomic orbitals as part of the LCAO method.

3) Construct the secular determinant of this molecule, taking as its parameters

$$\alpha_O = \alpha + 0.7\beta \quad ; \quad \alpha_C = \alpha + 0.2\beta$$

$$\beta_{CO} = 1.1\beta \quad ; \quad \beta_{CC} = 0.5\beta$$

where α and β are, respectively, the Coulombic integral and exchange integral in the ethylene molecule.

ANSWER

The Coulombic integrals in this molecule are α_O and α_C and the exchange integrals are β_{CO} and β_{CC}.

The secular equations become

$$\begin{cases} C_1(\alpha_O - \langle E\rangle) + C_2\beta_{CO} = 0 \\ C_1\beta_{CO} + C_2(\alpha_C - \langle E\rangle) + C_3\beta_{CC} = 0 \\ C_2\beta_{CC} + C_3(\alpha_C - \langle E\rangle) + C_4\beta_{CO} = 0 \\ C_3\beta_{CO} + C_4(\alpha_O - \langle E\rangle) = 0 \end{cases}$$

of which the secular determinant is

$$\begin{vmatrix} \alpha_O - \langle E\rangle & \beta_{CO} & 0 & 0 \\ \beta_{CO} & \alpha_C - \langle E\rangle & \beta_{CC} & 0 \\ 0 & \beta_{CC} & \alpha_C - \langle E\rangle & \beta_{CO} \\ 0 & 0 & \beta_{CO} & \alpha_O - \langle E\rangle \end{vmatrix} = 0$$

Using the particular values for glyoxal of α_O and β_{CO}, the determinant becomes

$$\begin{vmatrix} \alpha - \langle E \rangle + 0.7\beta & 1.1\beta & 0 & 0 \\ 1.1\beta & \alpha - \langle E \rangle + 0.2\beta & 0.5\beta & 0 \\ 0 & 0.5\beta & \alpha - \langle E \rangle + 0.2\beta & 1.1\beta \\ 0 & 0 & 1.1\beta & \alpha - \langle E \rangle + 0.7\beta \end{vmatrix} = 0$$

Dividing all the expression by β, we get

$$\begin{vmatrix} \dfrac{\alpha - \langle E \rangle}{\beta} + 0.7 & 1.1 & 0 & 0 \\ 1.1 & \dfrac{\alpha - \langle E \rangle}{\beta} + 0.2 & 0.5 & 0 \\ 0 & 0.5 & \dfrac{\alpha - \langle E \rangle}{\beta} + 0.2 & 1.1 \\ 0 & 0 & 1.1 & \dfrac{\alpha - \langle E \rangle}{\beta} + 0.7 \end{vmatrix} = 0$$

Now, putting

$$x = \frac{\alpha - \langle E \rangle}{\beta}$$

we obtain

$$\begin{vmatrix} x + 0.7 & 1,1 & 0 & 0 \\ 1.1 & x + 0.2 & 0.5 & 0 \\ 0 & 0.5 & x + 0.2 & 1.1 \\ 0 & 0 & 1.1 & x + 0.7 \end{vmatrix} = 0$$

4) Considering two types of solutions (symmetrical and antisymmetrical), determine the energy levels of this molecule.

ANSWER

To resolve this determinant, we can use the symmetry of the molecule. Consider the cisoid conformer given in **Fig. VII-T-39**.

We consider the median plane of the molecule plane as the plane of symmetry. In relation to this plane, we can consider two types of symmetries:

- symmetrical;
- antisymmetric.

These are the coefficients that will translate the symmetrical or antisymmetric character.

Symmetrical solutions

We have

$$C_1 = C_4 \quad \text{and} \quad C_2 = C_3$$

For symmetrical solutions, the secular equations take the form

$$\begin{cases} C_1(x+0.7)+1.1C_2 = 0 \\ 1.1C_1 + C_2(x+0.2)+0.5C_2 = 0 \end{cases}$$

i.e.

$$\begin{cases} C_1(x+0.7)+1.1C_2 = 0 \\ 1.1C_1 + C_2(x+0.7) = 0 \end{cases}$$

We can write a new determinant as

$$\begin{vmatrix} x+0.7 & 1.1 \\ 1.1 & x+0.7 \end{vmatrix} = 0$$

the solutions of which are

$$(x+0.7)^2-(1.1)^2 = 0$$

so that we obtain two solutions (symmetric)

$$x + 0.7 = -1.1 \;\; ; \;\; x + 0.7 = 1.1$$
$$x = -1.8 \;\; ; \;\; x = 0.4$$

which may be expressed in terms of α and β

$$\frac{\alpha - \langle E \rangle_{S_1}}{\beta} = -1.8 \;\; ; \;\; \frac{\alpha - \langle E \rangle_{S_2}}{\beta} = 0.4$$
$$\alpha - \langle E \rangle_{S_1} = -1.8\beta \;\; ; \;\; \alpha - \langle E \rangle_{S_2} = 0.4\,\beta$$
$$\langle E \rangle_{S_1} = \alpha + 1.8\beta \;\; ; \;\; \langle E \rangle_{S_2} = \alpha - 0.4\,\beta$$

Antisymmetric solutions

We have

$$C_1 = -C_4 \quad \text{and} \quad C_2 = -C_3$$

and

$$\begin{vmatrix} x+0.7 & 1.1 & 0 & 0 \\ 1.1 & x+0.2 & 0.5 & 0 \\ 0 & 0.5 & x+0.2 & 1.1 \\ 0 & 0 & 1.1 & x+0.7 \end{vmatrix} = 0$$

i.e.

$$\begin{cases} C_1(x+0.7) + 1.1C_2 = 0 \\ 1.1C_1 + C_2(x-0.3) = 0 \end{cases}$$

so that

$$\begin{vmatrix} x+0.7 & 1.1 \\ 1.1 & x-0.3 \end{vmatrix} = 0$$

i.e.

$$(x+0.7)(x-0.3)-(1.1)^2 = 0$$
$$x^2+0.4x-1.42 = 0$$

There are two solutions (antisymmetric)

$$x = 1.008 \;\; ; x = -1.408$$
$$\frac{\alpha-\langle E\rangle_{A_2}}{\beta} = -1.408 \quad ; \quad \frac{\alpha-\langle E\rangle_{A_1}}{\beta} = 1.008$$
$$\langle E\rangle_{A_1} = \alpha+1.408\ \beta \,;\, \langle E\rangle_{A_2} = \alpha-1.008\beta$$

so that the energies of the π system of glyoxal are

$$\langle E\rangle_{S_1} = \alpha+1.8\beta \;\; ; \;\; \langle E\rangle_{S_2} = \alpha-0.4\ \beta$$
$$\langle E\rangle_{A_1} = \alpha+1.408\ \beta \,;\, \langle E\rangle_{A_2} = \alpha-1.008\beta$$

Since the integrals α and β are negative, we have the following order of energy levels on an energy scale

$$\langle E\rangle_{A_2} = \alpha-1.008\beta$$
$$\langle E\rangle_{S_2} = \alpha-0.4\ \beta$$
$$\langle E\rangle_{A_1} = \alpha+1.408\ \beta$$
$$\langle E\rangle_{S_1} = \alpha+1.8\beta$$

5) Express the corresponding wave functions.

ANSWER

We know the sign and the relative value of the coefficients.

Thus, we have

$$
\begin{aligned}
|\Psi_4\rangle &= C_1|\varphi_1\rangle - C_2|\varphi_2\rangle + C_2|\varphi_2\rangle - C_1|\varphi_1\rangle \\
|\Psi_3\rangle &= C_1|\varphi_1\rangle - C_2|\varphi_2\rangle - C_2|\varphi_2\rangle + C_1|\varphi_1\rangle \\
|\Psi_2\rangle &= C_1|\varphi_1\rangle + C_2|\varphi_2\rangle - C_2|\varphi_2\rangle - C_1|\varphi_1\rangle \\
|\Psi_1\rangle &= C_1|\varphi_1\rangle + C_2|\varphi_2\rangle + C_2|\varphi_2\rangle + C_1|\varphi_1\rangle
\end{aligned}
$$

We start from the symmetrical expression of the secular equation

$$C_1(x + 0.7) + 1.1C_2 = 0$$

If we introduce the energy x = -1.8 in it

$$
\begin{aligned}
&C_1(-1.8 + 0.7) + 1.1C_2 = 0 \\
&C_1(-1.1) + 1.1C_2 = 0
\end{aligned}
$$

we deduce

$$C_1 = C_2$$

Given that the sum of the squared coefficients are equal to 1, we have for the state $|\Psi_1\rangle$

$$4C_1^2 = 1 \quad \text{then}\ C_1 = \tfrac{1}{2}$$

and the expression of the state may be written

$$|\Psi_1\rangle = \frac{1}{2}|\varphi_1\rangle + \frac{1}{2}|\varphi_2\rangle + \frac{1}{2}|\varphi_2\rangle + \frac{1}{2}|\varphi_1\rangle$$

Now, for the second level we have

$$x = -1.408$$

The secular equation is

$$C_1(x + 0.7) + 1.1C_2 = 0$$

and

$$C_1(-1.408 + 0.7) + 1.1C_2 = 0$$

$$C_1(-0.708) + 1.1C_2 = 0$$

$$C_1(0.708) = 1.1C_2$$

$$C_1\frac{(0.708)}{1.1} = C_2$$

$$0.644.C_1 = C_2$$

The second molecular orbital is

$$|\Psi_2\rangle = C_1|\varphi_1\rangle + 0.644\ C_1|\varphi_2\rangle - 0.644\ C_1|\varphi_2\rangle - C_1|\varphi_1\rangle$$

so that

$$2C_1^2(1 + 0.644^2) = 1$$

$$C_1^2 = \frac{1}{2 \times (1 + 0.644^2)} = 0.3534$$

$$C_1 = \sqrt{0.3534} = 0.5944$$

$$C_2 = 0.644 \times 0.5944 = 0.3828$$

$$|\Psi_2\rangle = 0.5944|\varphi_1\rangle + 0.3828|\varphi_2\rangle - 0.3828|\varphi_2\rangle - 0.5944|\varphi_1\rangle$$

For $|\Psi_3>$, we have

$$|\Psi_3\rangle = C_1|\varphi_1\rangle - C_2|\varphi_2\rangle - C_2|\varphi_2\rangle + C_1|\varphi_1\rangle$$

The secular equation is

$$C_1(x+0.7)+1.1C_2=0$$

with x = 0.4 we obtain

$$C_1(0.4+0.7)+1.1C_2=0$$

so that

$$C_1=C_2$$

and for |Ψ₃>, we have

$$|\Psi_3\rangle=\frac{1}{2}|\varphi_1\rangle-\frac{1}{2}|\varphi_2\rangle-\frac{1}{2}|\varphi_2\rangle+\frac{1}{2}|\varphi_1\rangle$$

At last, for |Ψ₄> if we take x = 1.008 as the solution, we get

$$C_1(1.008+0.7)+1.1C_2=0$$

then

$$1.708C_1+1.1C_2=0_*$$

$$C_1\frac{(1.708)}{1.1}=C_2$$

$$C_2=-1.5527C_1$$

$$\sum C_i^2 = 1$$

$$2C_1^2 + 2C_2^2 = 1$$

$$2C_1^2(1 + 1.5527^2) = 1$$

$$2C_1^2(1 + 1.5527^2)$$

$$6.82175458 C_1^2 = 1$$

$$C_1^2 = \frac{1}{6.8217} = 0.1466$$

$$C_1 = \sqrt{\frac{1}{6.8217}} = 0.3828$$

$$C_2 = -1.5527 \times 0.3828 = -0.5944$$

The expression of $|\Psi_4>$ is therefore

$$|\Psi_4\rangle = 0.3828|\varphi_1\rangle - 0.5944|\varphi_2\rangle + 0.5944|\varphi_2\rangle + 0.3828|\varphi_1\rangle$$

Finally, the π MOs of glyoxal take the following expressions

$$|\Psi_1\rangle = \frac{1}{2}|\varphi_1\rangle + \frac{1}{2}|\varphi_2\rangle + \frac{1}{2}|\varphi_3\rangle + \frac{1}{2}|\varphi_4\rangle$$

$$|\Psi_2\rangle = 0.5944|\varphi_1\rangle + 0.3828|\varphi_2\rangle - 0.3828|\varphi_3\rangle - 0.5944|\varphi_4\rangle$$

$$|\Psi_3\rangle = \frac{1}{2}|\varphi_1\rangle - \frac{1}{2}|\varphi_2\rangle - \frac{1}{2}|\varphi_3\rangle + \frac{1}{2}|\varphi_4\rangle$$

$$|\Psi_4\rangle = 0.3828|\varphi_1\rangle - 0.5944|\varphi_2\rangle + 0.5944|\varphi_3\rangle - 0.3828|\varphi_4\rangle$$

which may be put in a matrix of the form

$$\begin{bmatrix} |\Psi_1\rangle \\ |\Psi_2\rangle \\ |\Psi_3\rangle \\ |\Psi_4\rangle \end{bmatrix} = \begin{bmatrix} \frac{1}{2} & \frac{1}{2} & \frac{1}{2} & \frac{1}{2} \\ 0.5944 & 0.3828 & -0.3828 & -0.5944 \\ \frac{1}{2} & -\frac{1}{2} & -\frac{1}{2} & \frac{1}{2} \\ 0.3828 & -0.5944 & 0.5944 & -0.3828 \end{bmatrix} \times \begin{bmatrix} |\varphi_1\rangle \\ |\varphi_2\rangle \\ |\varphi_3\rangle \\ |\varphi_4\rangle \end{bmatrix}$$

6) Calculate the bond index π (bond order).

ANSWER

Let us recall the definition of the bond index or bond order in the ground state of glyoxal.

The ground state corresponds to the following configuration in which the two doublets π are found in MOs Ψ_1 and Ψ_2. For the bond index, we have

$$I_{ij} = \sum_k C_{ki} C_{kj} \times 2$$

then, for bond 12 of glyoxal we have **Fig. VII-T-41**.

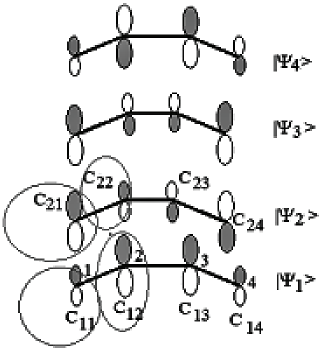


Figure VII-T-41: Calculation of the bond 12 order of glyoxal

Recall that the bond index of bond 12 is given by

$$I_{12} = (C_{11}C_{12} + C_{21}C_{22}) \times 2 \textit{ electrons} \text{ so that:}$$
$$I_{12} = \left(\tfrac{1}{2} \times \tfrac{1}{2} + 0.5944 \times 0.3828\right) \times 2 = \mathbf{0.9551}$$

similarly, for bond 23 we have

$$I_{23} = (C_{12}C_{13} + C_{22}C_{23}) \times 2 \textit{ electrons} \text{ so that}$$
$$I_{23} = \left(\tfrac{1}{2} \times \tfrac{1}{2} + 0.3828 \times -0.3828\right) \times 2 = \mathbf{0.2069}$$

7) Calculate the π electron populations in the ground state.

ANSWER

We can also determine the electron population carried by each atom. We have

$$q_i = 2e \sum_{j=1}^{N_{occ}} (C_{ij})^2$$

where N_{occ} represents the number of occupied MOs. For atoms 1 and 4 of glyoxal we have

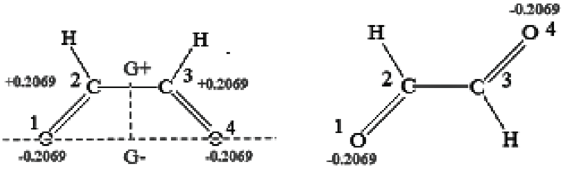
$$q_1 = 2\sum_{j=1}^{2}(C_{j1})^2 = 2\times\left((C_{11})^2+(C_{21})^2\right)$$
$$= 2\times\left(\left(\frac{1}{2}\right)^2+(0.5944)^2\right) = 1.2069 = q_4$$

Similarly, for atoms 2 and 3 we have

$$q_2 = 2\sum_{j=1}^{2}(C_{j2})^2 = 2\times\left((C_{12})^2+(C_{22})^2\right)$$
$$= 2\times\left(\left(\frac{1}{2}\right)^2+(0.3828)^2\right) = 0.7931 = q_3$$

$$Atom\ 1\ or\ 4 : Q_1 = 1-q_1 = 1-1.2069 = -0.2069$$
$$Atom\ 2\ or\ 3 : Q_2 = 1-q_2 = 1-0.7931 = 0.2069$$

so that, for the cisoid and transoid forms respectively, we have the π electron populations in the ground state



Cisoid form Transoid form

Figure VII-T-42: π electron populations in the ground state for glyoxal.

We can easily understand why only the cisoid form has a dipole moment.

CHAPTER VIII

CHEMICAL REACTIVITY AND MOLECULAR ORBITALS: ELECTROCYCLIC REACTIONS

In this last chapter, we shall show how the concepts discussed above can be applied to predict chemical reactivity.

Chemical reactivity is the way in which a chemical reaction transforms matter. During a reaction, the chemical species that constitute matter are modified. The species that are consumed are called reactants. The species formed during the reaction are called reaction products. Anyone investigating chemical reactivity is looking to determine, from a number of reagents, the ways they will turn into products. We shall see that the use of quantum theory makes it possible to predict the evolution of such reactions. This perspective defines a field of chemistry called theoretical chemistry or, more precisely, quantum chemistry because it studies chemical reactions in the light of mathematical theories such as quantum mechanics.

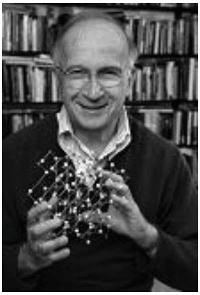
This course has undertaken a slow progression towards an elementary knowledge of quantum chemistry. The elements that we have acquired allow us now to approach the simple case of electrocyclic reactions.

We have seen, during the development of the theory of molecular orbitals, the importance of establishing correlation diagrams between atomic orbitals and molecular orbitals. These correlation diagrams, when applied to polyatomic molecules such as conjugated polyenes, make it possible to obtain important results concerning the evolution of reactants towards the products of a reaction. We shall therefore begin the study of electrocyclic reactions. Let us take for example, the reaction of cyclization of butadiene to cyclobutene and the reverse reaction of the opening of the cycle.

Consider a conjugated polyene with n double bonds. This polyene can undergo cyclization reactions (and conversely the opening of the cycles formed).

These reactions were called electrocyclic reactions by Woodward[1] and Hoffmann[2] who established predictive rules for the stereochemistry of these reactions.

R. Woodward



R. Hoffmann

These rules, called Woodward-Hoffmann rules, are based on the theory of molecular orbitals of systems, the principle characteristics of which we gave in the previous chapter

VIII-I. Electrocyclic Reactions

An electrocyclic reaction can be schematized as follows.

Where the chain connecting the ends of the molecule has n conjugated double bonds, that is to say alternated with single bonds, the ends each carrying a double bond.

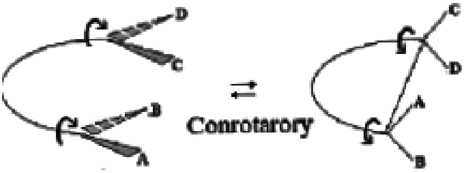


Figure VIII-1: Conrotatory process.

We can consider the type of cyclization-opening: in the *conrotatory* mode, the ends of the molecule rotate in the same direction, while in the *disrotatory* mode, the ends of the molecule rotate in opposite directions.

---

[1] Robert Burns Woodward (1917-1979). American theoretical chemist and winner of the Nobel Prize in Chemistry in 1965.

[2] Roald Hoffmann, born Roald Safran (born in 1937). American chemist and winner of the Nobel Prize in Chemistry in 1987.

We can see the importance of distinguishing between these two processes because the stereochemistry of the molecule obtained with this or that process is different, taking into account the differences between the substituents A, B, C, and D.

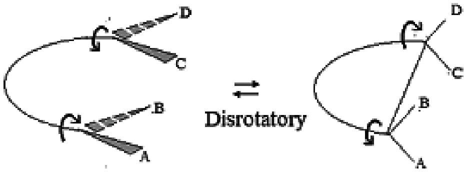


Figure VIII-2: Disrotaory process.

In general, electrocyclic reactions can be carried out thermally or photochemically, according to the conrotatory or disrotatory process.

The result of these reactions is not explained by the electrostatic (charge repulsion) or steric (bulk) effects of the substituents. Such interpretations often give results that are contrary to our predictions. This led Woodward and Hoffmann to propose that the stereochemistry of electrocyclic reactions is controlled by the symmetry of the highest occupied atomic orbital (HO) of the open product. This prediction is based on selection rules.

VIII-II. Woodward-Hoffmann's Selection Rules

We shall discuss here neutral molecules and ionic molecules.

1. Neutral molecules

a. Example of the cyclization of butadiene to cyclobutene

Consider for example the cyclization of butadiene to cyclobutene. The following figure shows the butadiene molecule (left) and the cyclobutene molecule (right) in interconversion.

We have shown the planes of symmetry of the molecule, in particular the P plane, with respect to which we shall define the symmetry of the atomic orbitals.

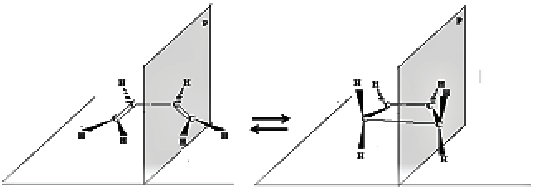


Figure VIII-3: Cyclization of butadiene.

In this type of reaction some orbitals undergo profound changes. These are the four molecular orbitals π of butadiene, Ψ_1, Ψ_2, Ψ_3, and Ψ_4, and the orbitals σ, σ*, π, and π* of cyclobutene, which can be represented schematically as follows (**Fig. VIII-4**).

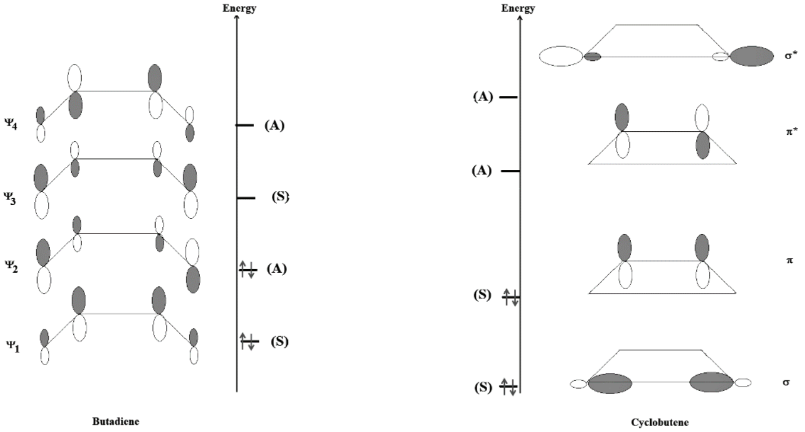


Figure VIII-4: Energy levels of butadiene and cyclobutene.

We have also included the scale of the energies as well as the symmetry of the orbitals with respect to plane P. Taking into account the signs of the coefficients in each orbital (gray = sign +; white = sign -) we can deduce the symmetry of the molecular orbital: (S) for symmetric and (A) for antisymmetric. This notation will be very useful to us in constructing the correlation diagram of the butadiene-cyclobutene reaction.

The separation limit (blue dotted line) between the occupied atomic orbitals and the vacant atomic orbitals in the system of orbitals that undergo the greatest transformations in the two molecules is indicated on this diagram. Among these orbitals, some will play an important role: the highest occupied atomic orbital (HO) and the lowest vacant atomic orbital (LV).

If the process is thermal, according to Woodward and Hoffmann, we start from the ground state of butadiene, which includes 2 electrons in the molecular orbital HO Ψ_2. The reaction is done by a binding interaction in the HO by overlapping the lobes of the same sign, the symmetry of the orbital being preserved throughout the process.

It can thus be seen that, in the case of butadiene, the HO being antisymmetric with respect to plane P, the reaction leading to the positive overlap of the lobes of the ends of the orbital ends of HO is the *conrotatory* movement.

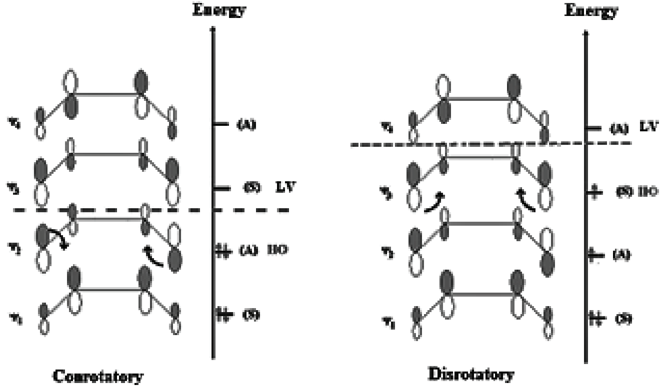


Figure VIII-5: Conrotatory (left) and disrotatory (right) processes of butadiene cyclization.

On the contrary, in a photochemical process, the HO has the orbital Ψ_3, which is symmetrical with respect to P. The movement will therefore be *disrotatory*.

In the thermal process the molecules react in their ground state.

If the molecule contains 4q electrons, then the HO has the orbital number 2q and is therefore an even-numbered orbital.

If the molecule contains 4q+2 electrons, the HO has the number 2q+1 and is an odd-numbered orbital.

Coulson has shown that the energies of molecular orbitals and the coefficients of linear polyenes can be predicted by the formulas that bear his name

$$\boxed{E_p = \alpha + 2\beta \cos\left(\frac{p\pi}{n+1}\right)}$$

$$\boxed{C_p^k = \sqrt{\frac{2}{n+1}}\,\sin\left(\frac{pk\pi}{n+1}\right)}$$

where n is the number of polyene atoms; p is the number of the molecular orbital counting from the lowest energy MO; and k is the number of the atom considered. For example, in butadiene we can calculate the coefficients of the extreme atoms of the HO orbital and thus realize the symmetry of the latter with respect to plane P. Thus, we find

$$C_2^1 = 0.601 \text{ and } C_2^4 = -0.601$$

and HO is therefore asymmetrical.

Using this formula, we can determine whether the HO is symmetrical or antisymmetric, which makes it possible to determine the disrotatory or conrotatory process of the reaction.

In photochemical reactions, molecules react in their first excited state. If the molecule contains 4q electrons, the HO in the first excited state has the number 2q+1 and is therefore odd.

If the molecule contains 4q+2 electrons, the HO of the first excited state has the number 2q+2 is and even.

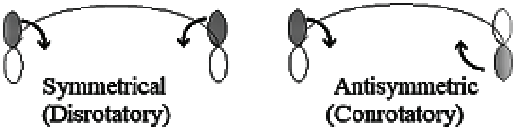


Figure VIII-6: Disrotatory (left) and conrotatory (right) movement.

b. Example of cyclization of hexatriene to cyclohexadiene.

Fig. VIII-7 presents the cyclization of hexatriene to cyclohexadiene.

Using Coulson's formulas, we can quickly determine the energy levels and coefficients of the π molecular orbitals for hexatriene.

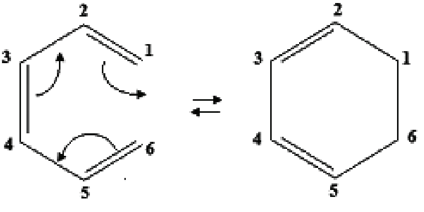


Figure VIII-7: Cyclization of hexatriene to cyclohexadiene.

For the energy levels we have

$$E_p = \alpha + 2\beta \cos\left(\frac{p\pi}{n+1}\right)$$

$$C_p^k = \sqrt{\frac{2}{n+1}} \sin\left(\frac{pk\pi}{n+1}\right)$$

Energies and coefficients obtained from the above formulas are given in **Table VIII-1**.

Table VIII-1: Energies and coefficients for hexatriene

E	C_1	C_2	C_3	C_4	C_5	C_6
$E_1 = \alpha + 1.802\beta$	0.232	0.418	0.521	0.521	0.418	0.232
$E_2 = \alpha + 1.247\beta$	0.418	0.521	0.232	-0.232	-0.521	-0.418
$E_3 = \alpha + 0.445\beta$	0.521	0.232	-0.418	-0.418	0.232	0.521
$E_4 = \alpha - 0.445\beta$	0.521	$-0,232$	$-0,418$	$0,418$	$0,232$	$-0,521$
$E_5 = \alpha - 1.247\beta$	0.418	-0.521	0.232	0.232	-0.321	0.418
$E_6 = \alpha - 1.802\beta$	0.232	-0.418	0.521	-0.521	0.418	-0.232

We can represent the OM of hexatriene as well, the size of the lobes being proportional to the importance of the coefficients.

It can clearly be seen that, taking into account the symmetry of the HO, the thermal cyclization in cyclohexadiene takes place according to a disrotatory process.

A photochemical process will affect the status of orbital Ψ_4, which becomes HO by the excitation of an electron. Therefore the overlap of the lobes at the extremities will happen according to a conrotatory process.

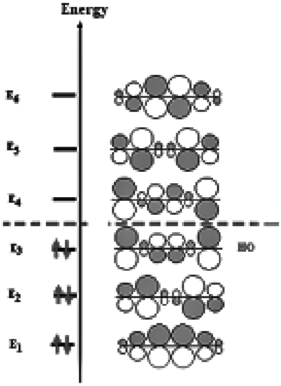


Figure VIII-8: Energies and MO coefficients of hexatriene.

2. Ionic molecules

The reasoning is the same for ionic molecules. It is sufficient to add or subtract the number of electrons from the ion and to consider the HO orbital under these conditions.

Consider the allyl cation $C_3H_5^+$, which is a π system with 3 carbon atoms and 2 electrons, as shown in **Fig. VIII-9**.

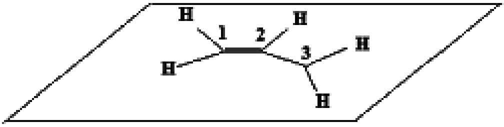


Figure VIII-9: Allyl system.

By applying the linear combination of the atomic orbital $2p_z$, we are led to the secular equations describing the system π

$$\begin{cases} C_1(\alpha - \langle E \rangle) + C_2\beta = 0 \\ C_1\beta + C_2(\alpha - \langle E \rangle) + C_3\beta = 0 \\ C_2\beta + C_3(\alpha - \langle E \rangle) + C_4\beta = 0 \end{cases}$$

The secular determinant is

$$\begin{vmatrix} \alpha - \langle E \rangle & \beta & 0 \\ \beta & \alpha - \langle E \rangle & \beta \\ 0 & \beta & \alpha - \langle E \rangle \end{vmatrix} = 0$$

Dividing these equations by β, we come to

$$\begin{vmatrix} \frac{\alpha - \langle E \rangle}{\beta} & 1 & 0 \\ 1 & \frac{\alpha - \langle E \rangle}{\beta} & 1 \\ 0 & 1 & \frac{\alpha - \langle E \rangle}{\beta} \end{vmatrix} = 0$$

and putting

$$x = \frac{\alpha - \langle E \rangle}{\beta}$$

the secular determinant becomes

$$\begin{vmatrix} x & 1 & 0 \\ 1 & x & 1 \\ 0 & 1 & x \end{vmatrix} = 0$$

so that:

$$x^3 - 2x = 0$$

This equation has the following solutions

$$x_1 = \sqrt{2}; \; x_2 = 0; \quad x_3 = -\sqrt{2}$$

i.e., for energies

$$\langle E \rangle_1 = \alpha + \beta\sqrt{2}$$

$$\langle E \rangle_2 = \alpha$$

$$\langle E \rangle_3 = \alpha - \beta\sqrt{2}$$

The coefficients of atomic orbitals can be obtained using the Coulson formula met above, i.e.

$$C_p^k = \sqrt{\frac{2}{n+1}}\,\sin\left(\frac{pk\pi}{n+1}\right)$$

in which n = 3. Then, for MO 1, we have

$$C_p^1 = \sqrt{\frac{2}{3+1}}\,\sin\left(\frac{p\pi}{3+1}\right)$$

$$C_2^1 = \sqrt{\frac{2}{3+1}}\,\sin\left(\frac{\pi}{3+1}\right) = 0.5$$

$$C_2^1 = \sqrt{\frac{2}{3+1}}\,\sin\left(\frac{2\pi}{3+1}\right) = 0.707$$

$$C_2^1 = \sqrt{\frac{2}{3+1}}\,\sin\left(\frac{3\pi}{3+1}\right) = 0.5$$

For MO 2

$$C_1^2 = \sqrt{\frac{2}{3+1}}\,\sin\left(\frac{2\pi}{3+1}\right) = 0.707$$

$$C_2^2 = \sqrt{\frac{2}{3+1}}\,\sin\left(\frac{2 * 2\pi}{3+1}\right) = 0$$

$$C_3^2 = \sqrt{\frac{2}{3+1}}\,\sin\left(\frac{3 * 2\pi}{3+1}\right) = -0.707$$

For MO 3

$$C_1^3 = \sqrt{\frac{2}{3+1}}\,\sin\left(\frac{3\times\pi}{3+1}\right) = 0.5$$

$$C_2^3 = \sqrt{\frac{2}{3+1}}\,\sin\left(\frac{3\times 2\times\pi}{3+1}\right) = -0.707$$

$$C_3^3 = \sqrt{\frac{2}{3+1}}\,\sin\left(\frac{3\times 3\times\pi}{3+1}\right) = 0.5$$

We therefore have the representation of the molecular orbitals π of the allyl cation (2 electrons) and the allyl anion (4 electrons).

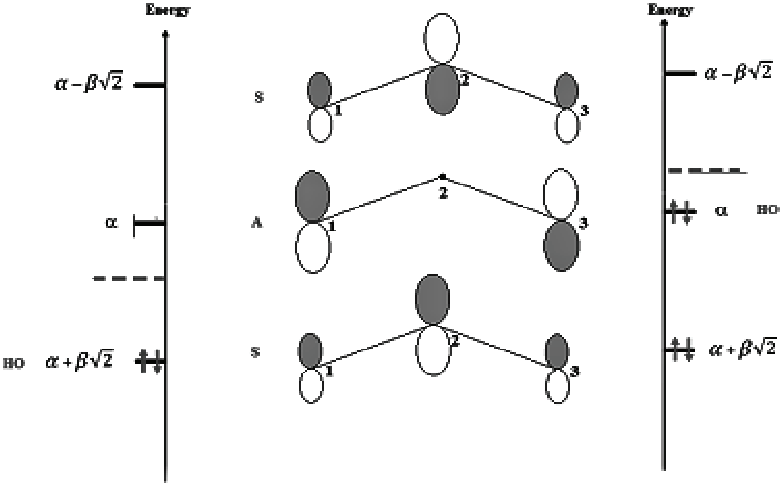


Figure VIII-10: π MOs of the cation (left) and of the allyl anion (right).

We can see that in the case of the allyl cation, the HO being symmetrical, the movement towards the thermal cyclization will be disrotatory, while the movement towards the photochemical cyclization will be conrotatory, since the HO will be the 2nd orbital, which is antisymmetric.

On the contrary in the case of the allyl anion, the HO being antisymmetrical, one can provide a conrotatory movement for thermal cyclization and a disrotatory movement for photochemical cyclization.

We have given here only a short overview of the possibilities of predicting chemical reactivity as represented by the Woodward-Hoffmann rules. In so doing, we have gone beyond the scope of the current work, the focus of which is an approach to the structure of matter and the theories involved.

CONCLUSION

In this didactic work, offering an introduction to the structure and energy of atoms and molecules, we have attempted a graduated presentation of current knowledge in this area, from simplest to most complicated.

In the **first chapter**, we enumerated the constituent elements of atoms. In the **second chapter**, we approached the study of light to demonstrate experimentally the character of both the wave-like and corpuscular nature of electromagnetic vibrations in general. This chapter allowed us to set up the basic formalism concerning wave phenomena.

All these notions have led us, in the **third chapter**, to look at material particles with an identical approach and consider both the corpuscular and wave-like behavior of matter in general.

The **fourth chapter** showed us how various experiments, such as the Franck-Hertz experiment or the spectra of the atomic hydrogen and the hydrogenic atoms, are explanatorily useful only if we consider that the energy of the electrons in the atom is quantized. This empirical hypothesis, born of experience, gradually acquired a theoretical explanation in the **fifth chapter** with the use of so-called semi-classical theories like that of the Bohr-Sommerfeld model, which is based on a classical approach, but where quantization elements are introduced to improve the accuracy. Despite great quantitative success, this theory cannot fully explain the energy stability of the atom when considered in the classical planetary model.

In the **sixth chapter**, we examined the full quantum theory of the atom in which all reference to a classic trajectory for the electron moving in the atom is abandoned. The electron is described as a stationary wave, represented by a wave function through the resolution of the Schrödinger equation, which allows us to specify the details of the quantization of energy with the model of the stationary states. This model, extended to atoms with several electrons, makes it possible to describe each atom by an electronic configuration and to account for the physicochemical properties by explaining the periodic classification of the elements.

The **seventh chapter**, the longest in this work, using the logic of what we know about atoms, is devoted to examining the chemical bond, both from the electronic point of view with the elementary Lewis theory, which made it possible to pose the principles defining a chemical bond between two atoms, and with the theory of molecular orbitals based on the linear combination of atomic orbitals. If we are interested in polyatomic molecules, the notion of geometry comes into play and the shape of molecules in space. The predictive nature of a theory such as the VSEPR method combined with the theory of hybridization of atomic orbitals and the theory of molecular orbitals has made it possible to obtain the most global image possible the molecule.

Finally, the **eighth chapter**, which goes beyond the framework of the study of matter, has looked at how the knowledge of molecules can be put to work when attempting to predict their reactivity. Thus, the use of the theory of π molecular orbitals of polyenes can account for the experimental results of electrocyclic and sigmatropic reactions.

This modest study has illustrated the path by which our knowledge of matter has progressed, showing the close link between experience and theory. We hope that it has given students, starting out on this path, the desire to learn more.

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