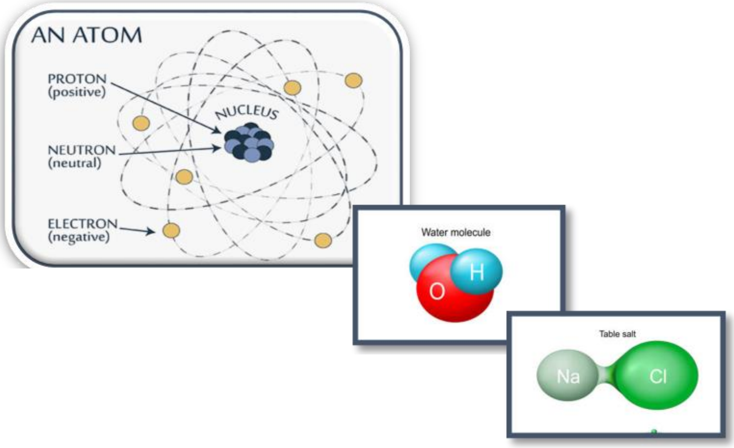
DEMOCRATIC AND POPULAR REPUBLIC OF ALGERIA

MINISTRY OF HIGHER EDUCATION AND SCIENTIFIC RESEARCH

ABDELHAFID BOUSSOUF University Center – Mila

Institute of Sciences and Technology



Structure of Matter courses

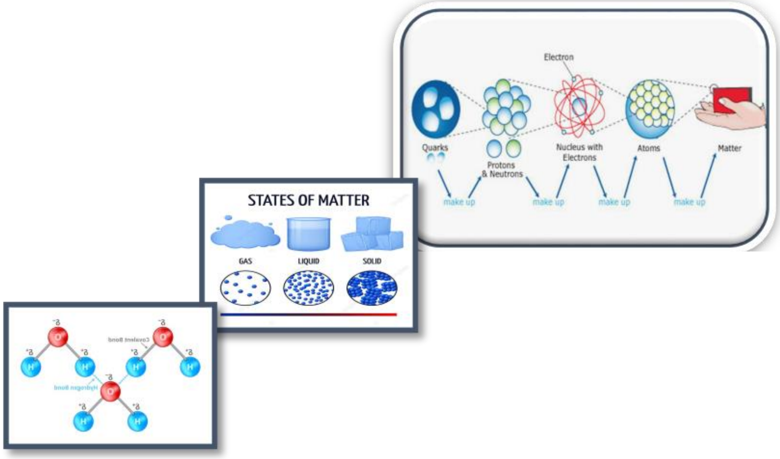


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Table of Contents

Summary

Introduction

Chapter N° I : Fundamental Concepts

Chapter N° II : Main components of matter

Chapter N° III : Radioactivity

Chapter N° IV : Atomic spectra and Bohr's atomic model

Chapter N° V : Periodic table

Chapter N° VI : Chemical Bonding

Bibliographic references

List of figures

Figure **page**

Introduction

Understanding the structure of matter is fundamental to unraveling the mysteries of the physical world. From the smallest subatomic particles to the complex materials that shape our daily lives, the study of matter forms the cornerstone of chemistry, physics, materials science, and engineering. This pedagogical booklet is designed to provide first-year students in the Sciences and Technology common core program with a clear and structured approach to mastering the essential concepts of atomic and molecular structure.

By exploring the composition of matter, its fundamental particles, and the forces that govern its behavior, this document aims to build a solid foundation for further scientific inquiry. Whether your interest lies in chemical reactions, material properties, or advanced technologies, a deep comprehension of matter's structure will be indispensable.

Organized into six comprehensive chapters, this document begins with fundamental principles, progresses through atomic theory and electronic configurations, and concludes with chemical bonding and the periodic table. Each section is crafted to enhance conceptual understanding while preparing students for practical applications in research and industry.

We hope this resource serves as a valuable guide in your academic journey, fostering both curiosity and competence in the fascinating study of matter's architecture.

Chapter I

Fundamental concepts

Chapter N° I :

Fundamental Concepts

1. Introduction :

Chemistry is the scientific study of matter: its composition, structure, properties, behavior, and the energy changes that accompany its transformations.

2. Definitions :

2.1. **Matter:** anything that has mass and takes up space.

2.1.1. States of Matter:

- **Gase :** have no definite shape or volume. They expand to fill whatever container they are placed in. They are highly compressible.
- **Liquid :** have no definite shape, but have a definite volume. They are slightly compressible.
- **Solid :** have definite shape and definite volume. They are incompressible.

Note: the state of a given sample of matter depends on the strength of the forces among the particles contained in the matter. Whether a substance is a gas, a liquid, or a solid depends on its temperature and pressure. We can convert state of matter from one form to another by changing temperature and pressure ; however, the chemical identity of substance does not change (physical change).

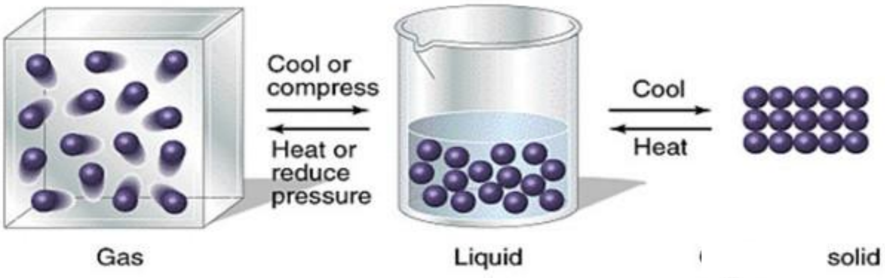


Figure 1 : The different states of matter and their transitions

2.1.2. Atom : The fundamental components of matter. They are the building blocks of everything that occupies space or has mass.

2.1.3. Molecule : The simplest unit of a chemical substance, usually a group of two or more atoms.

2.2. Mole (mol): The amount of a substance that contains as many elementary particles (atoms,molecules or ions), where each mole has number of 6.022×10^{23}particles.

1mole = 6.022×10^{23}particles = Avogadro's number N_a

1 mol (Al) = 6.022×10^{23} atoms

1 mol (CO_2) = 6.022×10^{23} molecules

1 mol (NaCl) = 6.022×10^{23} Na^+ ions = 6.022×10^{23} Cl^- ions

2.3. Avogadro's number : The number of formula units in a mole.

1 mole of hydrogen atoms = 6.022×10^{23} atoms of hydrogen

1 mole of water molecules = 6.022×10^{23} molecules of water

1 mole of Na^+ ions = 6.022×10^{23} ions of Na^+

2.4. Atomic mass unit (amu) : Atomic mass is expressed as a multiple of one-twelfth the mass of the ^{12}C, ($1.992646547\times10^{-23}$ g), which is assigned an atomic mass of exactly 12 units. On this scale, 1 atomic mass unit (amu) corresponds to $1.660539040\times10^{-24}$ gram. The atomic mass unit is also called the dalton (Da), after English chemist *John Dalton*.

2.5. Formula and molecular weight: is the sum of the atomic weights (in atomic mass units amu) of all atoms in the compound's formula, for both ionic and covalent compounds. The molecular weight (MW) is the same as the formula weight, however, it is used only for the covalent compounds.

Example :

MW of H_2SO_4 : 2 × (1 amu) for H + 1 × (32 amu) for S + 4 × (16 amu) for O = 98 amu.

MW or FW of $AlCl_3$: 1 × (27 amu) for Al + 3 × (35.5 amu) for Cl = 133.5 amu.

2.6. Molar mass : molar mass is defined as the mass of one mole of a substance, given in grams. It can be described as the formula weight of a substance expressed in grams.

Formula weight of H_2O = 18 amu → molar mass = 18 g (mass of 1 mole H_2O)
Formula weight of NaCl = 58.5 amu → molar mass = 58.5 g (mass of 1 mole NaCl)

2.7. Atomic weight (Atomic mass) : an element's atomic mass is the average mass of its atoms, measured in an atomic mass unit (amu, commonly known as *daltons* or Da). The atomic mass of an element is a weighted average of all its isotopes, calculated by multiplying the mass of each isotope by its relative abundance. Atomic mass is also known as atomic weight, but the term "mass" is more appropriate.

2.8. Molar volume : Is the volume occupied by one mole of a chemical element or chemical compound at standard temperature and pressure (STP), The molar volume (Vm).

2.9. Lavoisier's Law of Conservation of Mass : With the development of more precise ideas on elements, compounds and mixtures, scientists began to investigate how and why substances react. French chemist ***Antoine Lavoisier*** laid the foundation to the scientific investigation of matter by describing that substances react according to certain laws. These laws are called the laws of chemical combination and eventually formed the basis of Dalton's Atomic Theory of Matter.

Law of Conservation of Mass: According to this law, during any physical or chemical change, the total mass of the products remains equal to the total mass of the reactants.

$$\mathrm{HgO\ (s)} \ \rightarrow \mathrm{Hg\ (l)} + \frac{1}{2}\mathrm{O_2(g)}$$

$$100\ \mathrm{g} \qquad 92.6\ \mathrm{g} \qquad 7.4\ \mathrm{g}$$

This law is also known as the "law of indestructibility of matter."

2.10. Chemical Reactions :

$$\mathrm{Reactants} \ \rightarrow \mathrm{Products}$$

Chemical reactions occur when chemical bonds between atoms are formed or broken. The substances that go into a chemical reaction are called the reactants, and the substances produced at the end of the reaction are known as the products.

Example:

$$2\mathrm{HgO}\ (s) \rightarrow 2\mathrm{Hg}\ (l) + \mathrm{O}_2(g)$$

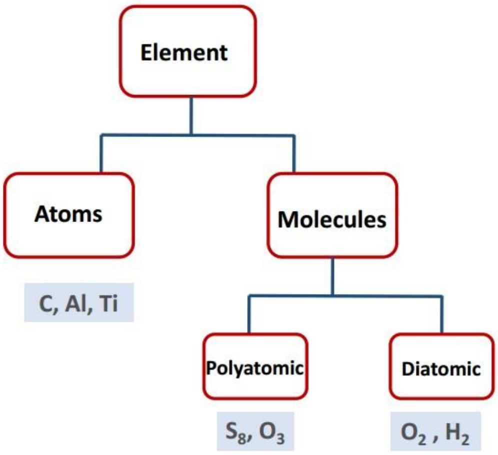
3. Qualitative Aspect of the Matter :

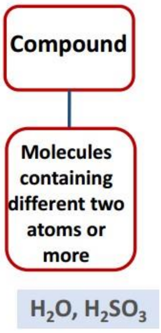
3.1. Element : A substance that consists of identical atoms (e.g., hydrogen, oxygen, and Iron). An element cannot be divided by chemical and physical methods. A total of 116 elements are known (88 occur in nature and chemist have synthesized the others in laboratories).

- **Symbols of elements**: Often an element's name is derived from a Greek, Latin, or German word that describes some property of the element. These symbols usually consist of the first letter or the first two letters of the elements name (F for fluorine and Ne for neon). Sometimes, however, the two letters used are not the first two letters in the name (Zn for zinc).

3.2. Pure Substance: A pure substance will always have the same composition and cannot be further refined. Pure substances can be either elements or compounds.

3.3. Compound: A pure substance made up of two or more elements in a fixed ratio by mass (for example, water H_2O and Sodium chloride NaCl).





3.4. Mixture: A combination of two or more pure substances. Mixtures are divided into two groups :

- **Homogeneous:** The mixture is uniform and throughout and no amount of magnification will reveal the presence of different substances (for example, air, and salt dissolved in water).
- **Heterogeneous:** The mixture is not uniform. Therefore, it contains regions that have different properties from those of other regions (for example, soup, milk, and blood).

Note : If we know the physical properties of individual substances in a heterogeneous mixture, we can use appropriate physical methods to separate the mixture into its component parts. Two methods of separation are distillation and filtration :

- **Distillation :** is a widely used method for separating mixtures based on differences in the boiling points of the components. To separate a mixture of liquids, the mixture can be heated to convert the components with lower boiling points into the gas phase. The vapor is then condensed back into liquid form and collected. Repeating the process on the collected liquid to improve the purity of the product is called double

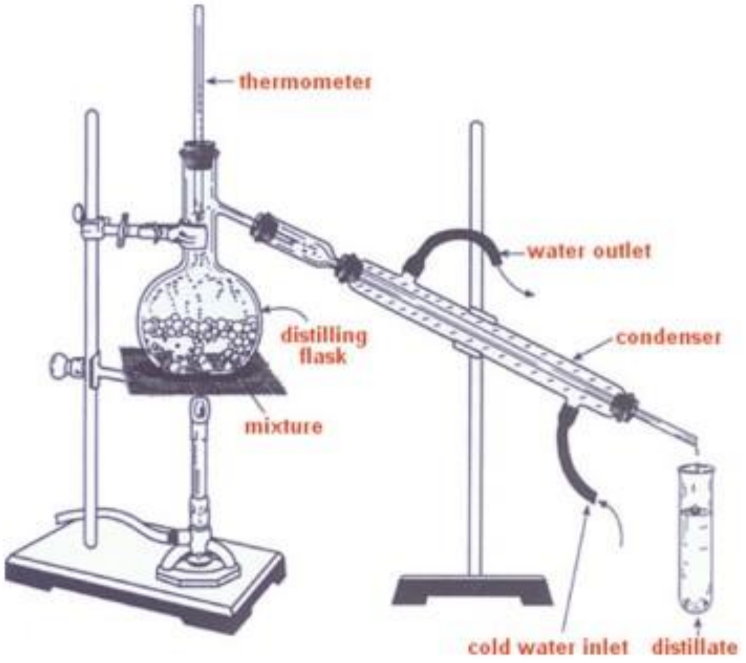


Figure 2 : Distillation setup.

- **Filtration:** Mechanical or physical process used to separate of solids from fluids (liquids or gases) by interposing a medium through which only the fluid can pass.
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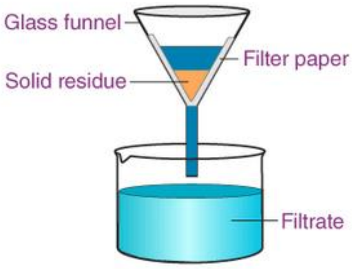

Figure 3: Filtration process

3.5.Solutions :

- **Solution:** A homogeneous mixture of two or more substances consist of :
    - **Solute:** The substance that is being dissolved (present in a smaller amount).
    - **Solvent:** The substance that dissolves the solute (present in a larger amount).

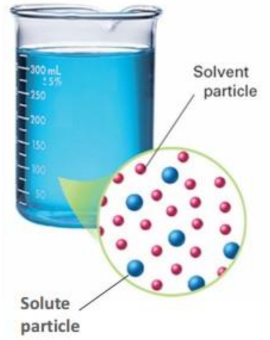

Figure 4: Solution components

- **Saturated solution :** A chemical solution containing the maximum concentration of a solute, that can be dissolved in the solvent at given conditions. Any additional solute will not dissolve.

- **Diluted Solution :** A solution with a relatively low concentration of solute. Dilution is the process of decreasing the concentration of a solute, usually by adding more solvent (e.g., adding more water to the solution). To dilute a solution means to add more solvent without adding more solute.

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4. Quantitative aspect of matter :

4.1. Concentrations : The amount of solute present in a given quantity of a solvent or solution.

4.2 Molarity (M): The number of moles of solute dissolved in one liter of solution.

Molarity *(M)*

$$M = \frac{\text{moles of solute}}{\text{liters of } \boxed{\text{solution}}}$$

Example : A solution has a volume of 2.0 L and contains 36.0 g of glucose ($C_6H_{12}O_6$). If the molar mass of glucose is 180 g/mol, what is the molarity of the solution ?

n glucose = wt (g) / Mw ($g.mol^{-1}$) = 36.0 g/ 180 $g.mol^{-1}$ = 0.2 mol

M = n (mol)/ V (L) = 0.2 mol / 2.0 L = 0.1 $mol.L^{-1}$

4.3. Molality (m): The number of moles of solute dissolved in one kilogram of solvent

Molality *(m)*

$$m = \frac{\text{moles of solute}}{\text{mass of } \boxed{\text{solvent}} \text{ (kg)}}$$

Example : What is the molality of a 5.86 M ethanol (C_2H_5OH) solution whose density is 0.927 g/mL?

$$m = \frac{\text{moles of solute}}{\text{mass of solvent (kg)}}$$

Assume 1 L of solution :

$$\text{Mass of solute} = 5.86 \text{ mol} \times 46.0 \text{ g}\cdot\text{mol}^{-1} = 270 \text{ g ethanol}$$

$$\text{Mass of solution} = 1000 \text{ mL} \times 0.927 \text{ g}\cdot\text{mL}^{-1} = 927 \text{ g}$$

$$\text{mass of solvent} = \text{mass of solution} - \text{mass of solute}$$

$$= 927 \text{ g} - 270 \text{ g} = 657 \text{ g} = 0.657 \text{ kg}$$

$$m = \frac{\text{moles of solute}}{\text{mass of solvent (kg)}} = \frac{5.86 \text{ moles } C_2H_5OH}{0.657 \text{ kg solvent}} = 8.92\ m$$

4.4. Normality : A solution is a homogenous mixture of two or more components. Each component of a homogenous solution has the same chemical composition. Therefore, the number of grams equivalent of an element dissolved in one litre of solution is the solution's normality.

- **Definition Normality and Its Formula :**

The term "normality" refers to the number of gram equivalents of solute dissolved in one liter of solution. It is commonly used in the preparation of acid or basic solutions. The units of normality are denoted by the symbols N, (eq/L).

$$\boldsymbol{N = \frac{Gram\ Equivalent\ of\ Solute}{volume\ of\ solution\ in\ litre}}$$

$$\boldsymbol{N = \frac{Weight}{Equivalent\ weight} \times \frac{1000}{V\ (mL)}}$$

$$\boldsymbol{Equivalent\ weight\ = \frac{\textbf{Molecular weight}}{X}}$$

- **Number of Gram Equivalent :** Let's get forward with understanding the concept of gram equivalence.

  We know that : **no of moles = Mass/Molecular weight**

  Number of gram equivalent = Mass/Equivalent weight

  Equivalent weight = Molecular weight / X

(X = valence factor, where valence factor for acids and bases is the number of H^+ and OH^- ions they release in the solution, respectively).

Example 1 : Find the number of gram equivalents present in 0.5 g of HCl.

HCl releases one H^+ ion in the solution, so X = 1.

The molecular weight of HCl = 36.46 g.

So, **equivalent weight =Molecular weight /X** = 36.46/1 = 36.46 g,

and Number of gram equivalent = Mass/Equivalent weight = 0.5/36.46 = 0.0137 eq

So, we get the **number of gram equivalent = 0.0137 eq**

Example 2: Let us take another example of 1.06 g of Na_2CO_3 to understand this concept clearly

the mass of Na_2CO_3 = 1.06 g.

Firstly, Find the equivalent weight of Na_2CO_3.

Since Na_2CO_3 is a **salt**, so the number of positive charges on the cation gives X = 2

Molecular weight = 106 g So, **Equivalent Weight = Molecular weight/X**= 106/2 = 53 g,

and **number of gram equivalent = Mass/Equivalent weight**= 1.06/53 = 0.02 eq

In a chemical equation, the number of grams equivalent of both reactions always remains the same.

The following simple relationship exists between normality, *N*, and molarity, M,

$$N = n \times M$$

M is the molecular weight of moles per litre, and n is some equivalents formed. The number of equivalents is an integer for acid-base reactions, but in a redox reaction.

4.5. Mole Fraction (X_i): Is a unit of concentration, defined to be equal to the number of moles of a component divided by the total number of moles of a solution. Because it is a ratio, mole fraction is a unitless expression. The mole fraction of all components of a solution, when added together, is equal 1.

$$X_i = \frac{n_i}{n_T}, \qquad \sum X_i = 1$$

4.6. Mass Concentration (ρ_i): ρ_i is defined as the mass of a constituent m_i divided by the volume of the mixture V. For a pure chemical the mass concentration equals its density (mass divided by volume), thus the mass concentration of a component in a mixture can be called the density of a component in a mixture. This explains the usage of ρ (the lower case Greek letter rho), the symbol most often used for density.

4.7. Mass Percentage Formula : Mass Percent Fomula can be defined as the way that is used to express a concentration. Mass percent is a way to express the concentration of a substance in a mixture. It can further be defined as the mass of a solute in a mixture divided by the total mass of the mixture, and multiplied by 100%:

$$\text{Mass Percentage} = \frac{\text{Mass of Solute}}{\text{Mass of Solution}} \times 100$$

Practical Exercises:

Exercise 1:

1. Calculate the number of moles and the mass present in:
   - a. 3.612×10^{24} atoms of Zinc (Zn = 65 g/mol)
   - b. 36.12×10^{21} molecules of NaOH (Na = 23 g/mol, O = 16 g/mol, H = 1 g/mol)

2. Calculate the value of the atomic mass unit (u.m.a) in grams and Avogadro's number (N_A), knowing that the mass of one atom of carbon-12 (^{12}C) is 1.99×10^{-23} g.

Exercise 2:

Arrange the following aqueous sulfuric acid (H_2SO_4) solutions in decreasing order of concentration. M(H_2SO_4) = 98 g/mol

a. 1 Normal (1N)
b. 1 Molar (1M)
c. 53 g of H_2SO_4 in 500 ml of solution.

Exercise 3:

The concentration of a sodium nitrate ($NaNO_3$) solution is C = 3 mol/L. It has a density (ρ) of 1159 g/L. Calculate:

1. The mass concentration (T) (M ($NaNO_3$) = 85 g/mol).
2. The mole fraction (X) and the mass percentage (W%).
3. The normality (N) and the molality (m).
4. The number of gram equivalents present in 500 ml of the solution.

Chapter II

Main components of matter

Chapter II :

Main Components of Matter

1. Introduction :

Dalton's Atomic Theory :

The English chemist ***John Dalton*** suggested that all matter is made up of atoms, which were indivisible and indestructible. He also stated that all the atoms of an element were exactly the same, but the atoms of different elements differ in size and mass.

Chemical reactions, according to *Dalton*'s atomic theory, involve a rearrangement of atoms to form products. According to the postulates proposed by *Dalton*, the atomic structure comprises atoms, the smallest particle responsible for the chemical reactions to occur.

The following are the postulates of his theory :

- Every matter is made up of atoms.
- Atoms are indivisible.
- A given element contains only one type of atom
- Each atom has its own constant mass that varies from element to element.
- Atoms undergo rearrangement during a chemical reaction.
- Atoms can neither be created nor destroyed but they can be transformed from one form to another.

Dalton's atomic theory successfully explained the Laws of chemical reactions, namely, the Law of conservation of mass, the Law of constant properties, the Law of multiple proportions and the Law of reciprocal proportions.

Demerits of *Dalton*'s Atomic Theory :

- The theory was unable to explain the existence of isotopes.
- Nothing about the structure of the atom was appropriately explained.
- Later, scientists discovered particles inside the atom that proved the atoms are divisible.

The discovery of particles inside atoms led to a better understanding of chemical species; these particles inside the atoms are called subatomic particles. The discovery of various subatomic particles is as follows:

2. Discovering the Electron :

2.1. Electrical Nature of Matter :

Michael Faraday discovered the two laws of electrolysis while proving that electricity produced by different methods is identical : The amount of chemical change (or decomposition) is directly proportional to the quantity of electricity passing through the solution, and the amounts of different substances deposited or dissolved by the same amount of electricity are proportional to their chemical equivalent weights. In 1833, together with the classicist William Whewell, *Faraday* devised a new nomenclature for electrochemical phenomena based on Greek terminology, which is still widely used today ion, electrode, etc.

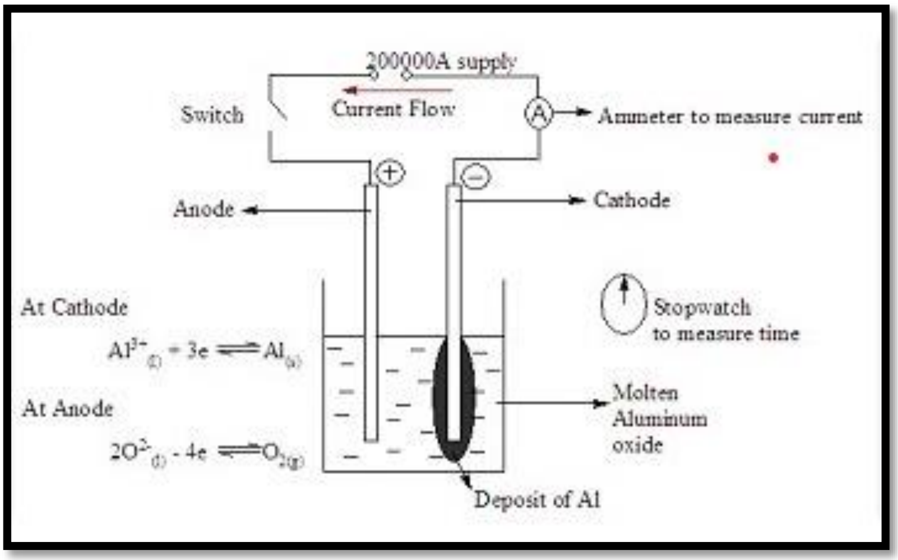


Figure 5 : Electrical Nature of Matter

2.2. Cathode Ray Experiment :

The first concepts concerning electrons emerged from tests with cathode-ray tubes. A typical cathode-ray tube is a partially evacuated glass tube with a piece of metal sealed in either end. The metal parts are referred to as electrodes; the cathode carries a negative charge, while the anode carries a positive charge.

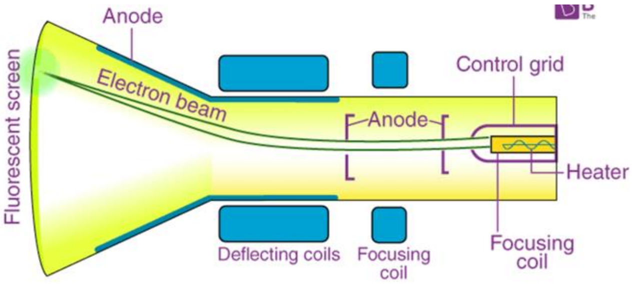


Figure 6 : Cathode ray tube experiment

Observations:

- If a high electrical voltage is applied to the electrodes, an electrical discharge is produced between them. This discharge appears to be a stream of particles emanating from the cathode (there are rays emerging from the cathode towards the anode). These cathode rays cause the residual gas and fluorescent materials to glow, and they can heat metal objects in their path to red heat. These rays were called cathode rays.
- When an external electric field is applied, the cathode rays get deflected towards the positive electrode, but in the absence of an electric field, they travel in a straight line.
- When rotor blades are placed in the path of the cathode rays, they seem to rotate. This proves that the cathode rays are made up of particles of a certain mass so that they have some energy.

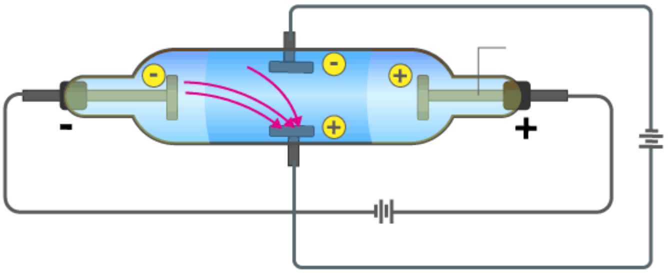


Figure 7 : The direction of cathode rays in absence of an electric field

- With all this evidence, *Thompson* concluded that cathode rays are made of negatively charged particles called “electrons”.

2.3. *J.J. Thomson’s* Experiment (Determination of the e/m Ratio) :

Thomson applied both electrical and magnetic fields to the cathode ray simultaneously. By knowing the strength of the applied fields and measuring the deflection of the particle stream. ***Thomson*** was therefore able to determine the mass-to-charge ratio (e/m) of the particles in the stream by measuring the ray's deflection while adjusting the two fields, and he discovered something astonishing. The negative particles had a mass-to-charge ratio almost 1,000 times lower than that of a hydrogen atom, indicating that they were extremely small - much smaller than the tiniest atom known. This discovery enabled Thomson to state unequivocally that the atom was not the fundamental building block of matter and that smaller (subatomic) particles exist. Thomson originally dubbed these particles corpuscles, but they were later referred to as electrons.

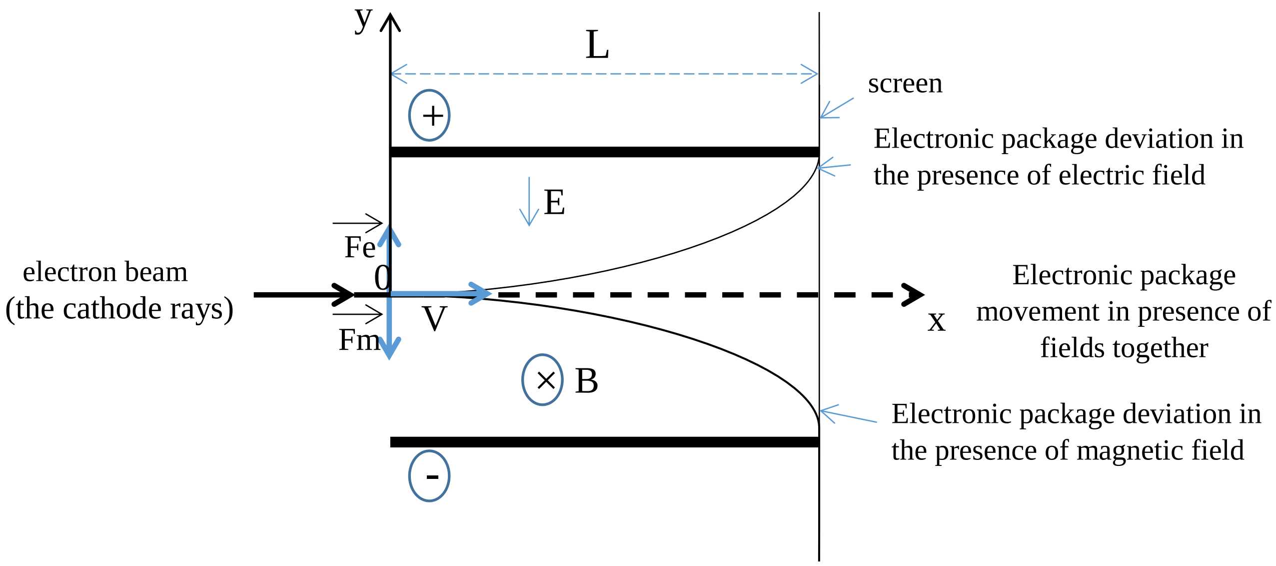


Figure 8 : *J.J. Thomson's* experiment

- The electron beam is deflected toward the positive plate due to electrical force

$\overrightarrow{Fe} = e\vec{E}$, This force acts perpendicular to the direction of the electron's velocity. According to the fundamental equation of dynamics :

$$\sum \vec{F} = m\vec{\gamma}$$

Motion along the ox axis :

The force applied to the electron in the direction of the **ox** the OX axis is zero :

$$F_x = 0 \Rightarrow \gamma_x = 0 \Rightarrow \frac{d^2x}{dt^2} = 0 \Rightarrow \frac{dx}{dt} = const$$

$$\frac{dx}{dt} = v \Rightarrow dx = vdt$$

By integration we obtain :

$$x = vt + c$$

- At $t = 0, \quad x = 0$, So :

$$x = vt \ldots\ldots\ldots..(1)$$

This is the time equation of the electron's motion along the **ox** axis, indicating that the motion along ox is regular.

Motion along the Oy axis :

$$\|\vec{F}\| = m\gamma_y = eE \Rightarrow \gamma_y = \frac{eE}{m} \Rightarrow \frac{dv}{dt} = \frac{eE}{m}$$

- Integrating once of acceleration γ_y gives the v_y velocity :

$$\Rightarrow v_y = \frac{eE}{m}t + c$$

At the moment of time $t = 0,$ $y = 0$, So:

$$\Rightarrow v_y = \frac{eEt}{m} = \frac{dy}{dt}$$

- Integrating a second time gives the distance y :

$$\int dy = \int \frac{eEt}{m}dt \Rightarrow y = \frac{1}{2}\frac{eE}{m}t^2 \dots\dots\dots\dots\dots (2)$$

This is if we consider the principle of y distance to be the entry point of the electron in the electric field t=0⇒y=0

Equation (**2**) is the time equation of electron movement towards the oy axis, and it is a regular accelerated movement.

- **Trajectory equation :**

From equation (**1)** we conclude that $t = \frac{x}{v}$ substituting into equation (**2**) gives :

$$y = \frac{1}{2}\frac{eE}{m}\frac{x^2}{v^2} \dots\dots\dots\dots\dots\dots..(3)$$

This is the equation of a parabola, giving y deviation to any distance x the electron travels under the electric field.

At the end of the electric field $x = L$, substituting into equation 3 we find :

$$y = \frac{1}{2}\frac{eE}{m}\frac{L^2}{v^2} \dots\dots\dots\dots\dots.(4)$$

- From this relationship we note :

1- The stronger the electric field, the greater the deflection.
2- The longer the deflecting plates, the greater the deflection.
3- The faster the electron the smaller the deflection.
4- The deflection is directly proportional to the charge and inversely proportional to the mass.

This can be summarized as follows :

- The measured deflection fits into the constant related to the device (E, L) which can be easily measured.
- The velocity of the electron can be measured by applying a suitable vertical magnetic field in addition to the electric field so that :

If the intensity of both forces is equal $F_e = F_m$ the following can be written :

$$\mathrm{q.v.B} = \mathrm{q.E} \Rightarrow v = \frac{E}{B}$$

With compensation in equation (**4**) we find :

$$\frac{e}{m} = \frac{2y}{L^2}\frac{E}{B^2} \dots\dots\dots\dots\dots.(5)$$

And since E = U/d:

d : Distance between the plates.

U : Potential difference between the plates.

$$\frac{e}{m} = \frac{2y}{L^2}\frac{U}{d}\frac{1}{B^2}$$

By conducting a numerical application of all values obtained experimentally we calculate the e/m ratio value where we find :

$$\boldsymbol{\frac{e}{m} = 1{,}759.10^{11}\ coulomb/K}$$

Thomson's experiments included the use of twenty different metals as cathodes and various gases to carry the discharge. Every metal-gas combination produced the same charge-to-mass ratio for cathode rays. This led to the conclusion that electrons are common to all of the metals employed in the studies, and most likely to all atoms in general.

2.4. The *Millikan* Experiment :

Millikan measured the charge of electrons. The experiment consisted of measuring the electric charge carried by tiny oil droplets suspended in an electric field. Using an atomizer, oil droplets were sprayed into the test chamber. As the droplets slowly settled through the air, high-energy X rays were passed through the chamber to charge the droplets negatively (the X rays caused air molecules to give up electrons to the oil). By using a beam of light and a small telescope, *Millikan* could study the motion of a single droplet. When the electrical charge on the plates was increased enough to balance the effect of gravity, a droplet could be suspended motionless. At this point, the gravitational force would equal the electrical force. Measurements made in the motionless state, when inserted into the equations for the forces acting on the droplet, enabled *Millikan* to calculate the charge carried by the droplet.

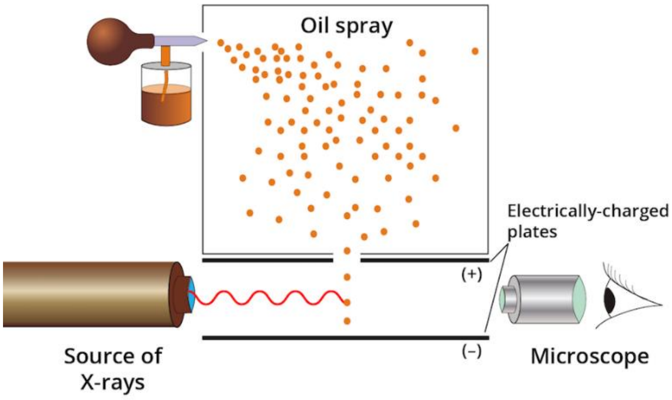
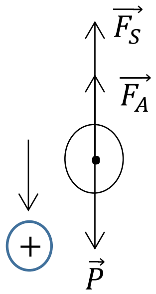


Figure 9 : *Millikan's* experiment

- To better understand exactly what's happening, let's follow the motion of a single drop of oil.
- the droplet falls rapidly with the effect of terrestrial gravity, but also quickly ceases to fall because air resistance increases by increasing speed, reaching its limit speed, becoming suspended (obviously the terminal velocity will vary from drop to drop depending on its mass).



There are three main forces affecting the oil droplet, the force of gravity downwards (the force of gravity), the force of Stokes (the force of air resistance), and the driving force of Archimedes (often neglected).

- When the oil droplet reaches its terminal velocity, its acceleration is zero :

$$F_S + F_A = P$$

$$F_S = 6\pi r\eta v, \quad F_A = \frac{4}{3}\pi r^3\rho_{air} g, \quad P = mg = \frac{4}{3}\pi r^3\rho_{oil} g$$

F_s : Stokes' drag force.

F_A: The driving force of Archimedes.

ρ_{oil} :Density of the oil.

m : Oil droplet mass.

g: gravitational acceleration.

ρ_{air} :density of air.

v : velocity of the droplet.

η : viscosity of air

r : Radius of the droplet.

$$F_S + F_A = P \Rightarrow 6\pi r\eta v_0 + \frac{4}{3}\pi r^3\rho_{air} g = \frac{4}{3}\pi r^3\rho_{oil} g$$

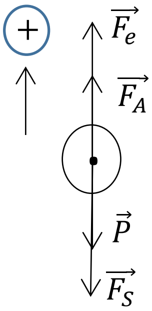
$$\Rightarrow \boldsymbol{v_0} = \frac{\boldsymbol{2r^2 g(\rho_{oil} - \rho_{air})}}{\boldsymbol{9\eta}}$$

Oil particles are of course equivalent, so *Millikan* exposed the room to X-rays.

• X-ray of air lost some of its electrons, which motivated the neutral particles to acquire them, becoming negative of the charge.

• After charging the room and having voltage teams, an electric field will be generated that affects the oil drops, the direction of the electric field from the top to the bottom, and because the oil drops are negative, the "opposite" of the field : from the bottom to the top.

In this case there are four main forces affecting the drop of oil which is the force of gravity, the electrical force to the top, the Stokes' drag force, the thrust of *archimides*.



$F_e = qE.$

F_e: electric force

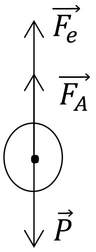
q: electric charge

E :electric field

$$F_e + F_A = P + F_S \Rightarrow qE + \frac{4}{3}\pi r^3 \rho_{air} g = \frac{4}{3}\pi r^3 \rho_h g + 6\pi r\tau v$$

$$\Rightarrow q = \frac{\frac{4}{3}\pi r^3 g(\rho_h - \rho_{air}) + 6\pi r\tau v}{E}$$

- The drop of oil will move upwards until the gravitational force is equal to the force the electric field affects, and here it will stop momentarily and remain stationary. In this case three forces affect the drop of oil (the force of Stokes here is non-existent) which is, the force of gravity, the electric force upwards and the thrust of *archimides*.



$$F_e + F_A = P \Rightarrow qE' + \tfrac{4}{3}\pi r^3 \rho_{air} g = \tfrac{4}{3}\pi r^3 \rho_h g$$

$$\Rightarrow q = \frac{\frac{4}{3}\pi r^3 g(\rho_h - \rho_{air})}{E'}$$

Some oil droplets are larger than others, which means they have the ability to capture more than one electron, which means they need a "stronger" electric field to stop them moving.

Thus, *Millikan* changed the amount of electric field to stop the oil particles, calculating the charge in each case based on the previous law.

Also, *Millikan* changed the power of X-ray ionizing air, which means changing the number of electrons he would catch.

Millikan and his team studied the movement, thousands of shipped oil drops, repeating all the steps from calculating the mass of each drop and calculating its boundary speed, and then changing the field and calculating its intensity to arrive at the amount of charge carried by each drop of oil.

Millikan found different amounts of negative charge on different drops, but the charge measured each time was always a whole-number multiple of a very small basic unit of charge. The largest common divisor of all charges measured by this experiment was 1.60 x 10^{-19} coulomb (the coulomb is a charge unit). *Millikan* assumed this to be the fundamental charge, which is the charge on the electron.

- **mass of the electron:**

An electron is a micro-minute with a negative charge, and *Millikan* defined its charge as a racial charge and equal to :

$$|e| = 1{,}602.10^{-19}C$$

With a good estimate of the charge on an electron and the ratio of charge-to-mass as determined by *Thomson* :

$$\frac{e}{m} = 1{,}759.10^{11}\ Coulomb/Kg$$

m is the mass of the electron and e charge it, we can calculate the mass of the electron as follows :

$$e\Big/\frac{e}{m} = m = \frac{1{,}602.10^{-19}C}{1{,}759.10^{8}C/g} = 9{,}108.10^{-28}g$$

$$\boldsymbol{m_e = 9{,}108.10^{-28}g = 9{,}1.10^{-31}Kg}$$

3. Discovery of the Proton :

3.1. *Rutherford* Discovering Proton

By 1918, scientists had begun to identify the nuclei of atoms and the smallest nuclei they had found was the hydrogen nucleus. Hydrogen nuclei were observed by shooting alpha particles at a tube full of hydrogen and occasionally the alpha particle would knock a hydrogen nucleus out of the atom. Those nuclei hit detectors that gave of twinkles of light when they were hit.

The way that Rutherford discovered the proton was in the following indirect way. He was shooting alpha particles through air, which is mostly nitrogen, with some oxygen and traces of other gasses. When he did this, he occasionally would see what looked like twinkles that occurred when the nuclei of hydrogen atoms hit his detector. The twinkles of the light were very clear.

3.2. *Rutherford*'s Experiments :

At that time, it could have been that what he was seeing was the alpha particles hitting hydrogen in the air, or maybe water molecules, which we know are made of two hydrogen atoms and one oxygen. So, he had to figure that all out.

He did so by repeating the experiment, this time with vials of pure nitrogen gas, pure oxygen gas, etc. What he found out was that it was the nitrogen that was the source of the hydrogen nuclei signal. He didn't see it very much at all with oxygen.

3.3. Findings from the Experiment :

So what he had done was use alpha particles to knock protons out of nitrogen nuclei, but he didn't know that of course. All he knew was that he could make hydrogen nuclei by hitting nitrogen nuclei and, of course, that's a bit puzzling. It took him a long time to figure it out.

Depending on how one reads the history in detail, it took between a year and six years for him to work through his thoughts. He saw the first creation of hydrogen nuclei in 1918 and it took until 1919 or perhaps until 1925 before he and others had put the entire picture together.

They realized that nitrogen nuclei must contain hydrogen nuclei and that they could be knocked out. Rutherford then coined the term proton, from the Greek word *protos*, which means *first.* The number of known constituents of the atom was now two. But there was a problem.

3.4. Problem of the 'Missing' Mass

Scientists had figured out the mass of the proton and the electron and they knew from the fact that the atom was electrically neutral that they had to come in equal quantities. The problem was that the masses didn't add up.

There were atoms with a known number of electrons, and therefore protons, and the mass of the atom was too big. There had to be another source of mass in the atoms and that source had to be electrically neutral. This is what we call the neutron these days, but they didn't know that back then.

Properties of Proton

Some of the basic properties of Protons can be given as

- The mass of the proton is 1.6726×10^{-27}kg
- It is around 1836 time the mass of the electron
- Charge of Proton +1
- The radius of the proton is approximately 1.11×10^{-15}m

4. Discovery of the Neutron :

Since the time of *Rutherford*, it had been known that the atomic mass number A of nuclei is a bit more than twice the atomic number Z for most atoms and that essentially all the mass of the atom is concentrated in the relatively tiny nucleus. In 1920 Rutherford proposed the existence of the third neutral particle in an atom. But up to 1930 proton-electron hypothesis was accepted. An experimental breakthrough came in 1930 with the observation by the German nuclear physicist Herbert Becker and Walther Bothe that bombardment of beryllium with alpha particles from a radioactive source produced neutral radiation which was penetrating but non-ionizing. They observed that the penetrating radiation was unaffected by electric fields and hence, they assumed it to be gamma radiation. In the year 1932, Frederic Joliot-Curie and Irene Joliot-Curie demonstrated that these rays have the potential to eject protons when it strikes paraffin or any H-containing compounds. The experiment proved that the assumption that the rays to be gamma rays was wrong. Because a photon that does not have mass cannot be capable to release a particle 1836 times heavier than an electron (protons). Therefore, it was concluded that the ejected rays cannot be photons.

4.1. *Chadwick*'s Experiment :

Neutron was discovered by Sir *James Chadwick* in 1932. He performed the same experiment performed by *Frederic Joliot-Curie* and Irene *Joliot-Curie* and used different bombardment targets other than paraffin.

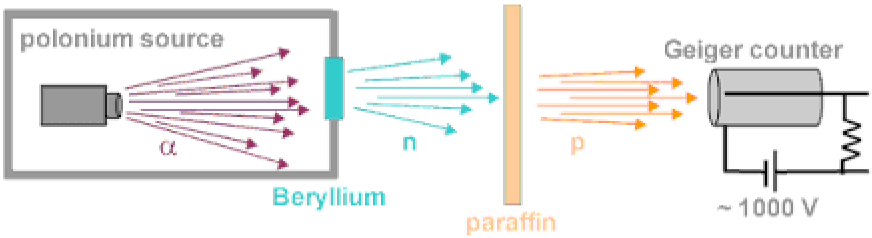


Figure 10 : *Chadwick*'s experiment

He fired alpha radiation at the beryllium sheet from a polonium source. This led to the production of an uncharged, penetrating radiation. These radiations were made incident on paraffin wax, having relatively high hydrogen content. The range of the liberated protons was measured and the interaction between the uncharged radiation and the atoms of several gases was studied by *Chadwick*. The particle ejected was found to have a mass equal to that at proton and no charge. He called these particles as neutrons.

$$\mathbf{{}_4^9Be + {}_2^4\alpha \longrightarrow [{}_6^{13}C] \longrightarrow {}_6^{12}C + {}_0^1n}$$

Properties of Neutrons :

Some of the basic properties of Neutron can be given as

- The mass of the electron is 1.6750×10^{-27} kg
- Charge of Neutron 0
- The radius of the neutron is approximately 1.11×10^{-15}m

5. Completing the Basic Structure of an Atom

With the discovery of the neutron, our understanding of basic structure of the atom was complete. Protons and neutrons are held together tightly in a small ball at the center of the atom called the nucleus. Surrounding the nucleus is a much larger volume-a trillion times larger in fact-where the electrons can be found.

With that model, scientists can work out the details of chemistry and nuclear physics. This very impressive achievement was all wrapped up by the early 1930s. Surely, scientists have made advances since then.

6. Different models of atom structure :

6.1. *Thomson* Atom Model (The 'Plum Pudding' model):

With the electron now discovered, Thomson went on to propose an entirely new model of the atom that was known as "The Plum Pudding Model." The model was so called since it mimicked the British desert of the same name that had dried fruit (primarily raisins not plums), dispersed in a body of suet and eggs that made a dough.

In his model *Thomson* proposed that the negatively charged electrons (analogous to the raisins) were randomly spread out among what he called "a sphere of uniform positive electrification" (analogous with the dough or body of the pudding).

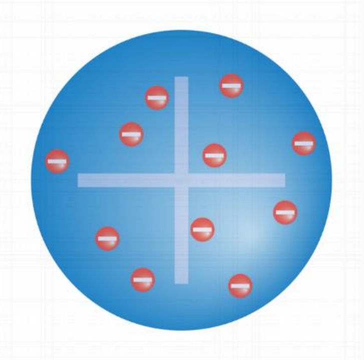


Figure 11 : *Thomson*'s "plum pudding model" of the atom, showing a positively-charged sphere containing many negatively-charged electrons in a random arrangement.

- **Limitations of *Thomson*'s Atomic Structure :**

  Thomson's atomic model does not provide a clear explanation for atomic stability. Furthermore, subsequent discoveries of other subatomic particles could not be accommodated within his atomic model.

6.2. *Rutherford* Atomic Theory

Rutherford, a student of *J. J. Thomson*, modified the atomic structure, where he did the next experiment.

Alpha Ray Scattering Experiment

Construction:

- A very thin gold foil of 1000 atoms thick is taken.
- Alpha rays (doubly charged Helium He^{2+}) were made to bombard the gold foil.
- ZnS screen is placed behind the gold foil.

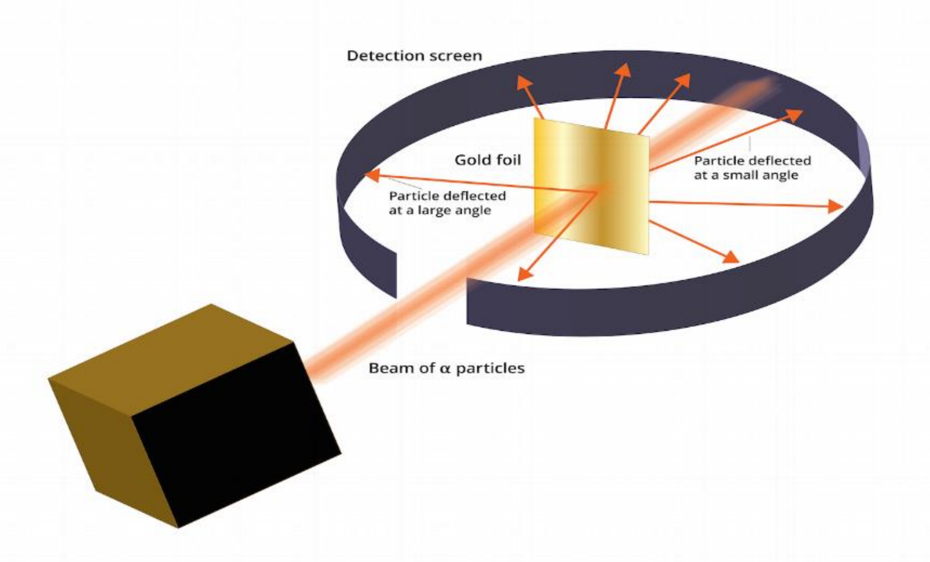
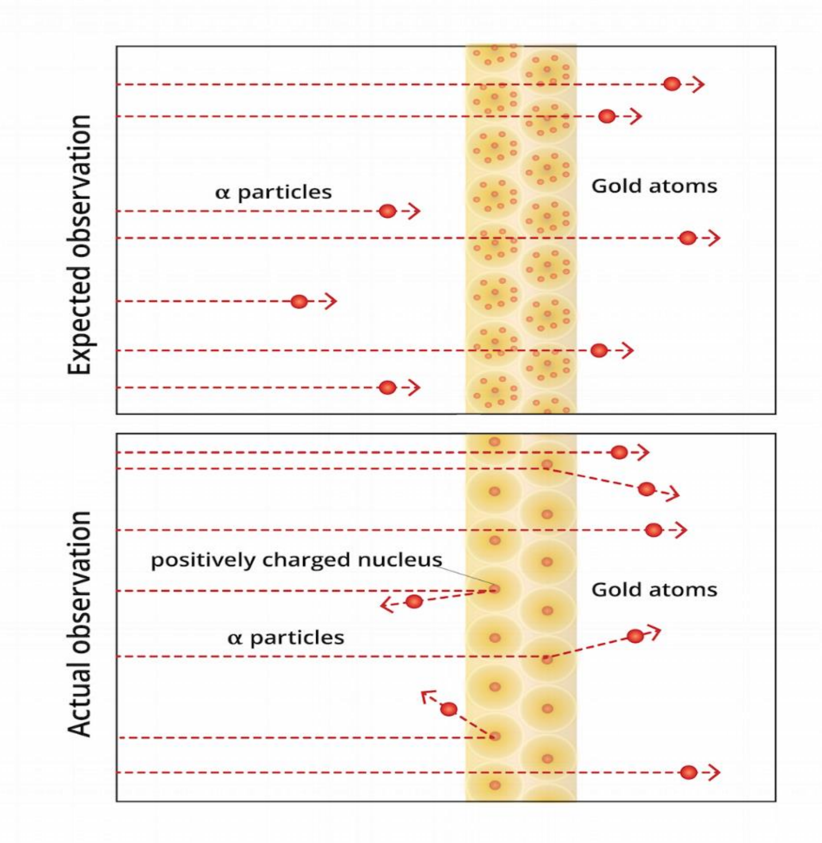


Figure 12 : *Rutherford* experiment

Observations:

- The majority of the photons passed through the gold foil, resulting in scintillations (bright spots) on the ZnS screen.
- A few photons were reflected after striking the gold foil.
- One in 1000 rays got reflected by an angle of 180° (retraced path) after hitting the gold foil.



Conclusions :

- *Rutherford* determined that the majority of the space inside the atom is vacant, as most rays pass through.
- Some rays were reflected due to repulsion between positive charges inside the atom.
- 1/1000th of the rays got strongly deflected because of a very strong positive charge in the centre of the atom. He called this strong positive charge “nucleus”.
- He said most of the charge and mass of the atom resides in the nucleus.

Rutherford’s Structure of Atom

Based on the foregoing findings and conclusions, Rutherford postulated his own atomic structure, which is shown below.

- The nucleus is the center of an atom and contains the majority of its charge and mass.
- The atomic structure is spherical.
- Electrons orbit the nucleus in a circular pattern, similar to how planets orbit the sun.

Limitations of the *Rutherford* Atomic Model

If electrons have to revolve around the nucleus, they will spend energy and that too against the strong force of attraction from the nucleus, a lot of energy will be spent by the electrons, and eventually, they will lose all their energy and will fall into the nucleus so the stability of atom is not explained.

6.3. *Bohr*'s Atomic Theory :

Keeping in view the defects in *Rutherford*'s Atomic Model, Neil Bohr presented another model of atom in 1913. The Quantum Theory of Max Planck was used as foundation for this model. According to Bohr's model, revolving electron in an atom does not absorb or emit energy continuously. The energy of a revolving electron is 'quantized' as it revolves only in orbits of fixed energy, called 'energy levels' by him.

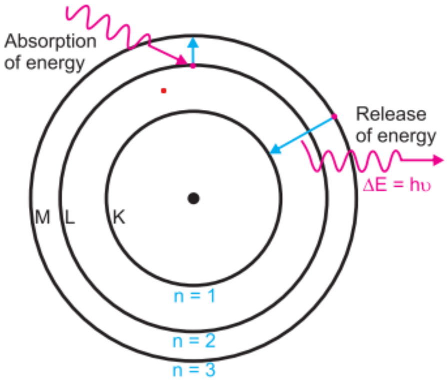
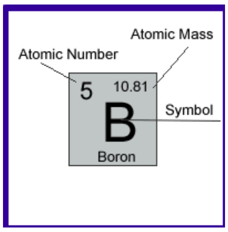


Figure 13 : The *Bohr*'s atomic model

7. Symbolic writing of atom :



- **Atomic Number :** Number of protons in nucleus
- **Mass Number (Atomic Mass) :** Number of protons + neutrons (Units are g/mol).

8. Isotopes:

8.1. Definition :

Isotopes are chemical elements that have the same number of protons and electrons but differ in the amount of neutrons. In other words, isotopes are element variations with different nucleon numbers (the total number of protons and neutrons) due to differences in the total number of neutrons in their respective nuclei.

Example:

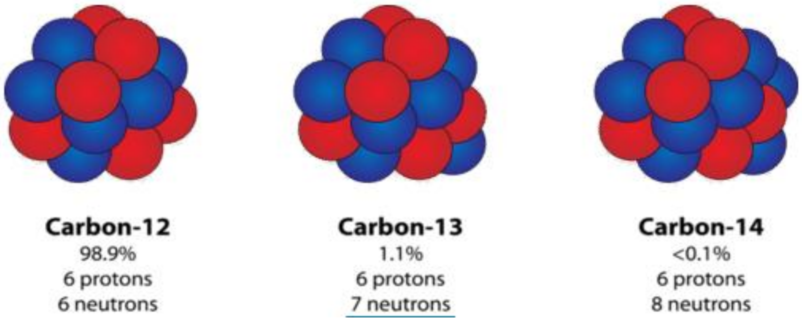


Figure 14 : Carbon isotopes

8.2. Average mass of isotopes :

An element's mass, as displayed in a periodic table or in a table of atomic masses, is a weighted average of all the isotopes present in a naturally occurring sample. This is the total of each isotope's mass multiplied by its fractional abundance, divided by 100.

$$\textbf{Average mass} = \sum i \ \textbf{(fractional abundance} \times \textbf{isotopic mass) / 100}$$

For example, the element **boron** is composed of two isotopes : About 19.9% of all **boron** atoms are ^{10}B with a mass of 10.0129 amu, and the remaining 80.1% are ^{11}B with a mass of 11.0093amu. The average atomic mass for **boron** is calculated to be :

$$\textbf{boron average mass} = (0.199\times10.0129) + (0.801\times11.0093) / 100 = 10.81\text{amu}$$

It is important to understand that no single **boron** atom weighs exactly 10.8 amu is the average mass of a large number of naturally occurring **boron** atoms. The individual **boron** atoms weigh either approximately 10 or 11 amu.

8.3. Isotope separation and identification of atomic blocks by mass spectrometry (*Bainbridge*):

The chemical properties of isotopes are identical and cannot be separated by classical chemical methods of this based on physical methods. These methods depend mainly on the different isotopes in the mass. Mass spectrometry is a device that allows :

- Separation of various strands by the application of an electric field and a magnetic field
- Measuring the e⁄m ratio of a given ion
- Determination of isotope mixture ingredients in percentages.

Among the types of spectometer :

- ***Bainbridge* Spectrometer :**

A device manifests its role in sorting ions with the same electric charge and different blocks using an electric field and a magnetic field, enabling the measurement of ion blocks with the same charge.

There are two types of fields used in Bainbridge mass spectrometer, electric and magnetic fields. Only ions having particular velocity are allowed to enter through the velocity selector. The force due to the magnetic field does not work, it only changes the direction of the moving particle.

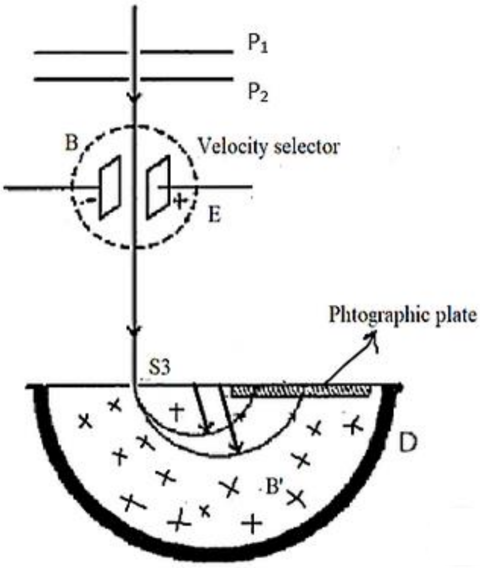


Figure 15 : *Bainbridge* Spectrometer

An instrument called *Bainbridge* mass spectrometer is used for the determination of atomic masses. If one or more electrons are removed from the atom then it has a net positive charge and it becomes a positive ion. Using two narrow slits ***S*1** and ***S*2**, a beam of positive ions produced in a discharge tube is collimated into a fine beam. This fine beam then enters into a velocity selector. Only the ions of a particular velocity are allowed to come out from the velocity selector. The velocity selector consists of two plane parallel plates $P1$ and $P2$, which produces a uniform electric field, it also has an electromagnet which produces a uniform magnetic field. These electric and magnetic fields are at right angles to each other and to the direction of the beam.

The electric field and magnetic field are so adjusted in such a way that the deflection produced by one field is nullified by the other so that the ions do not suffer any deflection within the velocity selector.

Let E be the electric field intensity, B be the magnetic induction respectively and **q** be the charge on the positive ion.

The force exerted by the electric field is :

$$FE = qE$$

The force exerted by the magnetic field is :

$$FB = qvB$$

Where v is the velocity of positive ions.

We have :

$$FE = FB$$

$$qE = qvB, \qquad v = E/B$$

The ions having this velocity are allowed to pass through the velocity selector. Then they pass through a slit $S3$ and then they enter in evacuated chamber D. The positive ions having the same velocity are again influenced by another strong uniform magnetic field of induction at right angles to the plane of the paper acting inwards. These ions then move in a circular path of radius R and strike the photographic plate. The centripetal force is provided by this magnetic field. Therefore,

$$mv/R = qvB', \quad m = qB'R/v$$

Using $v = E/B$, $D = 2R$ we get :

$$m = BB'qR/E \ \Rightarrow \ \frac{q}{m} = \frac{2E}{B.B_0.D}$$

Ions having different masses trace different semi-circular paths and produce dark lines on the plate. The distance between the opening of the chamber and the position of the dark line is equal to the diameter **2*R*** from which radius **R** can be calculated.

By knowing B, B', E and R, the mass of the positive ions and isotopic masses can be calculated.

Note : In this method, we can distinguish the ions based on their mass as ions having different masses trace semicircles of different radii.

9. Nuclear Binding Energy :

As a simple example of the energy associated with the strong nuclear force, consider the helium atom composed of two protons, two neutrons, and two electrons. The total mass of these six subatomic particles may be calculated as :

(2×1.0073amu) protons + (2×1.0087amu) neutrons + (2×0.00055amu) electrons = 4.0331amu

However, mass spectrometric measurements reveal that the mass of an ${}_2^4He$ atom is 4.0026 amu, less than the combined masses of its six constituent subatomic particles. This difference between the calculated and experimentally measured masses is known as the mass defect of the atom. In the case of helium, the mass defect indicates a "loss" in mass of 4.0331 amu – 4.0026 amu = 0.0305 amu. The loss in mass accompanying the formation of an atom from protons, neutrons, and electrons is due to the conversion of that mass into energy that is evolved as the atom forms. The nuclear binding energy is the energy produced when the atoms' nucleons are bound together ; this is also the energy needed to break a nucleus into its constituent protons and neutrons. In comparison to chemical bond energies, nuclear binding energies are *vastly* greater, as we will learn in this section. Consequently, the energy changes associated with nuclear reactions are vastly greater than are those for chemical reactions.

The conversion between mass and energy is most identifiably represented by the mass-energy equivalence equation as stated by ***Albert Einstein***:

$$\Delta E = \Delta m\, C^2$$

where ΔE is energy, Δm is mass of the matter being converted, and C is the speed of light in a vacuum. This equation can be used to find the amount of energy that results when matter is converted into energy. Using this mass-energy equivalence equation, the nuclear binding energy of a nucleus may be calculated from its **mass defect**, as demonstrated in Example.

A variety of units are commonly used for nuclear binding energies, including electron volts (eV), with 1 eV equaling the amount of energy necessary to the move the charge of an electron across an electric potential difference of 1 volt, making $1\text{eV}=1.602\times10^{-19}\text{J}$.

Example : Calculation of Nuclear Binding Energy

Determine the binding energy for the nuclide ${}_2{}^4\text{He}$ in :

a. joules per mole of nuclei
b. joules per nucleus
c. MeV per nucleus

Solution :

The mass defect for a He
Nucleus is 0.0305 amu, as shown previously. Determine the binding energy in joules per nuclide using the mass-energy equivalence equation. To accommodate the requested energy units, the mass defect must be expressed in kilograms (recall that 1 J = 1 kg m^2/s^2).

a) First, express the mass defect in g/mol. This is easily done considering the *numerical equivalence* of atomic mass (amu) and molar mass (g/mol) that results from the definitions of the amu and mole units (refer to the previous discussion in the chapter on atoms, molecules, and ions if needed). The mass defect is therefore 0.0305 g/mol. To accommodate the units of the other terms in the mass-energy equation, the mass must be expressed in kg, since 1 J = 1 kg m^2/s^2. Converting grams into kilograms yields a mass defect of 3.05×10–5kg/mol
. Substituting this quantity into the mass-energy equivalence equation yields :

b) The binding energy for a single nucleus is computed from the molar binding energy using Avogadro's number :

$$\Delta E = 2.74\times10^{12}\ Jmol^{-1}\times\ \frac{1mol}{6.022\times10^{23}nuclei} = 4.55\times10^{-12}J = 4.55J$$

c) that 1eV = 1.602×10^{-19}J

. Using the binding energy computed in part (b) :

$$\Delta E = 4.55\times10^{-12}J\times\frac{1eV}{1.602\times10^{-19}J} = 2.84\times10^{7}eV = 28.4\ MeV$$

10. Nuclear Stability

A nucleus is stable if it cannot be transformed into another configuration without adding energy from the outside. Of the thousands of nuclides that exist, about 250 are stable. A plot of the number of neutrons versus the number of protons for stable nuclei reveals that the stable isotopes fall into a narrow band.

represents nuclei that have a 1:1 ratio of protons to neutrons (n:p ratio). Note that the lighter stable nuclei, in general, have equal numbers of protons and neutrons. For example, nitrogen-14 has seven protons and seven neutrons. Heavier stable nuclei, however, have increasingly more neutrons than protons. For example : iron-56 has 30 neutrons and 26 protons, an n:p ratio of 1.15, whereas the stable nuclide lead-207 has 125 neutrons and 82 protons, an n:p ratio equal to 1.52. This is because larger nuclei have more proton-proton repulsions, and require larger numbers of neutrons to provide compensating strong forces to overcome these electrostatic repulsions and hold the nucleus together.

The relative stability of a nucleus is correlated with its binding energy per nucleon, the total binding energy for the nucleus divided by the number or nucleons in the nucleus. For instance, the binding energy for a ${}_{2}^{4}$He nucleus is therefore :

$$28.4\ \text{MeV} / 4\text{nucleons} = 7.10\ \text{MeV/nucleon}$$

The binding energy per nucleon of a nuclide on the curve shown in Figure :

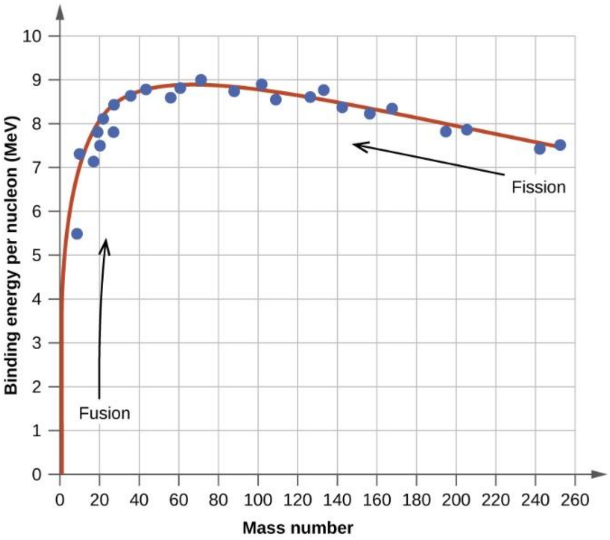


Figure 16 : Nuclear Stability

The binding energy per nucleon is largest for nuclides with mass number of approximately 56.

11. Summary

An atomic nucleus consists of protons and neutrons, collectively called nucleons. Although protons repel each other, the nucleus is held tightly together by a short-range, but very strong, force called the strong nuclear force. A nucleus has less mass than the total mass of its constituent nucleons. This “missing” mass is the mass defect, which has been converted into the binding energy that holds the nucleus together according to Einstein’s mass-energy equivalence equation, $E = mc^2$. Of the many nuclides that exist, only a small number are stable. Nuclides with even numbers of protons or neutrons, or those with magic numbers of nucleons, are especially likely to be stable. These stable nuclides occupy a narrow band of stability on a graph of number of protons versus number of neutrons. The binding energy per nucleon is largest for the elements with mass numbers near 56; these are the most stable nuclei.

Practical exercises

Exercise 1:

The electron package of the cathode tube is deviated under the influence of an electric field E. The deviation of this package (after measuring the amount of deviation Y_S) resulting from the electric field $E = 3,6 \cdot 10^4 V/m$ is abolished by the opposite of the magnetic field B = 9.10^{-4} Tesla, which affects in the same electric field vacuum.

1 . Find the expression for the e/m_e ratio of electrons in terms of E, B, L, Ys.

2. Determine the speed and kinetic energy of the electrons.

3. What is the value of the U voltage accelerator U that can be applied between the cathode and the anode so that the electrons acquire this Kinetic energy?

e = $1,6.10^{-19}$ C, me = $9,1.10^{-31}$ Kg

Exercise 2 :

Using the device used in ***Millikan's*** experiment, we observe the free fall of a spherical oil droplet in the air at a constant speed equal to $v_1 = 3.\ 10^{-4}$ m/s.

1. with negligent the Archimedes thruster. Calculate the radius of this droplet, its size and mass.

In the presence of the electric field E_1, the droplet rises toward the positive pole of the capacitor (upward) at a new speed $V_2 = 15,097.\ 10^{-4}$ m/s

2. What is the q_1 charge value that the droplet acquires if you know that the electric field value is E_1 = 3.106 v/m.

3. The electric charge of the droplet changes to q2. the droplet stabilizes between the two capacitor plates, when the value of the electric field E_2 = 331554.6 V/m . Calculate the value of the new electric charge q_2.

g = 9,81 m.s^{-2}, ρ_h = 900K g/m^3, $\eta = 17,3.10^{-6}$ Kg.m^{-1}.s^{-1}

Exercise 3:

Inside the mass spectrometer of ***Bainbridge*** observed that element X has 3 isotopes

The ions collide with the photographic board at a distance of: 41,50 cm; 45,65 cm and 37, cm from the collision point of the ions $^{12}C^{+}$ where the inside of the speed filter is applied electric field E = 5.104 $V.m^{-1}$.

1. Calculate the value of the appropriate magnetic field that allows ions with a speed of 2.10^{5} $m.s^{-1}$ pass to the filter without deviation.
2. Calculate the magnetic field inside the analyser knowing that the distance between the exit point from the speed filter and the point of collision of $^{12}C^{+}$ ions is 49.80 cm.
3. Select the X element and its isotopes knowing they are lighter than carbon

$N_A = 6,023.10^{23}$; $e=1.6 .10^{-19}C$

Chapter III

Radioactivity

Chapter III :

Radioactivity

1. Introduction :

During the nineteenth century, atomic theory assumed that nuclei had set compositions. However, in 1896, French scientist *Henri Becquerel* discovered that placing a uranium compound near a photographic plate resulted in an image on the plate, even when the compound was enveloped in black cloth. He reasoned that the uranium complex was generating radiation, which traveled through the cloth and exposed the photographic plate. Further examination revealed that the radiation was made up of particles and electromagnetic rays, with the atomic nucleus serving as the ultimate source. These emanations were eventually referred to as radioactivity.

Following *Becquerel*'s rather unexpected discovery of radioactivity, many notable scientists began to examine this new and exciting phenomenon. Among them were Marie Curie (the first woman to win a Nobel Prize and the only person to win two Nobel Prizes in different sciences-chemistry and physics), who coined the term "radioactivity," and Ernest Rutherford (famous for his gold foil experiment), who investigated and named three of the most common types of radiation. During the early twentieth century, several radioactive compounds were found, radiation properties were examined and quantified, and a solid understanding of radiation and nuclear decay was formed.

Radioactive decay occurs when an unstable nuclide spontaneously changes into another. The unstable nuclide is referred to as the parent nuclide, whereas the nuclide formed as a result of the decay is known as the daughter. The daughter nuclide may be stable or decay spontaneously. The radiation produced during radioactive decay causes the daughter nuclide to be closer to the band of stability than the parent nuclide, hence a nuclide's position relative to the band of stability can be used to predict the type of decay it will undergo.

There are around 270 stable isotopes and 50 naturally occurring radioisotopes (radioactive isotopes). Thousands of more radioisotopes have been created in the laboratory.

2. Natural radioactivity :

It is an atomic property of some materials where the latter emit different radiation on their own, and these radiation are accompanied by the disintegration of the nucleus, called the radioactive nucleus, while the nucleus that does not disintegrate is called the stable nucleus. Radiation disintegration is usually accompanied by a change in A and Z.

3. Major Forms of Radioactivity :

3.1. Alpha Particle (α) :

*Rutherford'*s experiments demonstrated that there are three main forms of radioactive emissions. The first is called an **alpha particle**, which is symbolized by the Greek letter α. An alpha particle is composed of two protons and two neutrons and is the same as a helium nucleus. (We often use $_2{}^4He$ to represent an alpha particle.) It has a 2+ charge. When a radioactive atom emits an alpha particle, the original atom's atomic number decreases by two (because of the loss of two protons), and its mass number decreases by four (because of the loss of four nuclear particles). We can represent the emission of an alpha particle with a chemical equation-for example, the alpha-particle emission of uranium-235 is as follows:

$$^{235}_{92}U \longrightarrow \underbrace{^{4}_{2}He}_{\alpha \text{ particle}} + \, ^{231}_{90}Th$$

3.2. Beta Particle (β) :

The second type of radioactive emission is called a **beta particle**, which is symbolized by the Greek letter β. A beta particle is an electron ejected from the nucleus (not from the shells of electrons about the nucleus) and has a -1 charge. We can also represent a beta particle as $_{-1}{}^0e$. The net effect of beta particle emission on a nucleus is that a neutron is converted to a proton. The overall mass number stays the same, but because the number of protons increases by one, the atomic number goes up by one. Carbon-14 decays by emitting a beta particle:

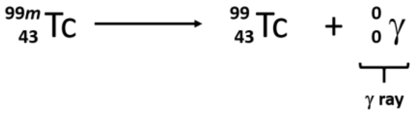
$$^{14}_{6}C \longrightarrow \, ^{14}_{7}N + \underbrace{^{0}_{-1}e}_{\beta \text{ Particle}}$$

3.3.Gamma Radiation (γ) :

The third major type of radioactive emission is not a particle but rather a very energetic form of **electromagnetic radiation** called **gamma rays**, symbolized by the Greek letter γ. In gamma decay, depicted, a nucleus changes from a higher energy state to a lower energy state through the emission of electromagnetic radiation (photons).

The number of protons (and neutrons) in the nucleus does not change in this process, so the parent and daughter atoms are the same chemical element. In the gamma decay of a nucleus, the emitted photon and recoiling nucleus each have a well-defined energy after the decay. The characteristic energy is divided between only two particles.

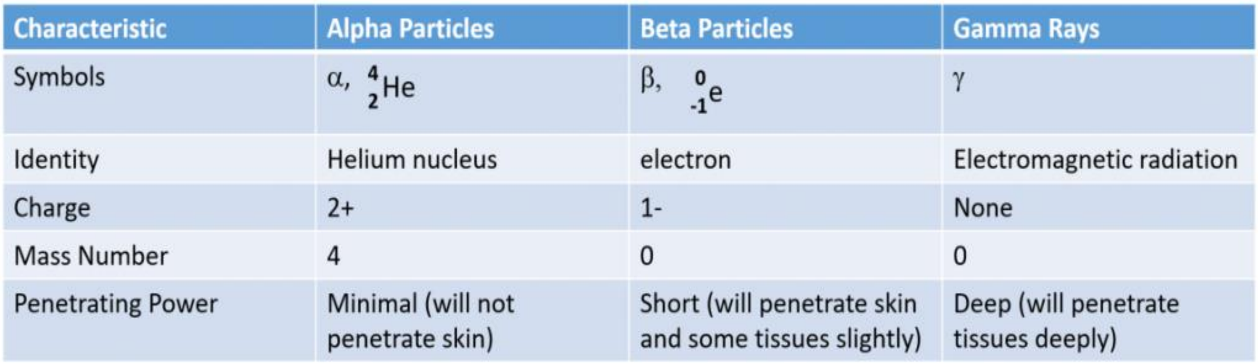
For example, in the decay of radioactive technetium-99, a gamma ray is emitted. Note that in radioactive decay where the emission of gamma radiation occurs, that the identity of the parent material does not change, as no particles are physically emitted.



$${}^{99m}_{43}\mathrm{Tc} \longrightarrow {}^{99}_{43}\mathrm{Tc} + \underbrace{{}^{0}_{0}\gamma}_{\gamma\ \text{ray}}$$

Alpha, beta, and gamma emissions have distinct penetration rates. The relatively big alpha particle can easily be stopped by materials. Beta particles only permeate materials for a few millimeters at most. Gamma rays have the ability to penetrate deeply into materials and transmit a significant amount of energy into it. Table 1 explains the attributes of the three major forms of radioactive emissions, whereas the following picture shows each radioactive type's capacity to permeate matter.

The Three Main Forms of Radioactive Emissions



Characteristic	Alpha Particles	Beta Particles	Gamma Rays
Symbols	α, ${}^{4}_{2}\mathrm{He}$	β, ${}^{0}_{-1}\mathrm{e}$	γ
Identity	Helium nucleus	electron	Electromagnetic radiation
Charge	2+	1-	None
Mass Number	4	0	0
Penetrating Power	Minimal (will not penetrate skin)	Short (will penetrate skin and some tissues slightly)	Deep (will penetrate tissues deeply)

4. Radioactivity Laws:

4-1. Law of Radioactive Disintegration :

- Atoms of all radioactive elements undergo spontaneous disintegration and form new radioactive elements. The disintegration is accompanied by the emission of **α**, **β**, or **γ**-rays.
- The disintegration is at random, every atom has equal chance for disintegration at any time.
- The number of atoms that disintegrate per second is directly proportional to the number of remaining unchanged radioactive atoms present at any time. The disintegration is independent of all physical and chemical conditions like temperature, pressure chemical combination etc.

$$dN/dt \propto N \ (1)$$

N: number of atoms present at time t.

Removing proportionality sign, we get

$$dN/dt = -\lambda N \ (2)$$

λ: decay constant of the element.

Negative sign indicates that as t increases N decreases.

Rewriting Eq. (2) as $dN/dt = -\lambda dt$

Integrating both sides, we have $dN/N = -\lambda \quad dt$

$$\int_{N_0}^{N_t} \frac{dN}{N} = -\lambda \int_0^t dt$$

at t = 0 N $= N_0$, we get :

N_0 is the initial quantity of the substance that will decay (this quantity may be measured in grams, moles, number of atoms, etc.),

$$\ln N \Big]_{N_0}^{N_t} = -\lambda\, t \Rightarrow ln \frac{N_t}{N_0} = -\lambda\, t$$

$\Rightarrow \frac{\boldsymbol{N_t}}{\boldsymbol{N_0}} = \boldsymbol{e^{-\lambda\, t}} \Rightarrow \boldsymbol{N_t} = N_0$ It's the law of radioactivity.

4-2. Half-life :

half-life, in radioactivity, the interval of time required for one-half of the atomic nuclei of a radioactive sample to decay (change spontaneously into other nuclear species by emitting particles and energy), or, equivalently, the time interval required for the number of disintegrations per second of a radioactive material to decrease by one-half.

This half-life is a time that is unique time to each radioisotope of an element. Half-lives can range from less than a millionth of a second to millions of years. The half-life can be mathematically expressed as the point in time when N(t) is one half of N_0.

Replacing this expression in the law of radioactivity, where $t_{1/2}$ is the half-life, gives:

$$N_t = N_0 e^{-\lambda\, t_{\frac{1}{2}}} \Rightarrow \frac{N_0}{2} = N_0 e^{-\lambda\, t_{\frac{1}{2}}} \Rightarrow \frac{1}{2} = e^{-\lambda\, t_{\frac{1}{2}}}$$

Taking the logarithm of both sides of the above equation and solving for the half-life t1/2 gives:

$$\ln 2 = \lambda\, t_{\frac{1}{2}} \Rightarrow t_{\frac{1}{2}} = \frac{\ln 2}{\lambda}$$

4-3. Activity (A):

The number of radioactive nuclei cannot be measured directly. One can only determine the rate of transformation called the activity by measuring the particles emitted. It is proportional to the number of atoms :

$$A = -\, dN/dt = -\lambda N$$

The activity represents the number of disintegrations per second and it is measured in Becquerel Bq. [Bq] = dps. The old unit of activity was Curie Ci and represented the activity of 1g of Radium-226. 1Ci = $3.7 \cdot 10^{10}$ Bq, so 1 mCi = 37 MBq; and 1 µCi = 37 kBq.

4-4. The relationship between disintegration and activity :

$$N_t = N_0 e^{-\lambda t}$$

$$A = \lambda N \Rightarrow N = \frac{A}{\lambda} \Rightarrow$$

$$\frac{A}{\lambda} = \frac{A_0}{\lambda} e^{-\lambda t} \Rightarrow A_t = A_0 e^{-\lambda t}$$

4-5. The relationship between disintegration and mass :

$$N = \frac{m.\mathrm{N_A}}{M}, \qquad N_0 = \frac{m_0.\mathrm{N_A}}{M}$$

$$N_t = N_0 e^{-\lambda t} \Rightarrow \frac{m.\mathrm{N_A}}{M} = \frac{m_0.\mathrm{N_A}}{M} e^{-\lambda t}$$

$$\Rightarrow m_t = m_0 e^{-\lambda t}$$

5- Artificial radioactivity and nuclear reactions :

These reactions happen when stable isotopes are hit with particles like neutrons. This approach of causing a nuclear reaction to proceed is known as artificial radioactivity. This allowed for the observation of new nuclear reactions that would not have occurred naturally.

5-1. Types of Nuclear Reactions :

Although the number of possible nuclear reactions is enormous, nuclear reactions can be sorted by type. Most nuclear reactions are accompanied by gamma emissions. Some examples are :

- **Capture reaction :** The capture reaction is one of the two possible absorption reactions that may occur. Capture reactions result in the loss of a neutron coupled with the production of one or more gamma rays. The resulting nucleus may also undergo a subsequent decay, such as beta decay in this example, which is a very important reaction in nuclear fuel.

$$\mathbf{{}^{238}U\ (n,\gamma)\ {}^{239}U}$$

- **Transfer Reaction :** Transfer reactions are nuclear reactions in which one or more nucleons are transferred to the other nucleus. Transfer reactions can occur from the projectile to the target; stripping reactions, or from the target to the projectile; pick-up reactions. These reactions are common in particle accelerators and astrophysics.

$$\mathbf{{}^{4}He\ (\alpha,\ p)\ {}^{7}Li}$$

- **Fission reactions :** Nuclear fission is a nuclear reaction in which the nucleus of an atom splits into smaller parts (lighter nuclei). The fission process often produces free neutrons and photons (in the form of gamma rays) and releases a large amount of energy.

$$\mathbf{{}^{235}U\ (n,\ 3n)}\ \textit{\textbf{fission products}}$$

- **Fusion reactions :** Occur when two or more atomic nuclei collide at a very high speed and join to form a new type of atomic nucleus. The fusion reaction of deuterium and tritium is exciting because of its potential of providing energy for the future.

$$\mathbf{{}^{3}T\ (d,\ n)\ {}^{4}He}$$

5-2. Energy of a nuclear reaction :

During nuclear changes, either some mass is converted into energy or some energy is converted into mass. Which occurs is dependent upon the specifics of the individual reaction. From this change in mass we can calculate its energy equivalent using Einstein's equation, $\Delta E = mc^2$.

- **Determining the Energy Change of a Nuclear Reaction :**

To find the energy change for a nuclear reaction you must know the masses of each species in the equation for the reaction. To calculate the energy change for a nuclear reaction:

- Calculate the sum of the masses of all of the products, and the sum of the masses of all the reactants,
- Calculate the change in mass by subtracting the combined mass of the reactants from the combined mass of the products,
- Convert the change in mass into its equivalent change in energy using *Einstein*'s equation.

- Convert the energy change from J/atom to kJ/mol of atoms.

Example: Calculate the energy change for the following nuclear reaction. The masses of each species are given below.

$$1 \text{ neutron} + {}^{235}\text{U} \rightarrow {}^{89}\text{Rb} + {}^{144}\text{Ce} + 3 \text{ electrons} + 3 \text{ neutrons}$$

Masses :

neutron = 1.00867 amu
electron = 0.00055 amu
uranium-235 = 234.9934 amu
rubidium-89 = 88.8913 amu
cerium-144 = 143.8817 amu

- Calculate the combined masses of the products and of the reactants.

Mass of Products = 88.8913 amu + 143.8817 amu + 3 (0.00055 amu) + 3 (1.00867 amu) = 235.8007 amu

Mass of Reactants = 1.00867 amu + 234.9934 amu = 236.0021 amu

- Calculate the change in mass for the reaction (mass of products - mass of reactants).

Δm = 235.8007 amu - 236.0021 amu = - 0.2014 amu

- Convert the change in mass into energy using *Einstein*'s equation. Remember to change the mass into kilograms.

$\Delta E = (-\ 0.2014 \text{ amu})\ (1.6606 \times 10^{-27} \text{ kg/amu})\ (2.9979 \times 10^{8} \text{ m/s})^2 = -\ 3.006 \times 10^{-11} \text{ J}$

- Convert the energy change per atom of uranium-235 into kJ/mol of uranium-235.

$(-\ 3.006 \times 10^{-11} \text{ J/atom})(1 \text{ kJ}/1000 \text{ J})(6.023 \times 10^{23} \text{ atoms/mol}) = -\ 1.811 \times 10^{10}$ kJ/mol of U-235

Note : The negative sign indicates that this nuclear reaction is **exothermic**.

6- Radioactive families :

Scientists have found four principal families, or decay series, of radioactive substances: the ***uranium-radium*** family**,** the ***actinium*** family**,** the ***thorium*** family and the ***neptunium*** family.

When it decays, a radionuclide transforms into a different atom - a decay product. The atoms keep transforming to new decay products until they reach a stable state and are no longer radioactive. The majority of radionuclides only decay once before becoming stable. Those that decay in more than one step are called series radionuclides. The series of decay products created to reach this balance is called the radioactive family.

Each series has its own unique decay chain. The decay products within the chain are always radioactive. Only the final, stable atom in the chain is not radioactive. Some decay products are a different chemical element.

Every radionuclide has a specific decay rate, which is measured in terms of "." Radioactive half-life is the time required for half of the radioactive atoms present to decay. Some radionuclides have half-lives of mere seconds, but others have half-lives of hundreds or millions or billions of years.

Exemple : Uranium-238 decay chain is shown below :

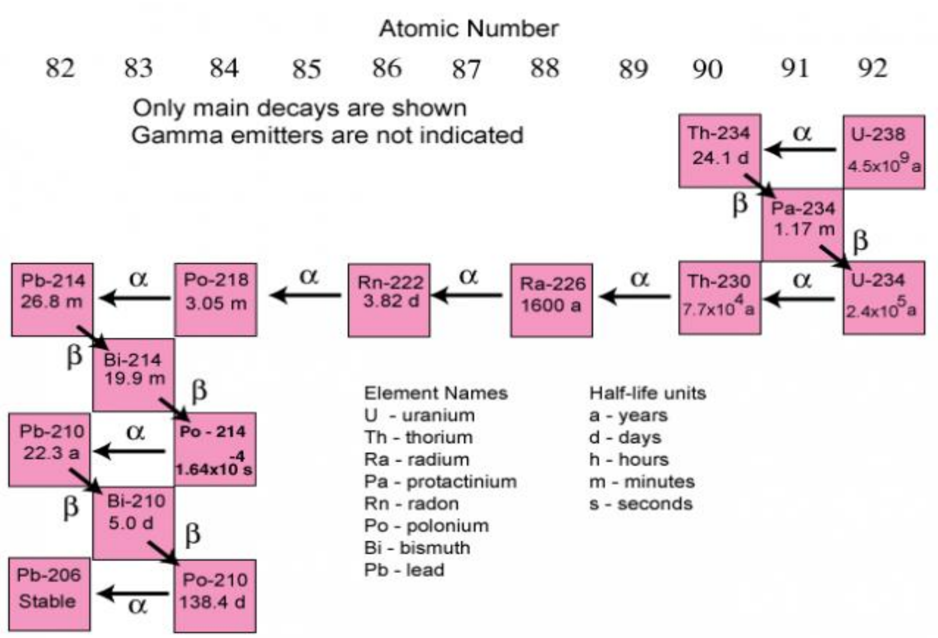


Figure 17 : Uranium-238 decay chain

7- radioactivity Applications :

- **Use of radioactive isotope :**

Radioactive isotopes have many useful applications. In medicine, as tracers for diagnostic purposes as well as in research on metabolic processes.

- **Uses of radioactivity :**

1. Medical use: Many diseases such as cancer are cured by radio therapy. Sterilization of medical instruments and food is another common application of radiation.
2. Scientific use: Alpha particles emitted from the radio isotopes are used for nuclear reactions.
3. Industrial use: Radio isotopes are used as fuel for atomic energy reactors.

- **Explain the applications of radio-isotopes :**

The applications of radio-isotopes are as follows:
1. Cobalt-60 is extensively employed as a radiation source to arrest the development of cancer.
2. Iodine-131 has proved effective in treating hyperthyroidism.
3. In industry, radioactive isotopes of various kinds are used for measuring the thickness of metal or plastic sheets; their precise thickness is indicated by the strength of the radiations that penetrate the material being inspected.

Practical exercises

Exercise 1:

Consider the following nuclear reaction:

$$2\,{}^{1}_{1}H + 2\,{}^{1}_{0}n \longrightarrow {}^{4}_{2}He$$

1) Calculate the change in mass Δm, The masses of each species are given below.
2) Calculate the binding energy in MeV
3) Calculate the binding energy per nucleon in J and eV .
4) Calculate the binding energy in joules and calories per mole of nucleons.

Masses:

neutron = 1.00866 amu

proton = 1.0073 amu

helium = 4.0026 amu

Exercise 2:

A) Write the balanced equation for the nuclear reactions:

${}^{130}_{52}Te(d,2n){}^{130}_{53}I$, ${}^{40}_{18}Ar(\alpha,P){}^{43}_{19}K$, ${}^{55}_{25}Mn(n,\gamma){}^{56}_{25}Mn$, ${}^{15}_{8}O(\beta^{+}){}^{15}_{7}N$, ${}^{14}_{6}C(\beta^{-}){}^{14}_{7}N$

B) Write the balanced equation for the nuclear reaction ${}^{56}_{25}Mn(\beta^{-}){}^{56}_{26}Fe$

1) It was found that in 7.5 hours, 1 mole of ^{56}Mn decays to gives 49 g of ^{56}F. What is the half-life time of manganese?

2) Calculate the mass of a sample of manganese. Its activity is 2 x 10^{6} Ci.

3) Calculate the energy resulting from disintegration a nucleus of Mn, and then for 1 mole.

Given ^{56}Mn = 55,93948 mau, ^{56}Fe =55,93493 mau

Exercise 3:

The Thorium ${}^{232}_{90}Th$ disintegrates to gives ${}^{208}_{82}Pb$, Calculate the number of α and β^{-} particles emitted during this disintegration.

Chapter IV

Atomic spectra and Bohr's atomic model

Chapter IV:

Atomic spectra and Bohr's atomic model

I- Electronic composition of atom using classic and quantitative mechanics

1- Introduction :

Rutherford’s planetary model of the atom was based upon classical physics, a system that deals with physical particles, force, and momentum. Unfortunately, this same system predicted that electrons orbiting in the manner that Rutherford described would lose energy, give off radiation, and ultimately crash into the nucleus and destroy the atom. However, for the most part, atoms are stable, lasting literally billions of years. Furthermore, the radiation predicted by the *Rutherford* model would have been a continuous spectrum of every color, in essence white light that when passed through a prism would display all of the colors of the rainbow.

But when pure gases of different elements are excited by electricity, as they would have been when placed in the newly discovered electric-discharge tube, they emit radiation at distinct frequencies. In other words, different elements do not emit white light, they emit light of different colors, and when that light is passed through a prism it does not produce a continuous rainbow of colors, but a pattern of colored lines, now referred to as line spectra. Clearly, *Rutherford*’s model did not fit with all of the observations, and *Bohr* made it his business to address these inconsistencies.

Did you know that atoms could not be described accurately until quantum theory as developed ?

Quantum theory offered a fresh way of thinking about the universe at the atomic level. After tremendous advances in quantum mechanics in the last century, the position of electrons and other infinitesimal particles can be predicted with confidence.

As discussed in our Atomic Theory II module, at the end of 1913 Niels Bohr facilitated the leap to a new paradigm of atomic theory – quantum mechanics. Bohr’s new idea that electrons could only be found in specified, quantized orbits was revolutionary (Bohr, 1913). As is consistent with all new scientific discoveries, a fresh way of thinking about the universe at the atomic level would only lead to more questions, the need for additional experimentation and collection of evidence, and the development of expanded theories. As such, at the beginning of the second decade of the 20th century, another rich vein of scientific work was about to be mined.

2- wave nature of light :

Most of the time, light behaves as a wave, categorized as one of the electromagnetic waves because it is made of electric and magnetic fields. Electromagnetic fields perpendicularly oscillate to the direction of wave travel and are perpendicular to each other. As a result of which, they are known as transverse waves

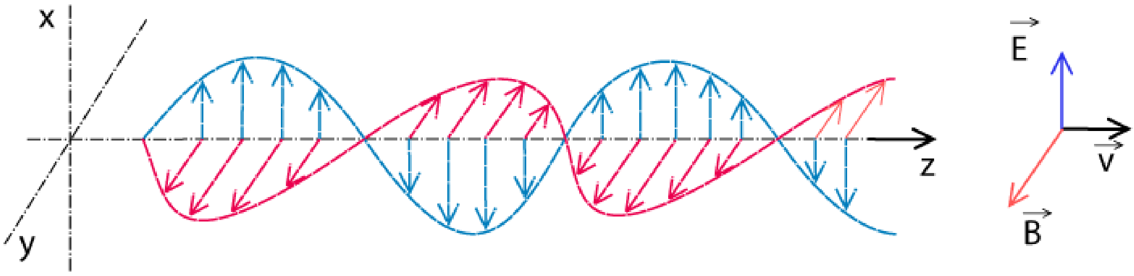
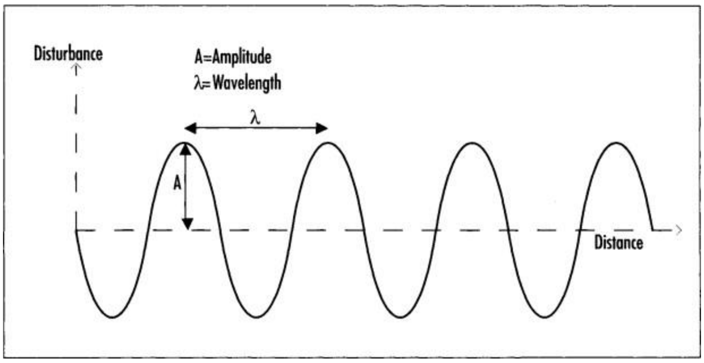


Figure 18 : Electromagntic wave propagation

This wave can be filmed at any moment in time and we get the following shape :



This waveform movement is known as :

2.1. Wavelength (λ) : distance between corresponding points of two consecutive waves. “Corresponding points” refers to two points or particles in the same phase.

2.2. The period (T): In physics, the period of a wave is the amount of time it takes for a wave to complete one wave cycle or wavelength, which is the distance from peak to peak or trough to trough.

2.3. Frequency (υ) : The frequency of a wave is the number of waves that pass by each second, and is measured in Hertz (Hz).

$$\upsilon = \frac{C}{\lambda} = \frac{1}{T}$$

2.4. Wave amplitude (A): The amplitude of a wave is the distance from the centre line (or the still position) to the top of a crest or to the bottom of a trough.

2.5. light speed : speed of light, speed at which light waves propagate through different materials. In particular, the value for the speed of light in a vacuum is now defined as exactly **299,792,458 metres per second**. The speed of light is considered a fundamental constant of nature.

2.6. Wave number $(\bar{\upsilon})$: It is the number of waves present per meter and is equal to the reciprocal of wavelength.

$$\bar{\boldsymbol{\upsilon}} = \frac{1}{\lambda}(cm^{-1}, m^{-1} \ldots)$$

3- The physical nature of light (*Planck* theory):

The wave theory of light failed to explain some physical phenomena, such as the distribution of energy emanating from a very hot (reddish) body and the photoelectric effect :

3.1. At the beginning of the twentieth century, the Planck world was able to explain why energy emanating from a very hot (reddish) body was distributed since the energy released was supplemented by specific amounts of photons, the energy of which is E: $E=h\upsilon$, h, the constant of Planck, equal to $6,62.10^{-34}$J.s and υ the frequency of light (photon).

3.2.Photoelectric Effect :

The photoelectric effect is a phenomenon in which electrons are ejected from the surface of a metal when light is incident on it. These ejected electrons are called photoelectrons. It is important to note that the emission of photoelectrons and the kinetic energy of the ejected photoelectrons is dependent on the frequency of the light that is incident on the metal's surface. The process through which photoelectrons are ejected from the surface of the metal due to the action of light is commonly referred to as photoemission.

The photoelectric effect occurs because the electrons at the surface of the metal tend to absorb energy from the incident light and use it to overcome the attractive forces that bind them to the metallic nuclei. An illustration detailing the emission of photoelectrons as a result of the photoelectric effect is provided below :

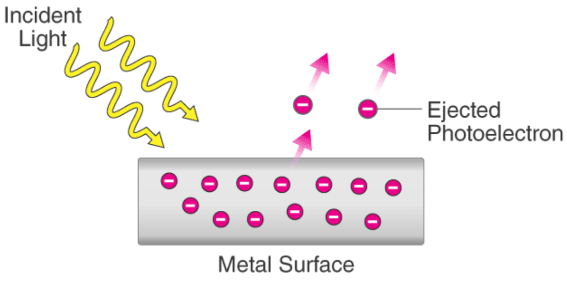


Figure 19 : Photoelectric effect

• Explaining the Photoelectric Effect: The Concept of Photons

The photoelectric effect cannot be explained by considering light as a wave. However, this phenomenon can be explained by the particle nature of light, in which light can be visualised as a stream of particles of electromagnetic energy. These 'particles' of light are called **photons**. The energy held by a photon is related to the frequency of the light via *Planck*'s equation.

$$\mathbf{E = h\nu = hc/\lambda}$$

Where,

- E denotes the energy of the photon
- h is Planck's constant
- ν denotes the frequency of the light
- c is the speed of light (in a vacuum)

- λ is the wavelength of the light.

Thus, it can be understood that different frequencies of light carry photons of varying energies. For example, the frequency of blue light is greater than that of red light (the wavelength of blue light is much shorter than the wavelength of red light). Therefore, the energy held by a photon of blue light will be greater than the energy held by a photon of red light.

- **Threshold Energy for the Photoelectric Effect**

For the photoelectric effect to occur, the photons that are incident on the surface of the metal must carry sufficient energy to overcome the attractive forces that bind the electrons to the nuclei of the metals. The minimum amount of energy required to remove an electron from the metal is called the **threshold energy** (denoted by the symbol Φ). For a photon to possess energy equal to the threshold energy, its frequency must be equal to the **threshold frequency** (which is the minimum frequency of light required for the photoelectric effect to occur). The threshold frequency is usually denoted by the symbol ν_0, and the associated wavelength (called the threshold wavelength) is denoted by the symbol λ_0. The relationship between the threshold energy and the threshold frequency can be expressed as follows :

$$\mathbf{\Phi = h\nu_0 = hc/\lambda_0}$$

- **Relationship between the Frequency of the Incident Photon and the Kinetic Energy of the Emitted Photoelectron :**

Therefore, the relationship between the energy of the photon and the kinetic energy of the emitted photoelectron can be written as follows:

$$\mathbf{E_{photon} = \Phi + E_{electron}}$$

$$\mathbf{\Rightarrow h\nu = h\nu_0 + \tfrac{1}{2}m_e v^2}$$

Where,

- E_{photon} denotes the energy of the incident photon, which is equal to $h\nu$
- Φ denotes the threshold energy of the metal surface, which is equal to $h\nu_0$
- $E_{electron}$ denotes the kinetic energy of the photoelectron, which is equal to $\frac{1}{2}m_e v^2$ (m_e = Mass of electron = $9.1*10^{-31}$ kg).

If the energy of the photon is less than the threshold energy, there will be no emission of photoelectrons (since the attractive forces between the nuclei and the electrons cannot be overcome). Thus, the photoelectric effect will not occur if $\nu < \nu_0$. If the frequency of the photon is exactly equal to the threshold frequency ($\nu = \nu_0$), there will be an emission of photoelectrons, but their kinetic energy will be equal to zero. An illustration detailing the effect of the frequency of the incident light on the kinetic energy of the photoelectron is provided below :

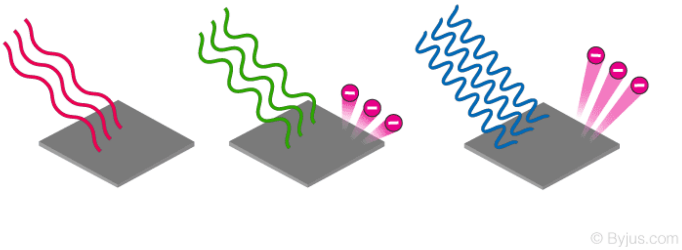


Figure 20 : the effect of the frequency of the incident light on the kinetic energy of the photoelectron

We note through the photo :

- The photoelectric effect does not occur when the red light strikes the metallic surface because the frequency of red light is lower than the threshold frequency of the metal.
- The photoelectric effect occurs when green light strikes the metallic surface, and photoelectrons are emitted.
- The photoelectric effect also occurs when blue light strikes the metallic surface. However, the kinetic energies of the emitted photoelectrons are much higher for blue light than for green light. This is because blue light has a greater frequency than green light.

It is important to note that the threshold energy varies from metal to metal. This is because the attractive forces that bind the electrons to the metal are different for different metals. It can also be noted that the photoelectric effect can also take place in non-metals, but the threshold frequencies of non-metallic substances are usually very high.

- **Experimental Study of the Photoelectric Effect :**

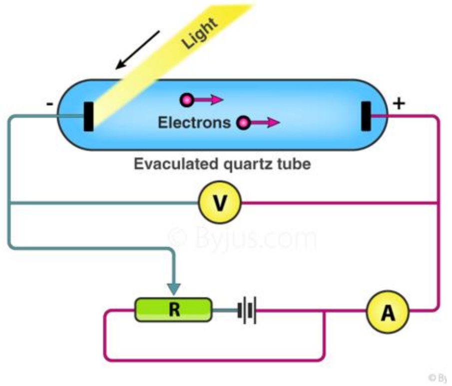


Figure 21 : Photoelectric effect experiment

Photoelectric Effect : Experimental Setup :

The given experiment is used to study the photoelectric effect experimentally. In an evacuated glass tube, two zinc plates, C and D, are enclosed. Plates C acts as an anode, and D acts as a photosensitive plate.

Two plates are connected to battery B and ammeter A. If the radiation is incident on plate D through a quartz window, W electrons are ejected out of the plate, and current flows in the circuit. This is known as photocurrent. Plate C can be maintained at desired potential (+ve or –ve) with respect to plate D.

Characteristics of the Photoelectric Effect :

- The threshold frequency varies with the material, it is different for different materials.
- The photoelectric current is directly proportional to the light intensity.
- The kinetic energy of the photoelectrons is directly proportional to the light frequency.
- The stopping potential is directly proportional to the frequency, and the process is instantaneous.

4. Electromagnetic ray spectrum :

Electromagnetic spectrum, the entire distribution of electromagnetic radiation according to frequency or wavelength. Although all electromagnetic waves travel at the speed of light in a vacuum, they do so at a wide range of frequencies, wavelengths, and photon energies. The electromagnetic spectrum comprises the span of all electromagnetic radiation and consists of many subranges, commonly referred to as portions, such as visible light or ultraviolet radiation. The various portions bear different names based on differences in behaviour in the emission, transmission, and absorption of the corresponding waves and also based on their different practical applications. There are no precise accepted boundaries between any of these contiguous portions, so the ranges tend to overlap.

The entire electromagnetic spectrum, from the lowest to the highest frequency (longest to shortest wavelength), includes all radio waves (e.g., commercial radio and television, microwaves, radar), infrared radiation, visible light, ultraviolet radiation, X-rays, and gamma rays. Nearly all frequencies and wavelengths of electromagnetic radiation can be used for spectroscopy.

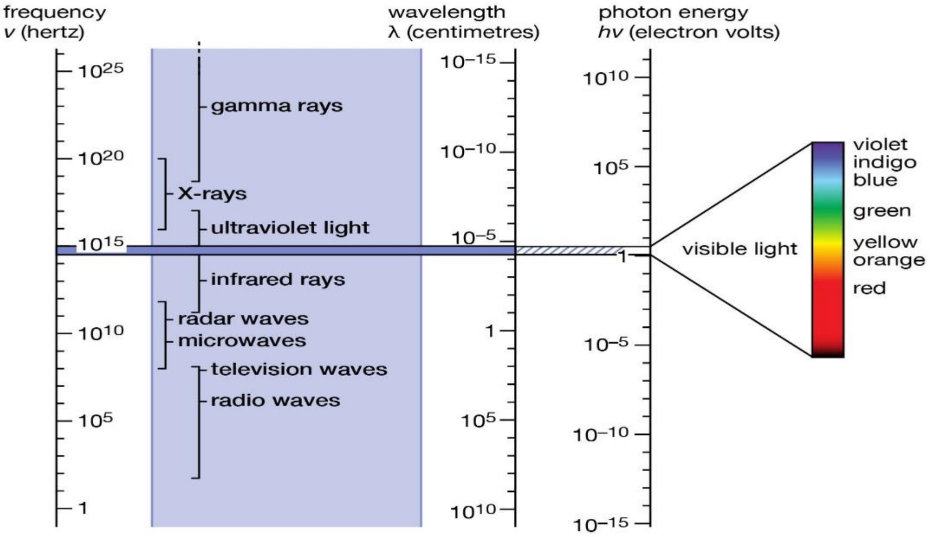


Figure 22 : Electromagnetic ray spectrum

5. Atomic Spectra

❒When an element in the vapour or the gaseous state is heated in a flame or a discharge tube, the atoms are excited (energised) and emit light radiations of a characteristic colour. The colour of light produced indicates the wavelength of the radiation emitted.

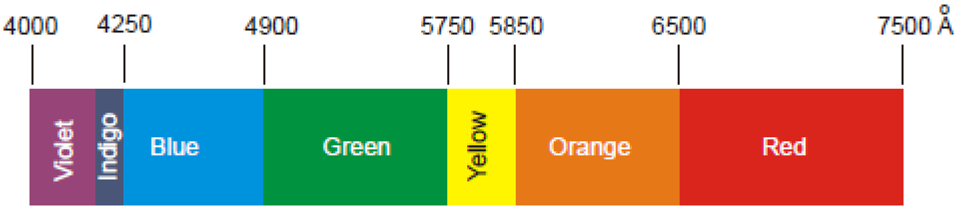


Figure 23: Wavelength range of colour bands in A° of continuous spectrum

❒ For example, a Bunsen burner flame is coloured yellow by sodium salts, red by strontium and violet by potassium. In a discharge tube, neon glows orange-red, helium-pink, and so on. If we examine the emitted light with a Spectroscope (a device in which a beam of light is passed through a prism and received on a photograph), the spectrum obtained on the photographic plate is found to consist of bright lines.

❒ Such a spectrum in which each line represents a specific wavelength of radiation emitted by the atoms is referred to as the Line spectrum or Atomic Emission spectrum of the element. The emission spectra of some elements are shown in the following figure. An individual line of these spectra is called a Spectral line.

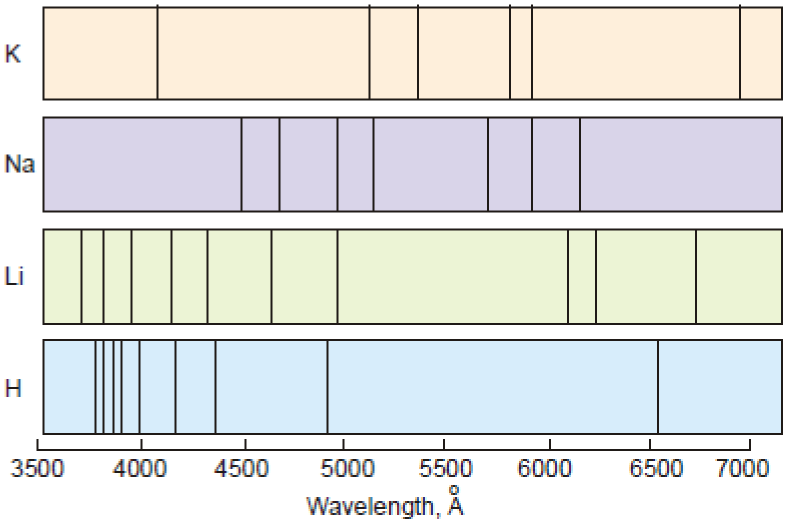


Figure 24 : Emission spectra of K, Na, Li and H

❒ When white light composed of all visible wavelengths, is passed through the cool vapour of an element, certain wavelengths may be absorbed. These absorbed wavelengths are thus found missing in the transmitted light.

❒ The spectrum obtained in this way consists of a series of dark lines which is referred to as the Atomic Absorption spectrum or simply Absorption spectrum. The wavelengths of the dark lines are exactly the same as those of bright lines in the emission spectrum. The absorption spectrum of an element is the reverse of emission spectrum of the element.

- Atomic spectral lines are emitted or absorbed not only in the visible region of the electromagnetic spectrum but also in the infrared region (IR spectra) or in the ultraviolet region (UV spectra).

- Since the atomic spectra are produced by emission or absorption of energy depending on the internal structure of the atom, each element has its own characteristic spectrum.

- Today spectral analysis has become a powerful method for the detection of elements even though present in extremely small amounts.

- The most important consequence of the discovery of spectral lines of hydrogen and other elements was that it led to our present knowledge of atomic structure.

5.1. Atomic Spectrum of Hydrogen (Balmer Series) :

- The emission line spectrum of hydrogen can be obtained by passing electric discharge through the gas contained in a discharge tube at low pressure.

- The light radiation emitted is then examined with the help of a spectroscope. The bright lines recorded on the photographic plate constitute the atomic spectrum of hydrogen.

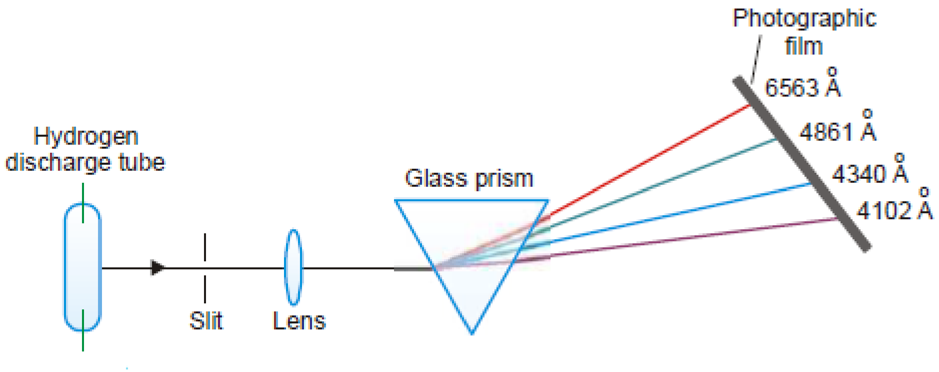


Figure 25 : Examination of the atomic spectrum of Hydrogen with a spectroscope

- In 1884 *J.J. Balmer* observed that there were four prominent coloured lines in the visible hydrogen spectrum :

(1) a red line with a wavelength of 6563 Å.
(2) a blue-green line with a wavelength 4861 Å.
(3) a blue line with a wavelength 4340 Å.
(4) a violet line with a wavelength 4102 Å.

❒The above series of four lines in the visible spectrum of hydrogen was named as the *Balmer* Series. By carefully studying the wavelengths of the observed lines, *Balmer* was able empirically to give an equation which related the wavelengths (λ) of the observed lines.

❒The *Balmer* Equation is:

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

R is a constant called the *Rydberg* Constant which has the value 109, 677 cm^{-1}.
n = 3, 4, 5, 6 etc. That is, if we substitute the values of 3, 4, 5 and 6 for n, we get, respectively, the wavelength of the four lines of the hydrogen spectrum.

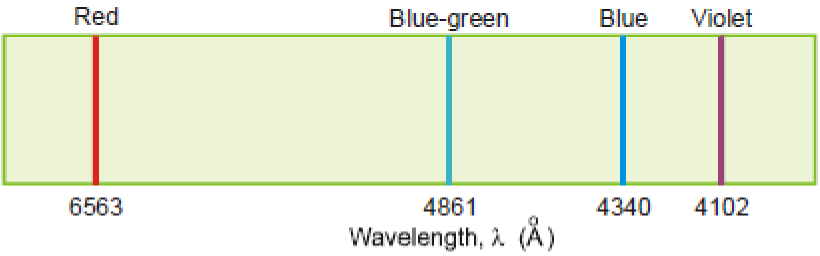
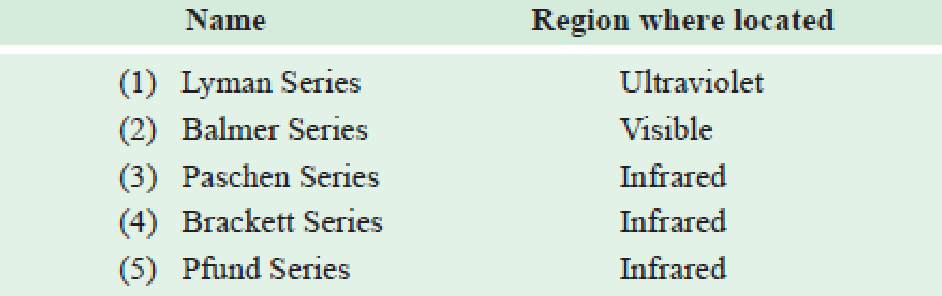


Figure 26 : Balmer series in the Hydrogen spectrum

❒In addition to Balmer Series, four other spectral series were discovered in the infrared and ultraviolet regions of the hydrogen spectrum. These bear the names of the discoverers. Thus in all we have Five Spectral Series in the atomic spectrum of hydrogen :



Name	Region where located
(1) Lyman Series	Ultraviolet
(2) Balmer Series	Visible
(3) Paschen Series	Infrared
(4) Brackett Series	Infrared
(5) Pfund Series	Infrared

❒*Balmer* equation had no theoretical basis at all. Nobody had any idea how it worked so accurately in finding the wavelengths of the spectral lines of hydrogen atom. However, in 1913 Bohr put forward his theory which immediately explained the observed hydrogen atom spectrum.

5.2. *Bohr*'s Explanation of Hydrogen Spectrum :

❒The solitary electron in hydrogen atom at ordinary temperature resides in the first orbit ($n = 1$) and is in the lowest energy state (ground state).

❒When energy is supplied to hydrogen gas in the discharge tube, the electron moves to higher energy levels viz., 2, 3, 4, 5, 6, 7, etc., depending on the quantity of energy absorbed. From these high energy levels, the electron returns by jumps to one or other lower energy level. In doing so the electron emits the excess energy as a photon. This gives an excellent explanation of the various spectral series of hydrogen.

❒Lyman series is obtained when the electron returns to the ground state i.e., $n = 1$ from higher energy levels ($n_2 = 2, 3, 4, 5$, etc.). Similarly, Balmer, Paschen, Brackett and Pfund series are produced when the electron returns to the second, third, fourth and fifth energy levels respectively as shown in the following figure :

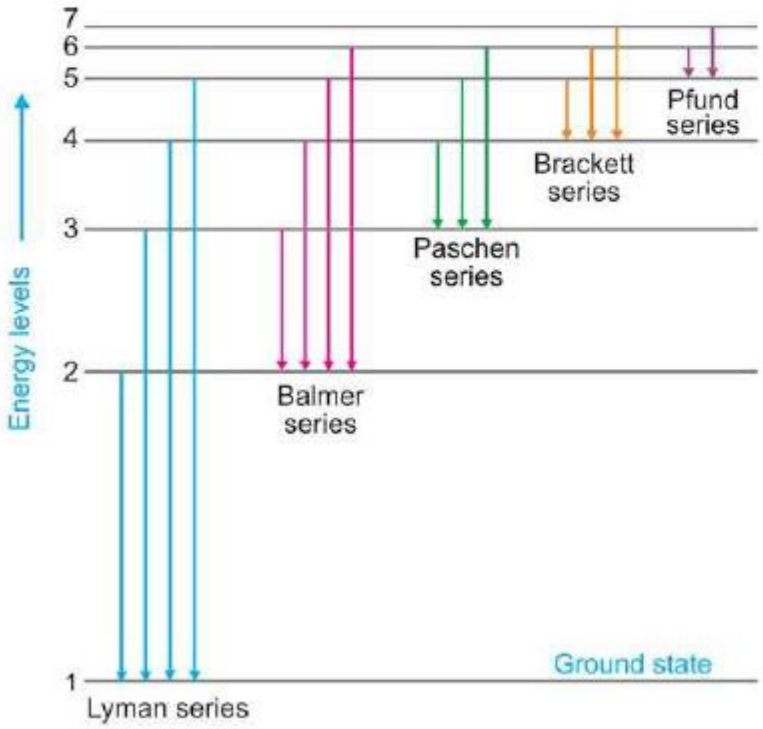
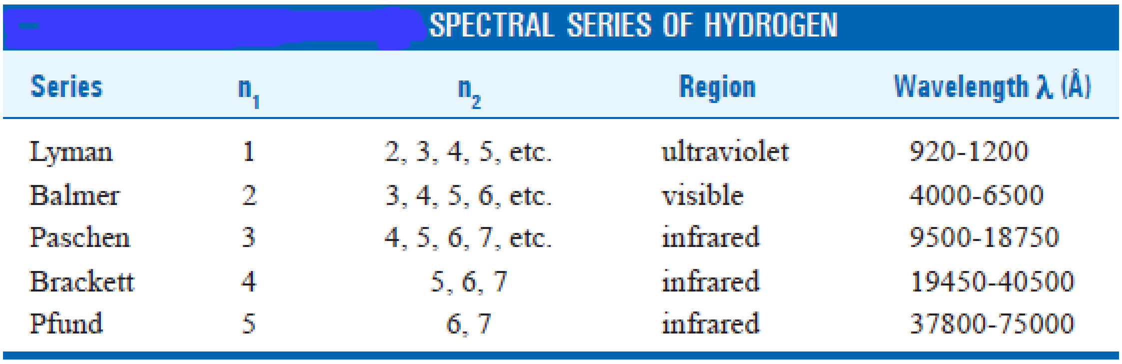


Figure 27 : Hydrogen spectral series on a Bohr atom energy diagram

Spectral series vary according to n_1 values :



[redacted] SPECTRAL SERIES OF HYDROGEN

Series	n_1	n_2	Region	Wavelength λ (Å)
Lyman	1	2, 3, 4, 5, etc.	ultraviolet	920-1200
Balmer	2	3, 4, 5, 6, etc.	visible	4000-6500
Paschen	3	4, 5, 6, 7, etc.	infrared	9500-18750
Brackett	4	5, 6, 7	infrared	19450-40500
Pfund	5	6, 7	infrared	37800-75000

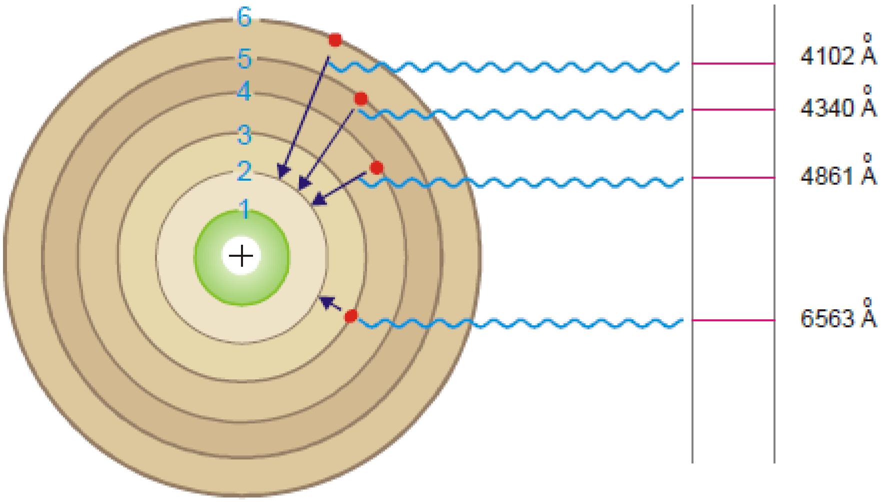


Figure 28 : Explanation of spectral lines of Hydrogen in visible region.

Value of *Rydberg*'s constant is the same as in the original empirical *Balmer*'s equation.

☐According to equation (1), the energy of the electron in orbit n_1 (lower) and n_2 (higher) is

$$E_{n_1} = -\frac{2\pi^2 me^4}{n_1^2 h^2}$$

$$E_{n_2} = -\frac{2\pi^2 me^4}{n_2^2 h^2}$$

The difference of energy between the levels n_1 and n_2 is :

$$\Delta E = E_{n_2} - E_{n_1} = \frac{2\pi^2 me^4}{h^2}\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$$ ❶

According to *Planck*'s equation:

$$\Delta E = h\nu = \frac{hc}{\lambda}$$ ❷

Where λ is wavelength of photon and (c) is velocity of light. From equation (1) and (2), we can write :

$$\frac{hc}{\lambda} = \frac{2\pi^2 e^4 m}{h^2}\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$$

$$\frac{1}{\lambda} = \frac{2\pi^2 e^4 m}{h^3 c}\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$$

$$= R\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$$

③

Where R is *Rydberg* constant. The value of R can be calculated as the value of (e, m, h and c) are known. It comes out to be 109,679 cm^{-1}and agrees closely with the value of Rydberg constant in the original empirical Balmer's equation (109,677 cm^{-1}).

5.3. Calculation of wavelengths of the spectral lines of Hydrogen in the visible region :

❒These lines constitute the Balmer series when $n_1 = 2$. Now the equation (3) above can be written as :

$$\frac{1}{\lambda} = 109679\left[\frac{1}{2^2} - \frac{1}{n_2^2}\right]$$

❒Thus the wavelengths of the photons emitted as the electron returns from energy levels 6, 5, 4 and 3 were calculated by Bohr. The calculated values corresponded exactly to the values of wavelengths of the spectral lines already known. This was, in fact, a great success of the Bohr atom.

6. Application of Bohr theory to hydrogen atom :

This model (*Bohr* atomic model) is limited to the study of systems with a single electron, including hydrogen and hydrogenoids.

Hydrogenoid : Is similar to hydrogen, it have only electron, but differ in the number of protons (Z) such as: ${}_{2}^{4}He^{+}, {}_{3}^{6}Li^{+2}, {}_{4}^{9}Be^{3+}$

6.1. *Bohr* Model Postulates :

Bohr, in an attempt to understand the structure of an atom better, combined classical theory with the early quantum concepts and gave his theory in three postulates :

Postulate I

In a radical departure from the established principles of classical mechanics and electromagnetism, Bohr postulated that in an atom, electron/s could revolve in stable orbits without emitting radiant energy. Further, he stated that each atom can exist in certain stable states. Also, each state has a definite total energy. These are stationary states of the atom.

Postulate II

Bohr defined these stable orbits in his second postulate. According to this postulate :

- An electron revolves around the nucleus in orbits
- The angular momentum of the electron is calculated in the following relationship :

$$mvr = nh/2\pi$$

m: mass of the electron.
v: Electron speed.
r: Orbit radius.
n: Quantum number (n = 1, 2, 3...)

Postulate III

In this postulate, Bohr incorporated early quantum concepts into the atomic theory. According to this postulate, an electron can transition from a non-radiating orbit to another of a lower energy level. In doing so, a photon is emitted whose energy is equal to the energy difference between the two states. Hence, the frequency of the emitted photon is :

$$hv = E_i – E_f$$

(Ei is the energy of the initial state and Ef is the energy of the final state. Also, Ei > Ef).

6.1.1. Determination of the radius of *Bohr* orbits :

An electron with m mass moves at v_n speed and draws a stable orbit with a radius of r_n, this electron is subject to two forces equal in intensity and opposite in direction: the Colombian force $\overrightarrow{F_{col}}$ and the centrifugal force $\overrightarrow{F_c}$ as shown in the figure :

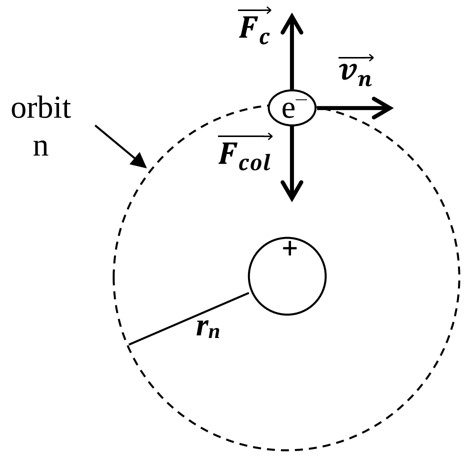
$$\overrightarrow{F_c} = \overrightarrow{F_{col}} \;\; et \;\; F_c = F_{col}$$

$$\text{où} \;\; F_c = \frac{m\,v^2}{r} \;\; et \;\; F_{col} = \frac{K\,Z\,e^2}{r^2}$$

$$\Rightarrow \frac{m\,v^2}{\cancel{r}} = \frac{K\,Z\,e^2}{r^{\cancel{2}}}$$

$$\Rightarrow mv^2 = \frac{K\,Z\,e^2}{r}$$

$$\Rightarrow m^2v^2 = \frac{K\,Z\,e^2 m}{r} \dots\dots (1)$$



Hydrogen atom

By Postulate II for bohr :

$$m\,v = \frac{h}{2\,\pi r} \dots\dots (2)$$

We compensate (2) in (1) we find :

$$\frac{K\,Z\,e^2 m}{\cancel{r}} = \frac{n^2\,h^2}{4\,\pi^2\,r^{\cancel{2}}} \quad \Rightarrow \quad r_n = \frac{n^2}{Z}\left(\frac{h^2}{4\,\pi^2\,m\,K\,e^2}\right) \dots\dots (3)$$

The r_1 of hydrogen atom radius is symbolized in its basic state:

$$\Rightarrow r_1 = \frac{1^2}{1}\left(\frac{(6{,}62 \times 10^{-34})^2}{4\,(3{,}14)^2\,(9{,}1 \times 10^{-31})\,(9 \times 10^9)\,(1{,}6 \times 10^{-19})^2}\right)$$

$$\Rightarrow r_1 = 0{,}53 \times 10^{-10}\,m = 0{,}53\,\text{Å}$$

Compensation in the equation (3) :

$$\Rightarrow \boldsymbol{r_n = \frac{n^2}{Z}\,(r_1)} \quad \textbf{où} \quad \boldsymbol{r_1 = 0,53}\ \text{Å}$$

It is the general relationship by which we calculate the radius of the hydrogen atom Z = 1 and the Z≠1 hydrogenoides in any orbit.

- For hydrogen $Z = 1,\ {}_1^1H$:

$$n = 1 \Rightarrow r_1 = \frac{1^2}{1}(0{,}53) = 0{,}53\ \text{Å}$$

$$n = 2 \Rightarrow r_2 = \frac{2^2}{1}(0{,}53) = 2{,}12\ \text{Å}$$

$$n = 3 \Rightarrow r_3 = \frac{3^2}{1}(0{,}53) = 4{,}77\ \text{Å}$$

For helium $Z = 2,\ {}_2^4He^+$:

$$n = 1 \Rightarrow r_1 = \frac{1^2}{2}(0{,}53) = 0{,}265\ \text{Å}$$

$$n = 2 \Rightarrow r_2 = \frac{2^2}{2}(0{,}53) = 1{,}06\ \text{Å}$$

$$n = 3 \Rightarrow r_3 = \frac{3^2}{2}(0{,}53) = 2{,}385\ \text{Å}$$

6.1.2. Determine the phrase "electron speed" in the *Bohr* atom :

By Postulate II for *bohr* :

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

And we have :

$$r_n = \frac{n^2}{Z}\left(\frac{h^2}{4\,\pi^2\,m\,K\,e^2}\right)$$

We compensate r_n in v_n we find :

$$v = \frac{\cancel{n}\,\cancel{h}}{\cancel{2}\,\cancel{\pi}\,\cancel{m}} \left(\frac{Z\,4\,\pi^{\cancel{2}}\,\cancel{m}\,K\,e^{2}}{n^{\cancel{2}}\,h^{\cancel{2}}} \right) \;\Rightarrow\; v_n = \frac{Z}{n} \left(\frac{2\,\pi\,K\,e^{2}}{h} \right) \ldots\ldots (4)$$

The v_1 for the speed of hydrogen atom electron in its basic state:

$$\Rightarrow v_1 = \frac{1}{1} \left(\frac{2\,(3{,}14)\,(9 \times 10^{9})\,(1{,}6 \times 10^{-19})^{2}}{(6{,}62 \times 10^{-34})} \right) = 2{,}18 \times 10^{6}\ m/s$$

Compensation in the equation (4):

$$\Rightarrow \boldsymbol{v_n = \frac{Z}{n}\,(v_1)} \ \ \textbf{où} \ \ \boldsymbol{v_1 = 2{,}18 \times 10^{6}\ m/s}$$

It is the general relationship by which we calculate the speed of the electron in the Bohr atom for hydrogen Z = 1 and the hydrogenoides Z≠1.

- For hydrogen $Z = 1,\ {}_{1}^{1}H$:

$$n = 1 \Rightarrow v_1 = \frac{1}{1}(2{,}18 \times 10^{6}) = 2{,}18 \times 10^{6}\ m/s$$

$$n = 2 \Rightarrow v_2 = \frac{1}{2}(2{,}18 \times 10^{6}) = 1{,}092 \times 10^{6}\ m/s$$

$$n = 3 \Rightarrow v_3 = \frac{1}{3}(2{,}18 \times 10^{6}) = 0{,}728 \times 10^{6}\ m/s$$

- For helium $Z = 2,\ {}_{2}^{4}He^{+}$:

$$n = 1 \Rightarrow v_1 = \frac{2}{1}(2{,}18 \times 10^{6}) = 4{,}36 \times 10^{6}\ m/s$$

$$n = 2 \Rightarrow v_2 = \frac{2}{2}(2{,}18 \times 10^{6}) = 2{,}18 \times 10^{6} m/s$$

$$n = 3 \Rightarrow v_3 = \frac{2}{3}(2{,}18 \times 10^{6}) = 1{,}453 \times 10^{6}\ m/s$$

6.1.3. Energy Electron Atom *Bohr* :

From *Bohr*'s hypothesis (orbits are stable means that their energy is constant), it means the electron is on the same dimension of the nucleus so energy is equal on all orbit points.

The total energy of any system consisting of kinetic energy E_c and latent energy E_P where

$$E_T = E_P + E_c$$

$$E_c = \frac{1}{2}\, m\, v^2 \;\; \text{و} \;\; E_P = -\,\frac{K\, Z\, e^2}{r}$$

We know that in order for the electron not to fall on the nucleus, There must be a parity between the attractive force and the centrifugal force :

$$\overrightarrow{F_{\text{الطاردة}}} = \overrightarrow{F_{\text{الكولومبية}}} \Rightarrow \frac{m\, v^2}{r} = \frac{K\, Z\, e^2}{r^2}$$

$$\Rightarrow m\, v^2 = \frac{K\, Z\, e^2}{r}$$

$$E_c = \frac{1}{2}\, m\, v^2 = \frac{K\, Z\, e^2}{2\, r}$$

$$E_c = \frac{K\, Z\, e^2}{2\, r} \;\; \text{أي}$$

$$E_T = E_c + E_p = \frac{K\, Z\, e^2}{2\, r} - \frac{K\, Z\, e^2}{r} \Rightarrow E_T = -\frac{K\, Z\, e^2}{2\, r}$$

to compensate r_n in the phrase E_T we find :

$$E_T = E_n = -\frac{K\, Z\, e^2}{\cancel{2}}\left(\frac{Z\, 4\, \pi^2\, m\, K\, e^2}{n^2\, h^2}\right)$$

$$E_n = \frac{Z^2}{n^2}\left(-\,\frac{2\, \pi^2\, m\, K^2\, e^4}{h^2}\right) \ldots\ldots (6)$$

Symbolized by E_1 for hydrogen atom energy in its basic state :

$$\Rightarrow\ E_1 = \frac{1^2}{1^2}\left(-\frac{2\,(3{,}14)^2\,(9{,}1\ \times\ 10^{-31})\,(9\ \times\ 10^{9})^2\,(1{,}6\ \times\ 10^{-19})^4}{(6{,}62\ \times\ 10^{-34})^2}\right)$$

$$\Rightarrow\ E_1 = -21{,}74\ \times\ 10^{-19}\,J = -13{,}6\,ev$$

Compensation in the equation (6) :

$$\Rightarrow \boldsymbol{E_n = \frac{Z^2}{n^2}\,(E_1)}\ \ \textbf{où}\ \ \boldsymbol{E_1 = -13{,}6\,ev}$$

On this basis, the energy of hydrogen atom electron levels according to Bohr's theory is as follows:

$$n = 1 \Rightarrow E_1 = \frac{1^2}{1^2}(-13{,}6) = -13{,}6\,ev$$

$$n = 2 \Rightarrow E_2 = \frac{1^2}{2^2}(-13{,}6) = -3{,}42\,ev$$

$$n = 3 \Rightarrow E_3 = \frac{1^2}{3^2}(-13{,}6) = -1{,}51\,ev$$

$$n = 3 \Rightarrow E_4 = \frac{1^2}{4^2}(-13{,}6) = -0{,}85\,ev$$

From it, the energy levels of hydrogen atom can be represented by *Bohr* :

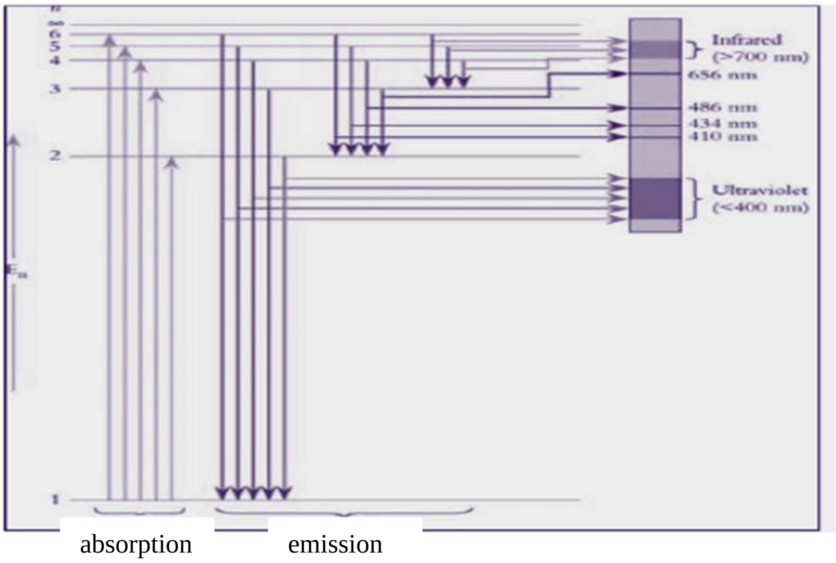


Figure 29 : Hydrogen emissin and absoption spectra

In the same way the energy of hydrogenoids can be represented by bohr.

- ***Rydberg*'s Formula :**

In atomic physics, *Rydberg*'s equation calculates the wavelength of the spectral line in a wide range of chemical elements. The equation is a generalisation of the *Balmer* series for all atomic hydrogen transitions. It is a unit of energy, explained in terms of the ground-state energy of the electron in the *Bohr* model of the hydrogen atom. In cgs, where “me” is electron mass, “e” is the charge of the electron, “Z” is the atomic number, and “n” is the principal quantum number of the electron state. It is easy to measure the spectral lines using the Rydberg formula.

The *Rydberg*'s Formula is :

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

Where,

R_H is the *Rydberg* constant (1,09737.10^7 m^{-1})

λ is the wavelength of light

Z is the atomic number

n_2 is the upper energy level

n_1 is the lower energy level

Single-electron atoms such as hydrogen have spectral series of Z = 1.

While the energy of the photon :

$$\Delta E = h\upsilon = \mathrm{h}\frac{C}{\lambda} = \mathrm{h}C\,\bar{\upsilon} \Rightarrow \Delta E = hCZ^2 R_H \left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

6.2. First line wavelength and final line:

Each of the previous five series features two main lines:

- **First line :**

Characterized by a smaller energy difference, smaller frequency and greater wavelength (most λ_{max}) where :

$$\frac{1}{\lambda_{\max}} = Z^2 R_H \left(\frac{1}{{n_1}^2} - \frac{1}{(n_1+1)^2}\right)$$

$$\frac{1}{\lambda_{\max}} = Z^2 R_H \left(\frac{(n_1+1)^2 - {n_1}^2}{{n_1}^2 (n_1+1)^2}\right)$$

$$\frac{1}{\lambda_{\max}} = Z^2 R_H \left(\frac{2n_1+1}{{n_1}^2 (n_1+1)^2}\right) \Rightarrow \qquad \boxed{\boldsymbol{\lambda_{\max} = \frac{{n_1}^2 (n_1+1)^2}{Z^2 R_H (2n_1+1)}}}$$

- **Final line :**

Characterized by greater energy difference, greater frequency and smaller wave length (most $\lambda_{\min}$) where:

$$\frac{1}{\lambda_{\min}} = Z^2 R_H \left(\frac{1}{{n_1}^2} - \frac{1}{\infty^2}\right)$$

$$\frac{1}{\lambda_{\min}} = Z^2 R_H \left(\frac{1}{{n_1}^2}\right) \Rightarrow \qquad \boxed{\boldsymbol{\lambda_{\min} = \frac{{n_1}^2}{Z^2 R_H}}}$$

6.3. Ionization energy of hydrogen atom and hydrogenoids :

The energy that is needed to remove the electron from the atom is called the ionization energy.

$$E_n = \frac{Z^2}{n^2} E_1, \quad E_i = E_\infty - E_n$$

Where :

$$1 \leq n < \infty$$

- For hydrogen atom in its basic state :

$$E_i = E_\infty - E_1$$

$$E_i = -\frac{Z^2}{n^2} E_1, \quad E_1 = -13{,}6\ eV$$

Ionization energy is always positive.

6.4. Shortcomings of The *Bohr* Atom :

(1) The great success of the *Bohr* theory was in its ability to predict lines in the hydrogen atom spectrum. But it was spectacularly unsuccessful for every other atom containing more than one electron.

(2) We no longer believe in well-defined electron orbits as was assumed by *Bohr*. In fact, in view of modern advances, like dual nature of matter, uncertainty principle, any mechanical model of the atom stands rejected.

(3) *Bohr*'s model of electronic structure could not account for the ability of atoms to form molecules through chemical bonds. Today we only accept Bohr's views regarding quantization as nobody has explained atomic spectra without numerical quantization and no longer attempted description of atoms on classical mechanics.

(4) *Bohr*'s theory could not explain the effect of magnetic field (*Zeeman* effect) and electric field (Stark effect) on the spectra of atoms.

- ***Sommerfeld*'s Modification of *Bohr* Atom :**

❐When spectra were examined with spectrometers, each line was found to consist of several closely packed lines. The existence of these multiple spectral lines could not be explained on the basis of Bohr's theory.

❐Sommerfeld modified *Bohr*'s theory as follows. Bohr considered electron orbits as circular but Sommerfeld postulated the presence of elliptic orbits also.

❐An ellipse has a major and minor axis. A circle is a special case of an ellipse with equal major and minor axis. The angular momentum of an electron moving in an elliptic orbit is also supposed to be quantized. Thus only a definite set of values is permissible. It is further assumed that the angular momentum can be an integral part of (h/2π) units, where h is Planck's constant. Or that,

$$\text{angular momentum} = \frac{kh}{2\pi}$$

❒where (k) is called the azimuthal quantum number, whereas the quantum number used in *Bohr*’s theory is called the principal quantum number. The two quantum numbers n and k are related by the expression :

$$\frac{n}{k} = \frac{\text{length of major axis}}{\text{length of minor axis}}$$

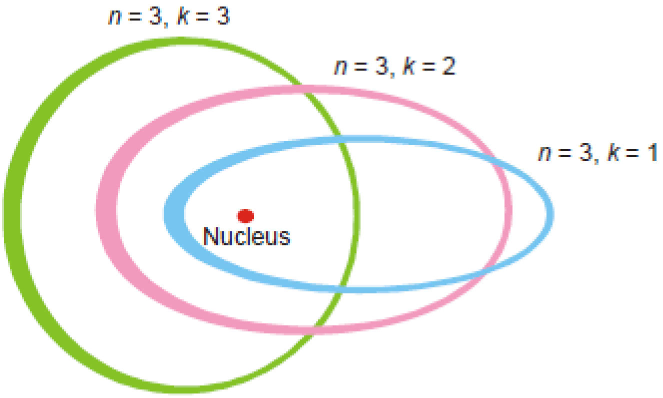


Figure 30 : *Sommerfeld* orbits in Hydrogen atom

❒The values of (k) for a given value of (n) are k = n – 1, n – 2, n – 3 and so on. A series of elliptic orbits with different eccentricities result for the different values of k. When n = k, the orbit will be circular. In other words (k) will have (n) possible values (n to 1) for a given value of (n). However, calculations based on wave mechanics have shown that this is incorrect and the Sommerfeld’s modification of Bohr atom fell through.

6.5. Quantum numbers :

A total of four quantum numbers are used to describe completely the movement and trajectories of each electron within an atom. The combination of all quantum numbers of all electrons in an atom is described by a wave function that complies with the Schrödinger equation. Each electron in an atom has a unique set of quantum numbers ; according to the *Pauli* Exclusion Principle, no two electrons can share the same combination of four quantum numbers. Quantum numbers are important because they can be used to determine the electron configuration of an atom and the probable location of the atom's electrons. Quantum numbers are also used to understand other characteristics of atoms, such as ionization energy and the atomic radius.

In atoms, there are a total of four quantum numbers : the principal quantum number (n), the orbital angular momentum quantum number (l), the magnetic quantum number (m_l), and the electron spin quantum number (m_s). The principal quantum number n.

6.5.1. The Principal Quantum Number (n) :

The principal quantum number, n, designates the principal electron shell. Because n describes the most probable distance of the electrons from the nucleus, the larger the number n is, the farther the electron is from the nucleus, the larger the size of the orbital, and the larger the atom is. n can be any positive integer starting at 1, as $n=1$ designates the first principal shell (the innermost shell). The first principal shell is also called the ground state, or lowest energy state. This explains why n can not be 0 or any negative integer, because there exists no atoms with zero or a negative amount of energy levels/principal shells. When an electron is in an excited state or it gains energy, it may jump to the second principle shell, where $n=2$. This is called absorption because the electron is "absorbing" photons, or energy. Known as emission, electrons can also "emit" energy as they jump to lower principle shells, where n decreases by whole numbers. As the energy of the electron increases, so does the principal quantum number, e.g., $n = 3$ indicates the third principal shell, $n = 4$ indicates the fourth principal shell, and so on. $n=1,2,3,4\ldots$

6.5.2. The Orbital Angular Momentum Quantum Number (l) :

The orbital angular momentum quantum number l determines the shape of an orbital, and therefore the angular distribution. The number of angular nodes is equal to the value of the angular momentum quantum number l. (For more information about angular nodes, see Electronic Orbitals.) Each value of l indicates a specific s, p, d, f subshell (each unique in shape.) The value of l is dependent on the principal quantum number n. Unlike n, the value of l can be zero. It can also be a positive integer, but it cannot be larger than one less than the principal quantum number ($n-1$): $l=0,1,2,3,4\ldots,(n-1)$

6.5.3. The Magnetic Quantum Number (ml) :

The magnetic quantum number ml determines the number of orbitals and their orientation within a subshell. Consequently, its value depends on the orbital angular momentum quantum number l. Given a certain l, ml is an interval ranging from $-l$ to $+l$, so it can be zero, a negative integer, or a positive integer.

$$ml=-l,(-l+1),(-l+2),\ldots,-2,-1,0,1,2,\ldots(l-1),(l-2),+l$$

6.5.4. The Electron Spin Quantum Number (*ms*) :

Unlike *n*, *l*, and m_l, the electron spin quantum number m_s does not depend on another quantum number. It designates the direction of the electron spin and may have a spin of +1/2, represented by↑, or –1/2, represented by ↓. This means that when m_s is positive the electron has an upward spin, which can be referred to as "spin up." When it is negative, the electron has a downward spin, so it is "spin down." The significance of the electron spin quantum number is its determination of an atom's ability to generate a magnetic field or not. (Electron Spin.)

$$m_s = \pm 1/2$$

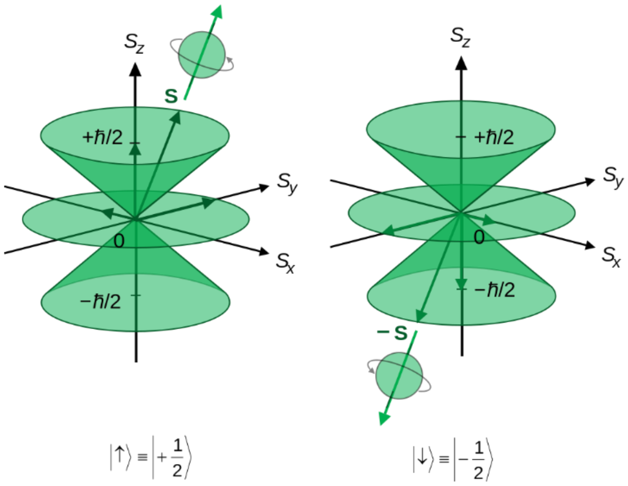


Figure 31 : Electron Spin

II- Electronic structure of atom by wave mechanics and quantitative mechanics

1- Introduction :

Atoms could not be described accurately until quantum theory as developed, Quantum theory offered a fresh way of thinking about the universe at the atomic level. After tremendous advances in quantum mechanics in the last century, the position of electrons and other infinitesimal particles can be predicted with confidence.

At the end of 1913 *Niels Bohr* facilitated the leap to a new paradigm of atomic theory – quantum mechanics. *Bohr*'s new idea that electrons could only be found in specified, quantized orbits was revolutionary (*Bohr*, 1913). As is consistent with all new scientific discoveries, a fresh way of thinking about the universe at the atomic level would only lead to more questions, the need for additional experimentation and collection of evidence, and the development of expanded theories. As such, at the beginning of the second decade of the 20th century, another rich vein of scientific work was about to be mined.

2- Wave-particle duality (*Lewis de Broglie*) :

he theory of wave--particle duality developed by *Louis-Victor de Broglie* eventually explained why the *Bohr* model was successful with atoms or ions that contained one electron. It also provided a basis for understanding why this model failed for more complex systems.

De *Broglie* started with the fact that light acts as both a particle and a wave. In many ways light acts as a wave, with a characteristic frequency, wavelength, and amplitude. *Einstein* argued, however, that light carries energy as if it contains discrete photons or packets of energy. In his doctoral thesis at the Sorbonne in 1924, de *Broglie* looked at the consequences of assuming that light simultaneously has the properties of both a particle and a wave. He then extended this idea to other objects, such as an electron.

When an object behaves as a particle in motion, it has an energy proportional to its mass (m) and speed with which it moves through space (s).

$$E = mc^2$$

When it behaves as a wave, however, it has an energy that is proportional to its frequency.

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

By simultaneously assuming that an object can be both a particle and a wave, de *Broglie*, he derived a relationship between one of the wave-like properties of matter and one of its properties as a particle.

$$\mathrm{E} = \frac{hC}{\lambda} = mc^2 \Rightarrow \lambda = \frac{h}{mC} = \frac{h}{P}$$

As noted in the previous section, the product of the mass of an object times the speed with which it moves is the momentum (p) of the particle. Thus, the de *Broglie* equation suggests that the wavelength (λ) of any object in motion is inversely proportional to its momentum.

De *Broglie* concluded that most particles are too heavy to observe their wave properties. When the mass of an object is very small, however, the wave properties can be detected experimentally. De *Broglie* predicted that the mass of an electron was small enough to exhibit the properties of both particles and waves. In 1927 this prediction was confirmed when the diffraction of electrons was observed experimentally by *C. J. Davisson*.

De *Broglie* applied his theory of wave-particle duality to the *Bohr* model to explain why only certain orbits are allowed for the electron. He argued that only certain orbits allow the electron to satisfy both its particle and wave properties at the same time because only certain orbits have a circumference that is an integral multiple of the wavelength of the electron, as shown below.

In 1923, *Louis de Broglie* predicted that since light exhibited both wave and particle behavior, particles should also. He proposed that all particles have a wavelength given by :

$$\lambda = \frac{h}{mC} = \frac{h}{P}$$

3- *Werner Heisenberg*'s Uncertainty Principle :

Heisenberg's Uncertainty principle, as published by *Werner Heisenberg* in 1927, states that it is impossible to determine both the position and momentum of any particle simultaneously. The equation of *Heisenberg*'s uncertainty principle is as follows :

$$\Delta\, p.\ \Delta\, x \geq h/2\pi.$$

Where h= *Planck*'s constant

Δ= Uncertainty.

Question: According to the *Heisenberg* uncertainty principle, it is impossible to calculate the position and velocity of an electron at the same time. Give reason.

Answer: According to *Bohr*'s model, the electron is a material particle and the calculation of its momentum and position at the same time is possible. However, *de-Broglie* declared the wave nature of the electron and concluded that it is impossible to simultaneously calculate the exact position and velocity of the electron. In 1927, *Heisenberg* gave his principle that states that the determination of both position and momentum of particles at the same time is impossible. This is simply because the electrons do not possess any definite position and direction of motion at the same time.

Question: A given proton has an uncertainty of 0.05 A°. Determine the uncertainty in the speed of protons using Heisenberg's uncertainty principle.

Solution: Mathematically, the *Heisenberg* uncertainty principle is :

$$\Delta\ x.\ \Delta\ p \geq h/2\pi$$

According to the question,

$$\Delta\ x = 0.05\ \text{A°}$$

Applying *Heisenberg*'s Uncertainty principle,

$$\Delta x = 0{,}05\ \times 10^{-10} m$$

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

$$\Delta x . m \Delta v = \frac{h}{2\pi}$$

$$\Delta v = \frac{h}{2\pi \times \Delta x \times m} = \frac{6{,}62.\,10^{-34}}{9{,}1.\,10^{-31} \times 2\pi \times 0{,}05\ \times 10^{-10}}$$

$$\Delta v = 2{,}31.10^{7} m/s$$

The uncertainty in the speed of protons using *Heisenberg*'s uncertainty principle is $2{,}31.10^{7} m/s$

Conclusion

Heisenberg's uncertainty principle states that it is impossible to determine the position and momentum of any particle at the same time with absolute accuracy. The principle was stated by the German physicist and philosopher, *Werner Heisenberg* in 1927, and is of great significance in quantum physics. The principle is based on the wave-particle duality, stating the dual nature of matter (waves and particles). Study the article to know about some of the Frequently Asked Questions on *Heisenberg*'s Uncertainty Principle.

4- Atomic Orbital Model :

In 1926, *Erwin Schrödinger* derived his now famous equation. For approximately 200 years prior to Schrödinger's work, the infinitely simpler *F = ma* (*Newton*'s second law) had been used to describe the motion of particles in classical mechanics. With the advent of quantum mechanics, a completely new equation was required to describe the properties of subatomic particles. Since these particles were no longer thought of as classical particles but as particle-waves, *Schrödinger*'s partial differential equation was the answer. In the simplest terms, just as Newton's second law describes how the motion of physical objects changes with changing conditions, the Schrödinger equation describes how the wave function (Ψ) of a quantum system changes over time. The *Schrödinger* equation was found to be consistent with the description of the electron as a wave, and to correctly predict the parameters of the energy levels of the hydrogen atom that *Bohr* had proposed.

The scientist *Schrödinger* re-examined the structure of the atom according to the *Bohr* model and added the hypothesis of *Lewis de Broglie*, where the electron kept pace with a stable wave.

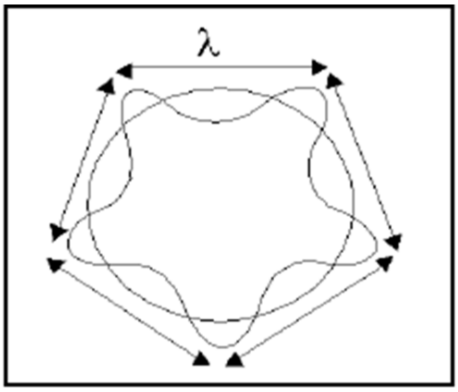


Figure 32 : hypothesis of *Lewis de Broglie*

$$2\pi \mathrm{r} = n\lambda$$

where *n* is a natural number ; $n \neq 0$

By offsetting *De Broglie*'s wavelength phrase we get :

$$2\pi \mathrm{r} = n\lambda = \frac{nh}{mv} \Rightarrow mvr = \frac{nh}{2\pi}$$

This phrase represents the angular momentum put by *Bohr* on the hydrogen atom electron.

4.1.Mathematic Description of Wave:

The latter leads to a second-degree differential equation, this equation is very important in waveform mechanics and its solution can determine the location of the electron in the atom :

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} + \frac{4\pi^2}{\lambda^2}\psi = 0$$

$$\Delta\psi + \frac{4\pi^2}{\lambda^2}\psi = 0$$

Where :

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

This equation controls the movement of stable waves spread in space.

4.2.The *Schrödinger* equation :

Schrödinger chose the mathematical equation that describes the spread of a stable wave based on a model of corn structure. Then insert in this phrase the hypothesis of De Brugley to get the following :

$$\Delta\psi + \frac{4\pi^2}{\left(\frac{h}{mv}\right)^2}\psi = 0$$

$$\Delta\psi + \frac{4\pi^2 m^2 v^2}{h^2}\psi = 0 \dots\dots\dots..(1)$$

Electron Kinetic Energy :

$$E = E_P + E_C \Rightarrow E_C = E - E_P$$

$$\Rightarrow \frac{1}{2}mv^2 = E - E_P$$

$$\Rightarrow mv^2 = 2(E - E_P)$$

$$\Rightarrow m^2v^2 = 2m(E - E_P)$$

Compensation in the equation(1) :

$$\Delta\psi + \frac{8\pi^2 m}{h^2}(E - E_P)\psi = 0, \qquad \text{It's } \textit{Schrödinger} \text{ 's equation.}$$

The probability of finding a particle at a particular location, then, is related to the wave associated with the particle. The larger the amplitude of the wave at a particular point, the larger the probability that the electron will be found there. Similarly, the smaller the amplitude the smaller the probability. In fact, the probability is proportional to the square of the amplitude of the wave.

All these ideas, that for very small particles both particle and wave properties are important, and that particle energies are quantized, only taking on discrete values, are the cornerstones of quantum mechanics. In quantum mechanics we often talk about the wave function ψ of a particle, the wave function is the wave discussed above, with the probability of finding the particle in a particular location being proportional to the square of the amplitude of the wave function.

The intensity of the probability of a precise presence in the racial size dV is given with the relationship :

$$dP = \psi^2 dV$$

Schrödinger's equation is perhaps most commonly used to define a three-dimensional area of space where a given electron is most likely to be found. Each area of space is known as an atomic orbital and is characterized by a set of three quantum numbers. These numbers represent values that describe the coordinates of the atomic orbital : including its size (*n*, the principal quantum number), shape (*l*, the angular or azimuthal quantum number), and orientation in space (*m*, the magnetic quantum number). There is also a fourth quantum number that is exclusive to a particular electron rather than a particular orbital (*s*, the spin quantum number).

Schrödinger's equation allows the calculation of each of these three quantum numbers. This equation was a critical piece in the quantum mechanics puzzle, since it brought quantum theory into sharp focus via what amounted to a mathematical demonstration of Bohr's fundamental quantum idea. The *Schrödinger* wave equation is important since it bridges the gap between classical Newtonian physics (which breaks down at the atomic level) and quantum mechanics. The *Schrödinger* equation is rightfully considered to be a monumental contribution to the advancement and understanding of quantum theory.

5. *Max Born* further interprets the *Schrödinger* equation :

German mathematician and physicist *Max Born* made a very specific and crucially important contribution to quantum mechanics relating to the *Schrödinger* equation. *Born* took the wave functions that *Schrödinger* produced, and said that the solutions to the equation could be interpreted as three-dimensional probability "maps" of where an electron may most likely be found around an atom (*Born*, 1926). These maps have come to be known as the *s, p, d*, and *f* orbitals (following figure) :

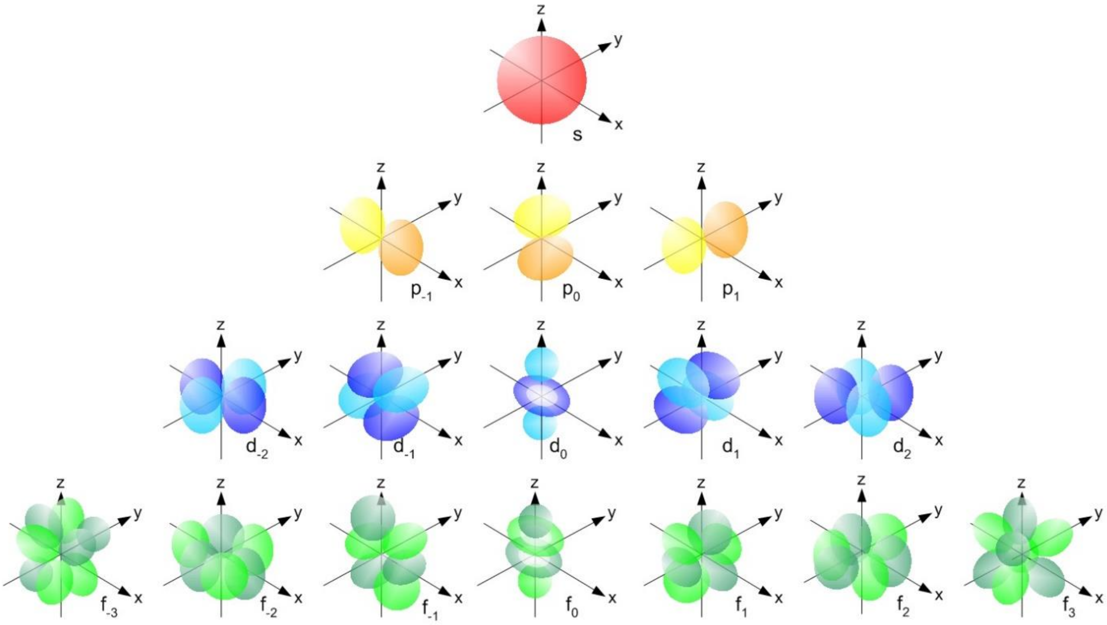


Figure 33 : Based on *Born*'s theories, these are representations of the three-dimensional probabilities of an electron's location around an atom. The four orbitals, in increasing complexity, are: *s, p, d,* and *f*. Additional information is given about the orbital's magnetic quantum number (*m*).

Practical exercises

Exercise 1:

Single Color Light Radiation Frequency .$\upsilon = 5{,}1 .10^{14}$ Hz.

1- Calculate the wave length **λ**, wave number **υ**, period **T**, and photon energy carried by this light radiation.

2- This light radiation hits a metal plate of zinc Zn with $E_0(Zn) = 3{,}4$ ev. Does photoelectric action occur?

3- This light radiation hits a metal plate of cesium Cs with $E_0(Cs) = 1{,}9$ ev. Does photoelectric action occur? If so, calculate the kinetic energy of the liberated electron, then calculate the speed of the electrons freed from the cesium metal.

given : **h** = $6{,}62 .10^{-34}$J.s, **C** = $3 .10^{8}$ m/s, **me** = $9{,}1 .10^{-31}$ Kg

Exercise 2:

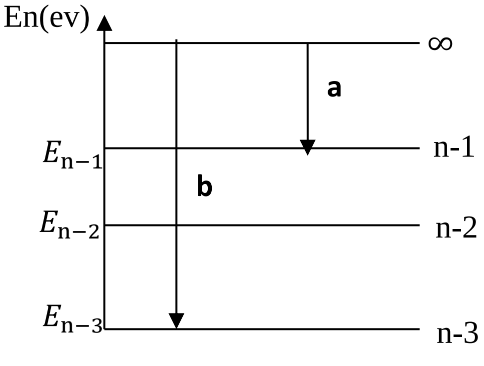
1- Calculate the wavelength approval of the first line and the boundary line of series: Lyman and Brackett.

2- Calculate the ionizing energy of the hydrogen atom in the first excited state.

3- Calculate radius $\mathbf{r_n}$, speed **Vn** and energy **En** for n = 1, 2, 3 according to Bohr model.

4- Represent on the energy diagram the transitions of the first line of absorption spectrum in the Lyman series and the second line of emission spectrum in the Paschen series.

5- We have transitions a and b shown on the following diagram, if $\frac{\Delta E_b}{\Delta E_a} = \frac{25}{9}$, Find the number **n** indicate on the energy diagram, then name each spectral series
For each transition.



Exercise 3:

1- If the wavelength of one line of hydrogen atom spectrum is $\lambda = 4868\ A°$, at what energy level the electron transits

2- It is assumed that this transitions was made on Hydrogenoid of $_3$Li.

a- Write the reactions that lead to the corresponding hydrogen.

b- Calculate the wavelength corresponding to the same previous transition.

c- Calculate the energy for the previous transition in two ways.

Exercise 4:

Considering that the hydrogenoid $_zX^{+q}$ is in a state of second excitation with total energy En=-24,17ev. find the number of charge Z and charge q for this hydrogenoid.

1- Calculate the wavelength $\lambda_{X^{+q}}$ for the assumed transition $(3 \rightarrow 4)$

2- Find the relation between λ_H and $\lambda_{X^{+q}}$ then calculate λ_H for transition$(3 \rightarrow 4)$

3- Calculate the ionization energy of H and $_zX^{+q}$ in the fundamental state, then in the second excitation.

4- find the quantum numbers n, l, m, s possible for the electron hydrogenoid $_zX^{+q}$ in second excitation. Then calculate the radius **a** and **b** according to Sommerfield.

Exercise 5:

1- Calculate the wavelength for the following cases

a- the weight of a human being is m = 65 kg and its speed is v = 5 km/h

b- Atom ^{63}Cu moves in vacuum by kinetic energy Ec = 7eV.

c- Electron of hydrogen atom in third excitation.

2- We consider electron to be its kinetic energy Ec = 10^2 eV and the absolute uncertainty of speed is 10^{-5}m/, calculate relative uncertainty on this speed and then absolute uncertainty on the position Δx.

3- Find the quantum numbers n, l, m, s of the main electronic layers M, N.

4- Find quantum numbers n, l for electronic layers ψ_{4d}, ψ_{4f}, ψ_{3p}, ψ_{2s}.

5- Write wave functions according to secondary electronic layers ψ_{52}, $\psi_{6331/2}$, ψ_{600}, $\psi_{1111/2}$

Chapter V

Periodic table

Chapter V :

Periodic table

1- Introduction :

Did you know that although electrons are minuscule compared to other parts of an atom, the way they are arranged around the nucleus is the biggest factor in determining the chemical properties of an element? The periodic chart is ordered by atomic number, but drastic shifts in chemical properties can occur from one element to the next. These shifts are explained by how the elements are displayed on the periodic table.

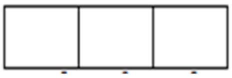
2- Electronic composition of atom :

2.1. Orbital Diagrams :

- **S** orbital consists of one quantum quase

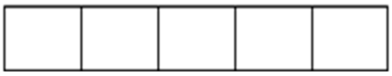
l = 0
(S)

- **P** orbital consists of three quantum quases



l = 1
(p)

- **d** orbital consists of five quantum quases



l = 2
(d)

- **f** orbital consists of seven quantum quases

l = 3
(f)

Two electrons can not have same four quantum numbers. The first three quantum numbers (n, l, and ml) can be the same, but the fourth must be different. A single orbital can only house two electrons with opposing spins. One electron spins up (ms = +1/2), while the other spins down (ms = -1/2).

$$\Psi_{100+\frac{1}{2}} \boxed{\uparrow\downarrow} \Psi_{100-\frac{1}{2}} \qquad ({}^{4}_{2}He)$$

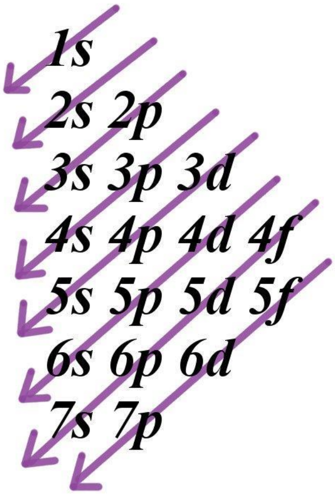
2.2. Rules for Assigning Electron Orbitals :

2.2.1. Occupation of Orbitals :

Electrons fill orbitals in a way to minimize the energy of the atom. Therefore, the electrons in an atom fill the principal energy levels in order of increasing energy (the electrons are getting farther from the nucleus). The order of levels filled looks like this :

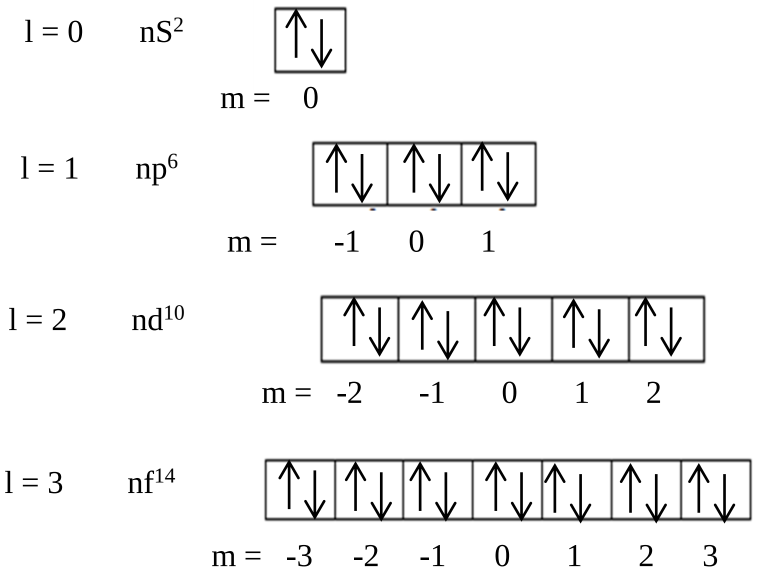
1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s, 4d, 5p, 6s, 4f, 5d, 6p, 7s, 5f, 6d, and 7p

One way to remember this pattern, probably the easiest, is to refer to the periodic table and remember where each orbital block falls to logically deduce this pattern.



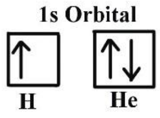
2.2.2. Pauli Exclusion Principle :

The Pauli exclusion principle states that no two electrons can have the same four quantum numbers. The first three (n, l, and m_l) may be the same, but the fourth quantum number must be different. A single orbital can hold a maximum of two electrons, which **must** have opposing spins ; otherwise they would have the same four quantum numbers, which is forbidden. One electron is spin up (m_s = +1/2) and the other would spin down (m_s = -1/2). This tells us that each subshell has double the electrons per orbital. The s subshell has 1 orbital that can hold up to 2 electrons, the p subshell has 3 orbitals that can hold up to 6 electrons, the d subshell has 5 orbitals that hold up to 10 electrons, and the f subshell has 7 orbitals with 14 electrons.



Example 1 : Hydrogen and Helium

The first three quantum numbers of an electron are n=1, l=0, m_l=0. Only two electrons can correspond to these, which would be either m_s = -1/2 or m_s = +1/2. As we already know from our studies of quantum numbers and electron orbitals, we can conclude that these four quantum numbers refer to the 1s subshell. If only one of the m_s values are given then we would have $1s^1$ (denoting hydrogen) if both are given we would have $1s^2$ (denoting helium). Visually, this is be represented as :



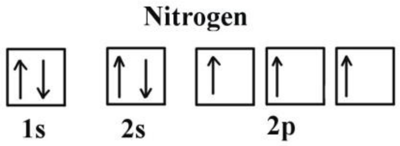
As shown, the 1s subshell can hold only two electrons and, when filled, the electrons have opposite spins.

2.2.3. Hund's Rule :

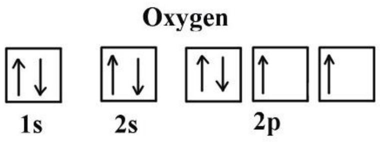
When assigning electrons in orbitals, each electron will first fill all the orbitals with similar energy (also referred to as degenerate) before pairing with another electron in a half-filled orbital. Atoms at ground states tend to have as many unpaired electrons as possible. When visualizing this processes, think about how electrons are exhibiting the same behavior as the same poles on a magnet would if they came into contact ; as the negatively charged electrons fill orbitals they first try to get as far as possible from each other before having to pair up.

Example 2 : Oxygen and Nitrogen

If we look at the correct electron configuration of the Nitrogen (Z = 7) atom, a very important element in the biology of plants : $1s^2\ 2s^2\ 2p^3$



We can clearly see that p orbitals are half-filled as there are three electrons and three p orbitals. This is because Hund's Rule states that the three electrons in the 2p subshell will fill all the empty orbitals first before filling orbitals with electrons in them. If we look at the element after Nitrogen in the same period, Oxygen (Z = 8) its electron configuration is: $1s^2\ 2s^2\ 2p^4$ (for an atom).



Oxygen has one more electron than Nitrogen and as the orbitals are all half filled the electron must pair up.

2.3. Writing Electron Configurations :

When writing an electron configuration, first write the **energy level** (the period), then the **subshell** to be filled and the **superscript**, which is the number of electrons in that subshell. The total number of electrons is the atomic number, Z. The rules above allow one to write the electron configurations for all the elements in the periodic table. Three methods are used to write electron configurations :

1. **orbital diagrams**
2. **spdf notation**
3. **noble gas notation**

Each method has its own purpose and each has its own drawbacks.

- ✓ **Orbital Diagrams :**

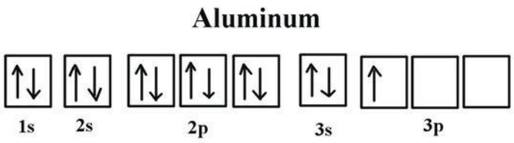
An orbital diagram, like those shown above, is a visual way to reconstruct the electron configuration by showing each of the separate orbitals and the spins on the electrons. This is done by first determining the subshell (s,p,d, or f) then drawing in each electron according to the stated rules above.

Example 4 : Aluminum and Iridium

Write the electron configuration for aluminum and iridium.

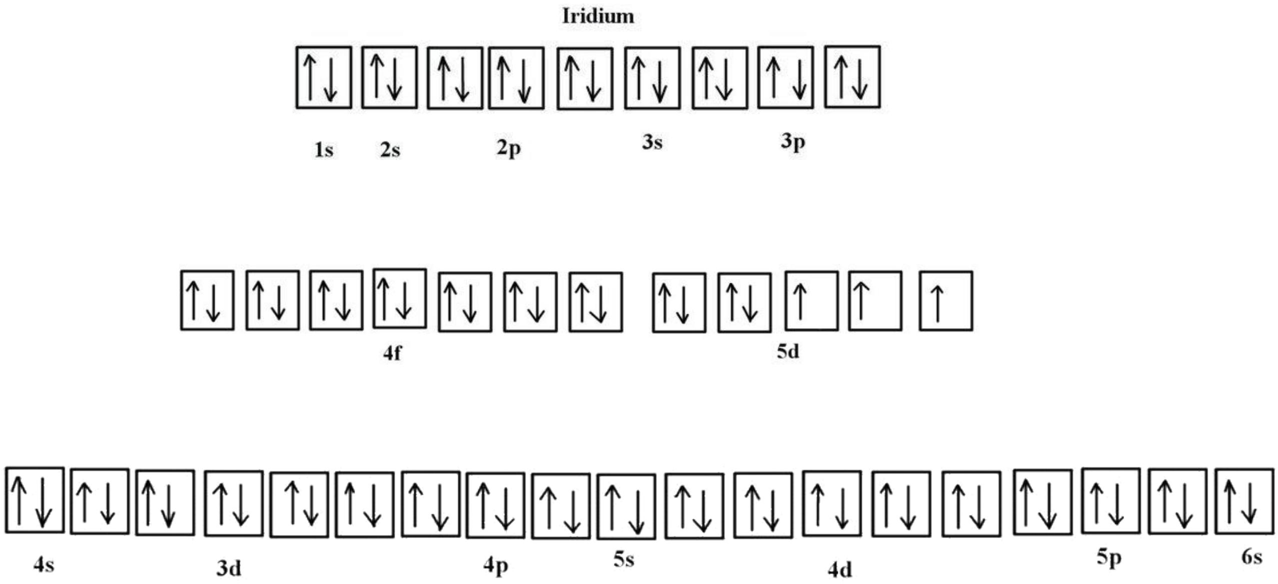
Solution :

Aluminum is in the 3rd period and it has an atomic number of Z=13. If we look at the periodic table we can see that its in the p-block as it is in group 13. Now we shall look at the orbitals it will fill : 1s, 2s, 2p, 3s, 3p. We know that aluminum completely fills the 1s, 2s, 2p, and 3s orbitals because mathematically this would be 2+2+6+2=12. The last electron is in the 3p orbital. Also another way of thinking about it is that as you move from each orbital block, the subshells become filled as you complete each section of the orbital in the period. The block that the atom is in (in the case for aluminum : 3p) is where we will count to get the number of electrons in the last subshell (for aluminum this would be one electron because its the first element in the period 3 p-block). This gives the following :



Note that in the orbital diagram, the two opposing spins of the electron can be visualized. This is why it is sometimes useful to think about electron configuration in terms of the diagram.

However, because it is the most time consuming method, it is more common to write or see electron configurations in spdf notation and noble gas notation. Another example is the electron configuration of iridium :



The electron configuration of iridium is much longer than aluminum. Although drawing out each orbital may prove to be helpful in determining unpaired electrons, it is very time consuming and often not as practical as the spdf notation, especially for atoms with much longer configurations. Hund's rule is also followed, as each electron fills up each 5d orbital before being forced to pair with another electron.

✓ **spdf Notation :**

The most common way to describe electron configurations is to write distributions in the spdf notation. Although the distributions of electrons in each orbital are not as apparent as in the diagram, the total number of electrons in each energy level is described by a superscript that follows the relating energy level. To write the electron configuration of an atom, identify the energy level of interest and write the number of electrons in the energy level as its superscript as follows: $1s^2$. This is the electron configuration of helium ; it denotes a full s orbital. The periodic table is used as a reference to accurately write the electron configurations of all atoms.

Example 5: Yttrium

Write the electronic configuration of Yttrium.

Solution :

Start with the straightforward problem of finding the electron configuration of the element yttrium. As always, refer to the periodic table. The element yttrium (symbolized Y) is a transition metal, found in the fifth period and in Group 3. In total it has thirty-nine electrons. Its electron configuration is as follows :

$$\mathbf{1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^{10}\ 4p^6\ 5s^2\ 4d^1}$$

This is a much simpler and more efficient way to portray electron configuration of an atom. A logical way of thinking about it is that all that is required is to fill orbitals across a period and through orbital blocks. The number of elements in each block is the same as in the energy level it corresponds. For example, there are 2 elements in the s-block, and 10 elements in the d-block. Moving across, simply count how many elements fall in each block. Yttrium is the first element in the fourth period d-block ; thus there is one electron in that energy level. To check the answer, verify that the subscripts add up to the atomic number. In this case, 2+2+6+2+6+2+10+6+2+1= 39 and Z=39, so the answer is correct.

A slightly more complicated example is the electron configuration of bismuth (symbolized Bi, with Z = 83). The periodic table gives the following electron configuration :

$$\mathbf{1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^{10}\ 4p^6 5s^2\ 4d^{10}\ 5p^6\ 6s^2\ 4f^{14}\ 5d^{10}\ 6p^3}$$

The reason why this electron configuration seems more complex is that the f-block, the Lanthanide series, is involved. Most students who first learn electron configurations often have trouble with configurations that must pass through the f-block because they often overlook this break in the table and skip that energy level. Its important to remember that when passing the 5d and 6d energy levels that one must pass through the f-block lanthanoid and actinoid series. Keeping this in mind, this "complex" problem is greatly simplified.

Another method (but less commonly used) of writing the spdf notation is the expanded notation format. This is the same concept as before, except that each individual orbital is represented with a subscript. The p, d, and f orbitals have different sublevels. The p orbitals are *px, py*, and *pz,* and if represented on the 2p energy with full orbitals would look like : $2p_x^2\ 2p_y^2\ 2p_z^2$. The expanded notation for neon (Ne, Z=10) is written as follows :

$$\mathbf{1s^2\ 2s^2\ 2p_x{}^2\ 2p_y{}^2\ 2p_z{}^2}$$

The individual orbitals are represented, but the spins on the electrons are not ; opposite spins are assumed. When representing the configuration of an atom with half filled orbitals, indicate the two half filled orbitals. The expanded notation for carbon is written as follows :

$$\mathbf{1s^2\ 2s^2\ 2p_x{}^1\ 2p_{y1}}$$

Because this form of the spdf notation is not typically used, it is not as important to dwell on this detail as it is to understand how to use the general spdf notation.

- ✓ **Noble Gas Notation :**

This brings up an interesting point about elements and electron configurations. As the p subshell is filled in the above example about the Aufbau principle (the trend from boron to neon), it reaches the group commonly known as the noble gases. The noble gases have the most stable electron configurations, and are known for being relatively inert. All noble gases have their subshells filled and can be used them as a shorthand way of writing electron configurations for subsequent atoms. This method of writing configurations is called the noble gas notation, in which the noble gas in the period above the element that is being analyzed is used to denote the subshells that element has filled and after which the valence electrons (electrons filling orbitals in the outer most shells) are written. This looks slightly different from spdf notation, as the reference noble gas must be indicated.

Example 6 : Vanadium

What is the electronic configuration of vanadium (V, Z=23) ?

Solution :

Vanadium is the transition metal in the fourth period and the fifth group. The noble gas preceding it is argon (Ar, Z=18), and knowing that vanadium has filled those orbitals before it, argon is used as the reference noble gas. The noble gas in the configuration is denoted E, in brackets : [E]. To find the valance electrons that follow, subtract the atomic numbers : 23 - 18 = 5. Instead of 23 electrons to distribute in orbitals, there are 5. Now there is enough information to write the electron configuration :

Vanadium, V : **[Ar] $4s^2$ $3d^3$**

This method streamlines the process of distributing electrons by showing the valence electrons, which determine the chemical properties of atoms. In addition, when determining the number of unpaired electrons in an atom, this method allows quick visualization of the configurations of the valance electrons. In the example above, there are a full s orbital and three half filled d orbitals.

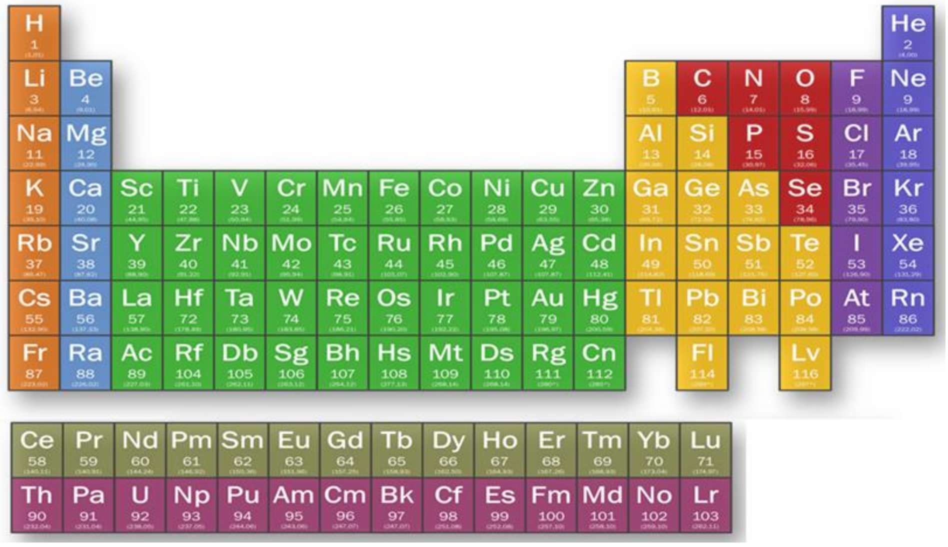
4. Modern Periodic Table :

In 1869, the Russian chemist Dmitri Mendeleev first proposed that the chemical elements exhibited a "periodicity of properties." Mendeleev had tried to organize the chemical elements according to their atomic weights, assuming that the properties of the elements would gradually change as atomic weight increased. What he found, however, was that the chemical and physical properties of the elements increased gradually and then suddenly changed at distinct steps, or periods. To account for these repeating trends, Mendeleev grouped the elements in a table that had both rows and columns.

The modern periodic table of elements is based on Mendeleev's observations ; however, instead of being organized by atomic weight, the modern table is arranged by atomic number (z).

3.1. Modern Periodic Law :

- Properties of elements are the periodic function to their atomic numbers.
- The periodicity in properties is due to repetition of similar outer shell electronic configuration at a certain regular intervals.
- In modern periodic table is based on modern periodic law in which elements are arranged in increasing order of their atomic numbers.
- In the modern periodic table, the elements are arranged in rows and columns. These rows and columns are known as periods and groups respectively.
- The table consists of 7 periods and 18 groups
- Period indicates the value of 'n' (principal quantum number) for the outermost or valence shell.
- Same number of electrons is present in the outer orbitals (that is, similar valence shell electronic configuration



H 1																	He 2
Li 3	Be 4											B 5	C 6	N 7	O 8	F 9	Ne 9
Na 11	Mg 12											Al 13	Si 14	P 15	S 16	Cl 17	Ar 18
K 19	Ca 20	Sc 21	Ti 22	V 23	Cr 24	Mn 25	Fe 26	Co 27	Ni 28	Cu 29	Zn 30	Ga 31	Ge 32	As 33	Se 34	Br 35	Kr 36
Rb 37	Sr 38	Y 39	Zr 40	Nb 41	Mo 42	Tc 43	Ru 44	Rh 45	Pd 46	Ag 47	Cd 48	In 49	Sn 50	Sb 51	Te 52	I 53	Xe 54
Cs 55	Ba 56	La 57	Hf 72	Ta 73	W 74	Re 75	Os 76	Ir 77	Pt 78	Au 79	Hg 80	Tl 81	Pb 82	Bi 83	Po 84	At 85	Rn 86
Fr 87	Ra 88	Ac 89	Rf 104	Db 105	Sg 106	Bh 107	Hs 108	Mt 109	Ds 110	Rg 111	Cn 112		Fl 114		Lv 116		

Ce 58	Pr 59	Nd 60	Pm 61	Sm 62	Eu 63	Gd 64	Tb 65	Dy 66	Ho 67	Er 68	Tm 69	Yb 70	Lu 71
Th 90	Pa 91	U 92	Np 93	Pu 94	Am 95	Cm 96	Bk 97	Cf 98	Es 99	Fm 100	Md 101	No 102	Lr 103

Figure 34 : Modern Periodic table

3.1.1. Characteristics of Periods :

- First period is called shortest period and contains only two elements. Second and third periods are called short periods containing eight elements each. Fourth and fifth periods are long periods containing eighteen elements each. Sixth period is the longest period with thirty-two elements. Seventh period is an incomplete period containing nineteen elements. Numbers 2, 8,8,18,18, 32 are called magic numbers.
- Lanthanide and actinide series containing 14 elements each are placed separately under the main periodic table. These are related to sixth and seventh periods of III group respectively.
- Elements of third period from sodium (Na) to Chlorine (Cl) are called representative or typical elements.
- From left to right in a period generally
    - Atomic weight, effective nuclear charge, ionisation potential, electronegativity and electron affinity of an element increases.
    - Atomic radius, electropositive character and metallic character of an element decreases.
- Diagonal relationship - Elements of second period Li, Be and B resemble closely with the elements Mg, Al and Si of third period in the next higher group.

Second Period	Li	Be	B	C
Third Period	Na	Mg	Al	Si

- Elements of second period are called bridge elements.

3.1.2. Characteristic of Groups :

- There are nine groups in modern periodic table and they are represented by roman numerals as I, II, III, IV, V, Vi, VII, VIII and zero.
- Groups I to VII are further divided into two subgroups A and B, Group VIII consists of three sets, each one containing three elements.
- Inert gases or noble gases are placed in zero group.
- The valency of an element in a group is equal to the group number.
- The elements of the groups which resemble the typical elements are called normal elements. For example IA, IIA, IIIA, IVA, VA, VIA, VIIA group elements are normal elements.
- Those elements of the groups which do not resemble the typical elements are called transition elements. For example- IB, IIB, IIIB, IVB, VB, VIB, VIIB, and VIII group elements are transition elements.Hydrogen is placed in both IA and VIIA groups.
- Atomic weight, atomic size, electropositive character and metallic character of elements increases down the group.
- Ionisation potential, electron affinity and electronegativity of elements decreases down the group.

3.1.3. Classification of Elements :

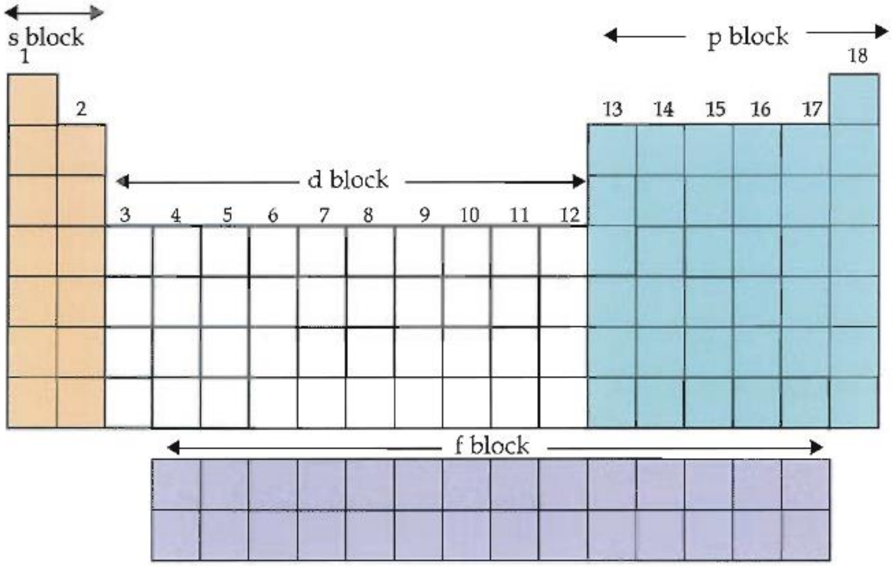


Figure 35 : s, p, d and f block elements

On the basis of electronic configuration, the elements may be divided into four groups :

s-block elements

- These are the elements in which last electron enters s subshell.
- These are present in the left part of the periodic table.
- These include 1 and 2 group elements.
- All the s- block elements are metals.
- The general electronic configuration of valence shell for s block elements is ns^{1-2} (n = 1 to 7).

p – block elements

- These are the elements in which last electron enters p subshell.
- These are present in the right part of the periodic table.
- These include 13 to 18 of the periodic table.
- Most of the p block elements are metalloids and non metals but some of them are metals also.
- The general electronic configuration of the valence shell is ns^2np^{1-6} (n = 2 to 7).
- ns^2 np^6 is stable noble gas configuration. The electronic configuration of He is Is^2.

d-Block Elements

- These are the elements in which last electron enters d-subshell.
- These are present in the middle part of the periodic table (between s & p block elements)
- d block elements include group 3 to 12 groups of the periodic table.
- All are d block elements are metals.
- The last electrons fills in (n – 1)d orbital.
- The outermost electronic configuration of d block elements is (n-1)d$^{1-10}$ ns$^{1-2}$ (n = 4 to 7).
- There are three series of d-block elements as under
  - 3d series – Sc(21) to Zn (30)
  - 4d series – Y (39) to Cd (48)
  - 5d series – La (57), Hf (72) to Hg (80).

f -Block Elements

- These are placed separately below the main periodic table.
- These are mainly related to IIIB i.e. group 3 of the periodic table
- There are two series of f-block elements as under
- 4f series – Lanthanides – 14 Elements i.e. Ce (58) to Lu (71)
- 5 f series – Actinides – 14 Elements i.e. Th (90) to Lw (103)
- the last electron fills in (n – 2) ¦-orbital
- Their general outermost electronic configuration is (n-2)¦$^{1-14}$ (n-1)s^{2} (n-1)p^{6} (n-1)d$^{0-1}$ns^{2} (n = 6 and 7).

4. Chemical families :

In the periodic table of elements, there are seven horizontal rows of elements. Each of these rows are called *periods*. The vertical columns of elements are called groups, or *families*. The most common way the periodic table is classified is by metals, nonmetals, and metalloids.

- Periods in the periodic table :

In each period (horizontal row), the atomic numbers increase from left to right. The periods are numbered 1 through 7 on the left-hand side of the table.

Elements that are in the same period have chemical properties that are not all that similar. Consider the first two members of period 3: sodium (Na) and magnesium (Mg). In reactions, they both tend to lose electrons (after all, they are metals), but sodium loses one electron, while magnesium loses two. Chlorine (Cl), down near the end of the period, tends to gain an electron (it's a nonmetal).

- **Families in the periodic table :**

Just like human families, members of the families (vertical columns) in the periodic table have similarities or similar properties. The families are labeled at the top of the columns in one of two ways :

- The older method uses Roman numerals and letters. Many chemists prefer and still use this method.
- The newer method uses the numbers 1 through 18.

So why do the elements in the same family have similar properties ? You can examine four families on the periodic table and look at the electron configurations for a few elements in each family.

- **Alkali Metals/Alkali Earth Metals :**

The Alkali metals are comprised of group 1 of the periodic table and consist of Lithium, Sodium, Rubidium, Cesium, and Francium. These metals are highly reactive and form ionic compounds (when a nonmetal and a metal come together) as well as many other compounds. Alkali metals all have a charge of +1 and have the largest atom sizes than any of the other elements on each of their respective periods.

Alkali Earth Metals are located in group 2 and consist of Beryllium, Magnesium, Calcium, Strontium, Barium, and Radium. Unlike the Alkali metals, the earth metals have a smaller atom size and are not as reactive. These metals may also form ionic and other compounds and have a charge of +2.

- **Transition Metals :**

The transition metals range from groups IIIB to XIIB on the periodic table. These metals form positively charged ions, are very hard, and have very high melting and boiling points. Transition metals are also good conductors of electricity and are malleable.

- **Lanthanides and Actinides :**

Lanthanides and Actinides, form the block of two rows that are placed at the bottom of the periodic table for space issues. These are also considered to be transition metals. Lanthanides are form the top row of this block and are very soft metals with high boiling and melting points. Actinides form the bottom row and are radioactive. They also form compounds with most nonmetals.

- **Metalloids :**

As mentioned in the introduction, metalloids are located along the staircase separating the metals from the nonmetals on the periodic table. Boron, silicon, germanium, arsenic, antimony, and tellurium all have metal and nonmetal properties. For example, Silicon has a metallic luster but is brittle and is an inefficient conductor of electricity like a nonmetal. As the metalloids have a combination of both metallic and nonmetal characteristics, they are intermediate conductors of electricity or "semiconductors".

- **Halogens :**

Halogens are comprised of the five nonmetal elements Flourine, Chlorine, Bromine, Iodine, and Astatine. They are located on group 17 of the periodic table and have a charge of -1. The term "halogen" means "salt-former" and compounds that contain one of the halogens are salts. The physical properties of halogens vary significantly as they can exist as solids, liquids, and gases at room temperature. However in general, halogens are very reactive, especially with the alkali metals and earth metals of groups 1 and 2 with which they form ionic compounds.

- **Noble Gases :**

The noble gases consist of group 18 (sometimes reffered to as group O) of the periodic table of elements. The noble gases have very low boiling and melting points and are all gases at room temperature. They are also very nonreactive as they already have a full valence shell with 8 electrons. Therefore, the noble gases have little tendency to lose or gain electrons.

5. Periodic Properties of the Elements :

The elements in the periodic table are arranged in order of increasing atomic number. All of these elements display several other trends and we can use the periodic law and table formation to predict their chemical, physical, and atomic properties. Understanding these trends is done by analyzing the elements electron configuration ; all elements prefer an octet formation and will gain or lose electrons to form that stable configuration.

5.1. Atomic Radius

We can never determine the atomic radius of an atom because there is never a zero probability of finding an electron, and thus never a distinct boundary to the atom. All that we can measure is the distance between two nuclei (internuclear distance). A covalent radius is one-half the distance between the nuclei of two identical atoms. An ionic radius is one-half the distance between the nuclei of two ions in an ionic bond. A metallic radius is one-half the distance between the nuclei of two adjacent atoms in a crystalline structure. The SI units for measuring atomic radii are the nanometer (nm) and the picometer (pm). $1nm=1\times10^{-9}m$ and $1pm=1\times10^{-12}m$.

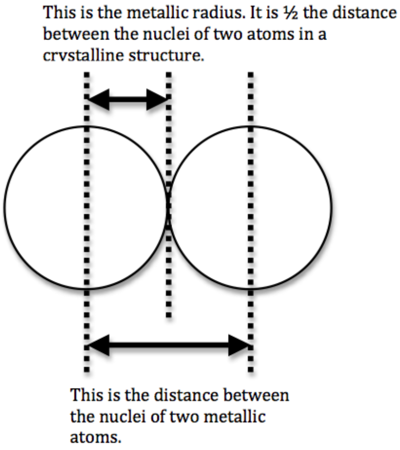
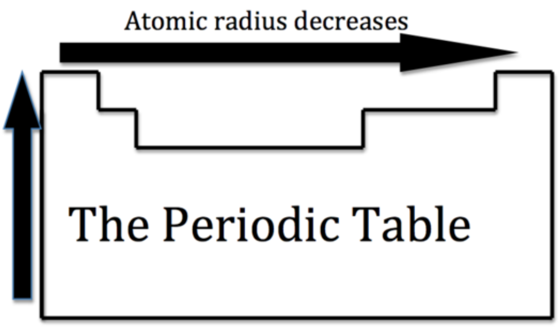


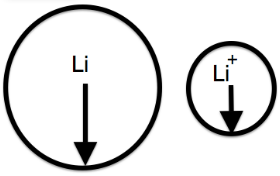
Figure 36 : Metallic Radii.

- **description the atomic radius trend in the periodic table :**

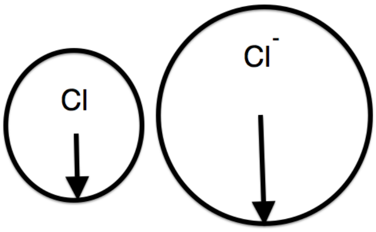
The atomic number increases moving left to right across a period and subsequently so does the effective nuclear charge. Therefore, moving left to right across a period the nucleus has a greater pull on the outer electrons and the atomic radii decreases. Moving down a group in the periodic table, the number of filled electron shells increases. In a group, the valence electrons keep the same effective nuclear charge, but now the orbitals are farther from the nucleus. Therefore, the nucleus has less of a pull on the outer electrons and the atomic radii are larger.



We can now use these concept to explain the atomic radius differences of cations and anions. A cation is an atom that has lost one of its outer electrons. Cations have a smaller radius than the atom that they were formed from. With the loss of an electron, the positive nuclear charge out powers the negative charge that the electrons exert. Therefore, the positive nucleus pulls the electrons tighter and the radius is smaller. An anion is an atom that has gained an outer electron. Anions have a greater radius than the atom that they were formed from. The gain of an electron does not alter the nuclear charge, but the addition of an electron causes a decrease in the effective nuclear charge. Therefore, the electrons are held more loosely and the atomic radius is increased.



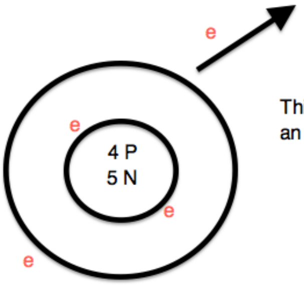
The Lithium Cations is significantly smaller than the Lithium atom



The Chlorine anion is significantly larger than the Chlorine atom

5.2. Ionization Energy (ionization potential) :

Expelling an electron from an atom requires enough energy to overcome the magnetic pull of the positive charge of the nucleus. Therefore, ionization energy (I.E. or I) is the energy required to completely remove an electron from a gaseous atom or ion. The Ionization Energy is always positive.



This image depicts an atom losing an electron. The ionization energy is the energy required to accomplish this.

The energy required to remove one valence electron is the first ionization energy, the second ionization energy is the energy required to remove a second valence electron, and so on.

- 1st ionization energy

$$\mathrm{Na}_{(g)} \longrightarrow \mathrm{Na}^{+}_{(g)} + e^{-}$$

- 2nd ionization energy

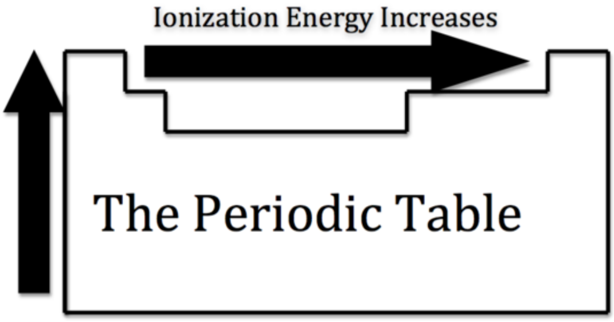
$$\mathrm{Na}^{+}_{(g)} \longrightarrow \mathrm{Na}^{2+}_{(g)} + e^{-}$$

Ionization energies increase relative to high effective charge. The highest ionization energies are the noble gases because they all have high effective charge due to their octet formation and require a high amount of energy to destroy that stable configuration. The highest amount of energy required occurs with the elements in the upper right hand corner. Additionally, elements in the left corner have a low ionization energy because losing an electron allows them to have the noble gas configuration. Therefore, it requires less energy to remove one of their valence electrons.

Ionization Energies of certain elements (1st IE, 2nd IE, etc)							
Element	**1st**	**2nd**	**3rd**	**4th**	**5th**	**6th**	**7th**
Na	496	4562					
Mg	738	1451	7733				
Al	577	1817	2745	11580			
Si	786	1577	3232	4356	16090		
P	1060	1903	2912	4957	6274	21270	
S	999.6	2251	3361	4564	7013	8496	27110
Cl	1256	2297	3822	5158	6542	9362	11020
Ar	1520	2666	3931	5771	7238	8781	12000

These are the ionization energies for the period three elements. Notice how Na after in the second I.E, Mg in the third I.E., Al in the fourth I.E., and so on, all have a huge increase in energy compared to the proceeding one. This occurs because the proceeding configuration was in a stable octet formation ; therefore it requires a much larger amount of energy to ionize.

Ionization Energies increase going left to right across a period and increase going up a group. As you go up a group, the ionization energy increases, because there are less electron shielding the outer electrons from the pull of the nucleus. Therefore, it requires more energy to out power the nucleus and remove an electron. As we move across the periodic table from left to right, the ionization energy increases , due to the effective nuclear charge increasing. This is because the larger the effective nuclear charge, the stronger the nucleus is holding onto the electron and the more energy it takes to release an electron.



The ionization energy is only a general rule. There are some instances when this trend does not prove to be correct. These can typically be explained by their electron configuration. For example, Magnesium has a higher ionization energy than Aluminum. Magnesium has an electron configuration of [Ne]3s2. Magnesium has a high ionization energy because it has a filled 3s orbital and it requires a higher amount of energy to take an electron from the filled orbital.

5.3. Electron Affinity :

Electron affinity (E.A.) is the energy change that occurs when an electron is added to a gaseous atom. Electron affinity can further be defined as the enthalpy change that results from the addition of an electron to a gaseous atom. It can be either positive or negative value. The greater the negative value, the more stable the anion is.

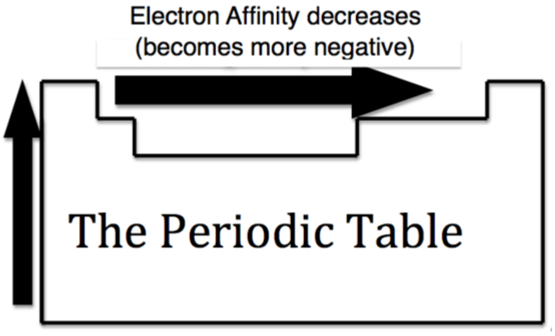
- (Exothermic) The electron affinity is positive

$$X_{(g)} + e^- \longrightarrow X^- + \text{Energy}$$

- (Endothermic) The electron affinity is negative

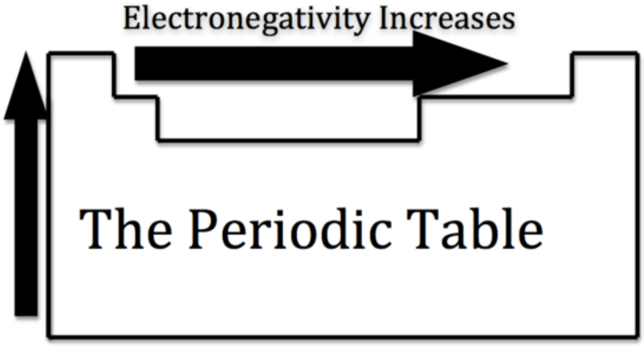
$$X_{(g)} + e^- + \text{Energy} \longrightarrow X^-$$

It is more difficult to come up with trends that describe the electron affinity. Generally, the elements on the right side of the periodic table will have large negative electron affinity. The electron affinities will become less negative as you go from the top to the bottom of the periodic table. However, Nitrogen, Oxygen, and Fluorine do not follow this trend. The noble gas electron configuration will be close to zero because they will not easily gain electrons.



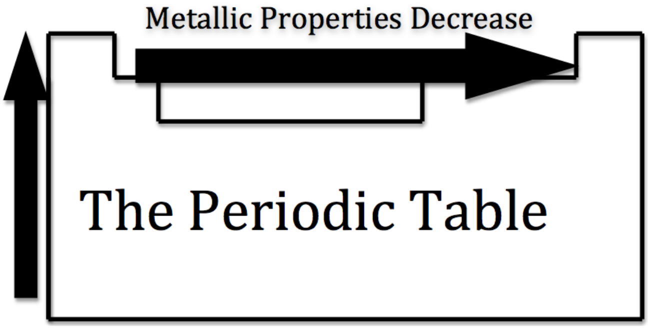
5.4. Electronegativity :

Electronegativity is the measurement of an atom to compete for electrons in a bond. The higher the electronegativity, the greater its ability to gain electrons in a bond. Electronegativity will be important when we later determine polar and nonpolar molecules. Electronegativity is related with ionization energy and electron affinity. Electrons with low ionization energies have low electronegativities because their nuclei do not exert a strong attractive force on electrons. Elements with high ionization energies have high electronegativities due to the strong pull exerted by the positive nucleus on the negative electrons. Therefore the electronegativity increases from bottom to top and from left to right.



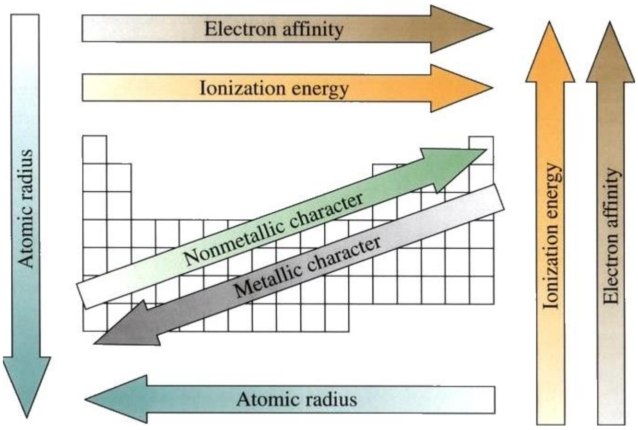
5.5. Metallic Character

The metallic character is used to define the chemical properties that metallic elements present. Generally, metals tend to lose electrons to form cations. Nonmetals tend to gain electrons to form anions. They also have a high oxidation potential therefore they are easily oxidized and are strong reducing agents. Metals also form basic oxides ; the more basic the oxide, the higher the metallic character.



As you move across the table from left to right, the metallic character decreases, because the elements easily accept electrons to fill their valance shells. Therefore, these elements take on the nonmetallic character of forming anions. As you move up the table, the metallic character decreases, due to the greater pull that the nucleus has on the outer electrons. This greater pull makes it harder for the atoms to lose electrons and form cations.

- **Summary of Periodic Trends :**



Practical exercises

Exercise 1:

We have the following elements $_{2}A$, $_{10}B$, $_{18}C$, $_{36}D$, $_{54}E$, $_{86}F$:

1- Give the period and the group for each element.

2- Attribute each element to an ionization energy of the following values:

15.7eV, 21.5eV, 12.13eV, 10.75eV, 24.58eV, 13.59eV

3- Rank these elements by decreasing atomic radius.

4- Using the ***Klechkowski*** rule, Arrange the following orbitals by increasing energy

1S, 2S, 2P, 3S, 3P, 3d, 4S, 4P, 4d, 4f, 5S, 5P, 6S

Exercise 2:

1. Write the electronic distribution of the following elements: $_{35}Br$, $_{47}Ag$, $_{38}Sr$.
2. Which element among the previous elements contains a single electron marked with the two quantitative numbers: ($l = 2$, $m = +2$)
3. And then which element contains a single electron marked with the two quantitative numbers: ($l = 0$, $m = 0$)
4. Among the previous elements, what elements belong to the alkali earth metals family.

Exercise 3:

1. The element zX belong to the fourth period and the V_B group, calculate the atomic number of this element.

2- Select the elements that their electrons number less than 18 and own two single electrons in the fondamental state (ground state). Among these elements are what elements belong to the period of 4Be and group of $_{32}Ge$

3- The element Y has 6 electrons in the outer layer with the ψ_{51} wave function, write the electronic distribution of this element in the fondamental state, then conclude his atomic number Z.

Exercise 4:

Write the electronic distribution of the following elements: $_{15}A$, $_{84}B$, $_{79}C$, $_{64}D$, $_{33}E$, $_{81}F$, $_{39}G$.

1- Select the period and the groupe for these elements.

2- Compare between B, C and D elements in terms of atomic radius.

3- Compare between C and A in terms of Ei (first ionization energy).

4- Compare between A, E and F in terms of electronegativity En.

5- Compare between the two ions (G^{3+}, E^{3-}) in terms of atomic radius.

Chapter VI

Chemical Bonding

Chapter VI :

Chemical Bonding

1. Introduction :

More than 118 elements on the periodic table combine to make millions and millions of chemical compounds. This is because chemical bonds between atoms result in new substances that are very different from the elements they are made of. For example, chlorine can be used as a chemical weapon and yet it combines with sodium, a highly reactive element, to make common table salt.

To summarize simply, a chemical bond is the attractive force holding atoms or ions together. This attractive interaction leads to a more stable state for the whole system compared to individual atoms.

Valence electrons play a fundamental role in chemical bonding. In the electron configuration of an atom, the outermost shell is called the valence shell, and the electrons in the valence shell (outermost shell) are known as valence electrons. Take the carbon atom for example : the electron configuration of carbon is $1s^22s^22p^2$. The outermost shell is the 2nd principal shell, so there are 4 valence electrons in carbon. Valence electrons are the electrons that are the furthest away from the nucleus, and thus they experience the least attraction from the nucleus and are the most reactive. They play the most important role in chemical bonding.

2. Types of chemical bonds :

What are the types of bonds in chemistry ? Let’s look at three of the most popular types of bonds – covalent bonds, ionic bonds, and metallic bonds.

2.1. Ionic bond :

The definition of **ionic bond**, is a bond between atoms where electrons are (mostly) transferred from one atom to another. We say mostly, because there is always some sharing of electrons between atoms, but in Ionic bonds, the sharing is very unequal. The less equal the sharing of the electrons, the more **ionic character** the bond has.

Ionic bonds occur between a metal and a non-metal. Unlike covalent bonds, ionic bonds transfer their valence electrons between atoms. In ionic bonding, the electronegativity difference between non-metals and metals exceeds 1.7. The metal atom transfers its electrons to the non-metal atom. Therefore, the metal atom becomes a positively charged cation and the non-metal atom becomes a negatively charged anion. Consequently, ionic bonds create two charged ions, the metal always donates its electron, and the non-metal always accepts the electron. An example of an ionic bond is the bond in sodium chloride, which is salt. Sodium's valence electron is transferred to the outer electron shell of chloride.

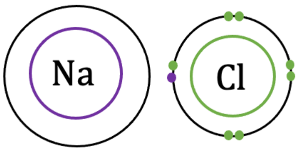


Figure 37 : Ionic bond

2.2. Covalent Bonds :

A covalent bond, or molecular bond, is a chemical bond formed between two atoms that share a pair of electrons ; the elements that form these bonds are generally non-metals. Some examples of oxygen, hydrogen and nitrogen in compounds like O_2 and H_2O). A defining characteristic of a covalent bond is that electron density is high in the middle of the bond. This means that electrons are more likely to be found in between the two atoms than at each end. Chemists sometimes describe and predict the ways that covalent bonds form using a model called molecular orbital theory.

2.2.1. Multiple Bonds :

Covalent bonds can be either single or multiple bonds. In a single bond, only one pair of valence electrons are being shared between two atoms. However, sometimes atoms share more than one electron pair, forming what is called a multiple bond. The common types of multiple bonds are double and triple, with higher order bonds forming only in certain exotic compounds of transition metals. The elements that most often participate in multiple bonding are : carbon, nitrogen, oxygen, phosphorus, and sulfur.

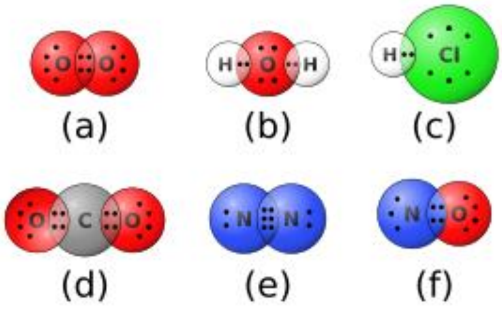


Figure 38 : Atoms engaging in **single** (b,c), **double** (a,d,f) and **triple** (e) covalent bonding

- ***Lewis* Theory of Chemical Bonding :**

In 1916, the American scientist *Gilbert N. Lewis* published a now famous paper on bonding entitled “The atom and the molecule” (*Lewis*, 1916). In that paper he outlined a number of important concepts regarding bonding that are still used today as working models of electron arrangement at the atomic level. Most significantly, Lewis developed a theory about bonding based on the number of outer shell, or valence, electrons in an atom. He suggested that a chemical bond was formed when two atoms shared a pair of electrons (later renamed a covalent bond by Irving Langmuir). His "Lewis dot diagrams" used a pair of dots to represent each shared pair of electrons that made up a covalent bond (following figure).

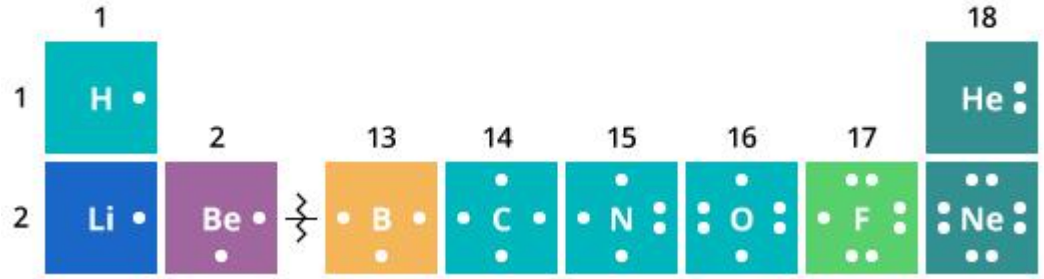


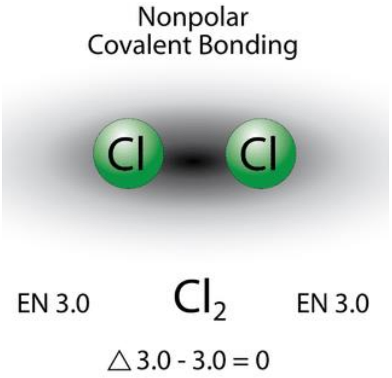
Figure 39 : *Lewis* dot structures for the elements in the first two periods of the periodic table

The structures are written as the element symbol surrounded by dots that represent the valence electrons.

Lewis also championed the idea of ‘octets’ (groups of eight), that a filled valence shell was crucial in understanding electronic configuration as well as the way atoms bond together. The octet had been discussed previously by chemists such as John Newland, who felt it was important, but Lewis advanced the theory.

2.2.2. Nonpolar Covalent Bonds :

A bond in which the electronegativity difference is less than 1.7 is considered to be mostly covalent in character. However, at this point we need to distinguish between two general types of covalent bonds. A **nonpolar covalent bond** is a covalent bond in which the bonding electrons are shared equally between the two atoms. In a nonpolar covalent bond, the distribution of electrical charge is balanced between the two atoms.



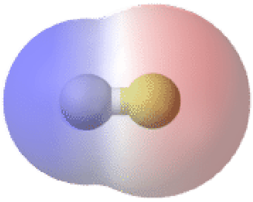
A nonpolar covalent bond is one in which the distribution of electron density between the two atoms is equal.

The two chlorine atoms share the pair of electrons in the single covalent bond equally, and the electron density surrounding the Cl_2

molecule is symmetrical. Note that molecules in which the electronegativity difference is very small (<0.4) are also considered nonpolar covalent. An example would be a bond between chlorine and bromine ($\Delta EN = 3.0-2.8=0.2$).

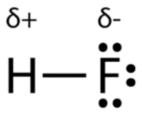
2.2.3. Polar Covalent Bonds :

A bond in which the electronegativity difference between the atoms is between 0.4 and 1.7 is called a polar covalent bond. A **polar covalent bond** is a covalent bond in which the atoms have an unequal attraction for electrons, and so the sharing is unequal. In a polar covalent bond, sometimes simply called a polar bond, the distribution of electrons around the molecule is no longer symmetrical.



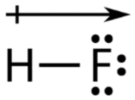
In the polar covalent bond of HF, the electron density is unevenly distributed. There is a higher density (red) near the fluorine atom, and a lower density (blue) near the hydrogen atom.

An easy way to illustrate the uneven electron distribution in a polar covalent bond is to use the Greek letter delta (δ).



Use of δ to indicate partial charge.

The atom with the greater electronegativity acquires a partial negative charge, while the atom with the lesser electronegativity acquires a partial positive charge. The delta symbol is used to indicate that the quantity of charge is less than one. A crossed arrow can also be used to indicate the direction of greater electron density.



Use of crossed arrow to indicate polarity.

What is Dipole Moment ?

A dipole moment arises in any system in which there is a separation of charge. They can, therefore, arise in ionic bonds as well as in covalent bonds. Dipole moments occur due to the difference in electronegativity between two chemically bonded atoms.

A bond dipole moment is a measure of the polarity of a chemical bond between two atoms in a molecule. It involves the concept of electric dipole moment, which is a measure of the separation of negative and positive charges in a system.

The bond dipole moment is a vector quantity since it has both magnitude and direction. An illustration describing the dipole moment that arises in an HCl (hydrochloric acid) molecule is provided below.

Dipole Moment has a Magnitude and a Direction

It can be noted that the symbols δ^+ and δ^- represent the two electric charges that arise in a molecule which are equal in magnitude but are of opposite signs. They are separated by a set distance, which is commonly denoted by 'd'.

Important Points :

- The dipole moment of a single bond in a polyatomic molecule is known as the bond dipole moment and it is different from the dipole moment of the molecule as a whole.
- It is a vector quantity, i.e. it has magnitude as well as definite directions.
- Being a vector quantity, it can also be zero as the two oppositely acting bond dipoles can cancel each other.
- By convention, it is denoted by a small arrow with its tail on the negative center and its head on the positive center.
- In chemistry, the dipole moment is represented by a slight variation of the arrow symbol. It is denoted by a cross on the positive center and arrowhead on the negative center. This arrow symbolizes the shift of electron density in the molecule.
- In the case of a polyatomic molecule, the dipole moment of the molecule is the vector sum of the all present bond dipoles in the molecule.

Dipole Moment Formula :

A dipole moment is the product of the magnitude of the charge and the distance between the centers of the positive and negative charges. It is denoted by the Greek letter ‘μ’.

Mathematically,

$$\textbf{Dipole Moment } (\mu) = \textbf{Charge } (Q) * \textbf{distance of separation } (r)$$

It is measured in *Debye* units denoted by ‘D’. 1 D = 3.33564×10^{-30} C.m, where C is Coulomb and m denotes a metre.

The bond dipole moment that arises in a chemical bond between two atoms of different electronegativities can be expressed as follows :

$$\mu = \delta . d$$

Where: μ is the bond dipole moment,

δ is the magnitude of the partial charges δ^+ and δ^-, And d is the distance between δ^+ and δ^-.

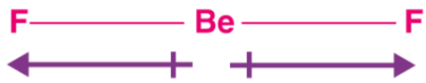
The bond dipole moment (μ) is also a vector quantity, whose direction is parallel to the bond axis. In chemistry, the arrows that are drawn in order to represent dipole moments begin at the positive charge and end at the negative charge.

When two atoms of varying electronegativities interact, the electrons tend to move from their initial positions to come closer to the more electronegative atom. This movement of electrons can be represented via the bond dipole moment.

Examples :

Dipole moment of BeF_2

In a beryllium fluoride molecule, the bond angle between the two beryllium-fluorine bonds is 180°. Fluorine, being the more electronegative atom, shifts the electron density towards itself. The individual bond dipole moments in a BeF_2 molecule are illustrated below.



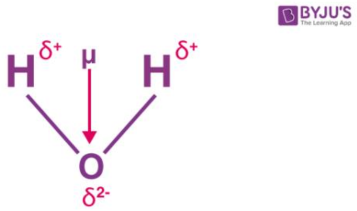
Bonds dipoles in **BeF_2**

Total bond moment in **BeF_2**

From the illustration provided above, it can be understood that the two individual bond dipole moments cancel each other out in a BeF_2 molecule because they are equal in magnitude but are opposite in direction. Therefore, the net dipole moment of a BeF_2 molecule is zero.

Dipole moment of H_2O (Water) :

In a water molecule, the electrons are localised around the oxygen atom since it is much more electronegative than the hydrogen atom. However, the presence of a lone pair of electrons in the oxygen atom causes the water molecule to have a bent shape (as per the VSEPR theory). Therefore, the individual bond dipole moments do not cancel each other out as is the case in the BeF_2 molecule. An illustration describing the dipole moment in a water molecule is provided below :



The bond angle in a water molecule is 104.5°. The individual bond moment of an oxygen-hydrogen bond is 1.5 D. The net dipole moment in a water molecule is found to be 1.84D.

2.2.4. Dative Covalent (Coordinate) Bonding :

A **Co-ordinate bond** is a type of alternate covalent bond that is formed by sharing of an electron pair from a single atom. Both shared electrons are donated by the same atom. It is also called a dative bond or dipolar bond.

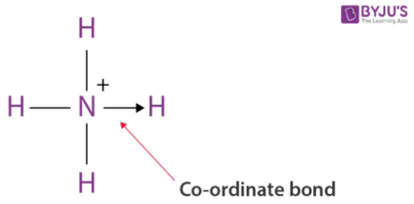
Co-ordinate covalent bonds are usually formed in reactions that involve two non-metals, such as a hydrogen atom or during bond formation between metal ions and ligands.

Characteristics of Coordinate Covalent Bond

1. In this type of bonding, the atom that shares an electron pair from itself is termed as the donor.
2. The other atom which accepts these shared pair of electrons is known as a receptor or acceptor.
3. The bond is represented with an arrow →, pointing towards the acceptor from the donor atom.
4. After sharing of electron pairs, each atom gets stability.
5. This type of bonding is central to the Lewis theory.
6. Getting a good understanding of co-ordinate covalent bonds can help in properly designing complex organic molecules.

Coordinate Bond Diagram :

Below, we have given a simple diagram of a co-ordinate bond. The bond is shown by an arrow which points in the direction where an atom is donating the lone pair to the atom that is receiving it.

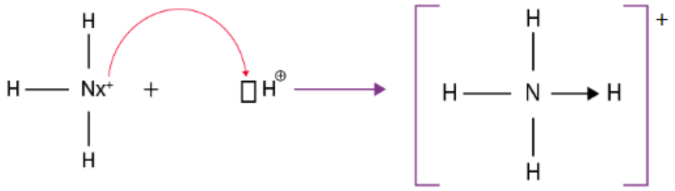


Co-Ordinate Bond Examples :

Here are a few examples of the coordinate covalent bond.

- Formation of Ammonium Ion :

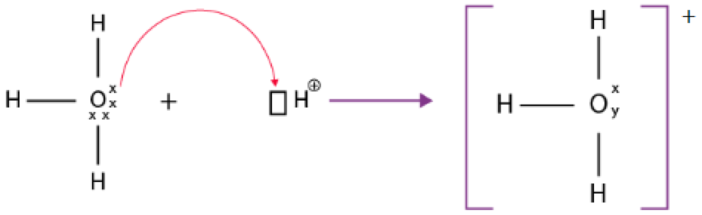
The nitrogen atom in Ammonia donates its electron pair to the empty orbital of the H^+ ion; thus, nitrogen is the donor, H^+ is the acceptor, and a co-ordinate bond is formed



Ammonium ion

- Formation of Hydronium Ion

An oxygen atom in water donates its one pair of electrons to the vacant orbital of the H^+ ion; thus, a dative bond is formed oxygen atom is the donor atom and the H^+ is the acceptor atom.



Hydronium ion

2.3. Metallic bonds :

Metallic bonds are chemical bonds among the atoms in a metal. Similar to a sea of freely moving electrons, these bonds connect all the atoms in the metal at once (in contrast to covalent bonds, in which atoms share discrete pairs of electrons over specific parts of a molecule). These chemical bonds are responsible for many properties of bulk metals, including their luster and electrical and thermal conductivity.

3. What are intermolecular forces ?

Intermolecular forces are electrostatic interactions between permanently or transiently (temporarily) charged chemical species. They are the attractive or repulsive forces between molecules. These forces are much weaker than the chemical bonds that hold atoms together within a molecule, but they can still have a significant impact on the properties of a substance. For example, intermolecular forces can affect the melting and boiling points of a substance, as well as its solubility and viscosity. There are several different types of intermolecular forces, including London dispersion forces, Van Der Waals forces (interactions), ion-dipole, dipole-dipole interactions, and hydrogen bonding. The strength of these forces depends on the type of molecules involved and the distance between them. Understanding intermolecular forces can help us predict and explain many of the physical properties of substances.

The term is usually used to refer only to attractive interactions, which hold molecules and ions together in condensed phases (liquid and solid). These forces govern many of the bulk physical properties of substances and mixtures, such as melting point, boiling point, and surface tension.

3.1. Types of intermolecular forces :

3.1.1. Van Der Waals forces

Van der Waals forces, aka Van der Waals interactions, are the weakest intermolecular force and consist of weak dipole-dipole forces and stronger London dispersion forces. They are names after the Dutch chemist Johannes van der Waals (1837-1923). The Van Der Waals equation, for non-ideal gases, takes into consideration these intermolecular forces. These forces determine whether a substance is a solid, liquid or gas at a given temperature.

3.1.2. Hydrogen bonding

Hydrogen bonding is a special type of dipole-dipole interaction. It can only occur when the molecules in question have a highly electronegative atom directly bonded to a hydrogen atom, leading to an unusually extreme dipole. For most purposes, these highly electronegative atoms are limited to only nitrogen, oxygen and fluorine.

Hydrogen bonding involves a “donor” molecule and an “acceptor” molecule. The donor provides the hydrogen atom for the bond, while the acceptor provides the electronegative atom. In the image below, the top two water molecules are both acting as donors, while the bottom molecule is acting as an acceptor. Some molecules can only act as acceptors.

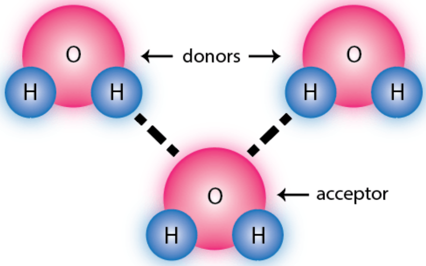


Figure 40 : Hydrogen bonding

Water molecules participate in hydrogen bonding. This gives water its characteristic high boiling point as well as low density in the solid state, which is why ice floats on liquid water. Hydrogen bonding is also directional – a bond can only qualify as a hydrogen bond if the three participating atoms are in roughly a straight line (180-degree angle). This sets it apart further from ordinary dipole-dipole bonding, which has no directionality.

4. Electronic structure of molecules :

Lewis's bond theory gives only a simple representation of the composition of molecules, and this representation cannot explain the shape or energy of molecular stations, nor can the geometric shape of molecules be predicted. In order to better study molecules, several new bond hypotheses have been developed based on quantum mechanics.

4.1. Molecular orbitals hypothesis :

Electrons in a molecule are assumed to obey the same laws as in an isolated atom, where each electron can be described by an Ø wave. The wave function satisfies the same conditions as the function ψ in the atom :

- $Ø^2$ represents the probability density of an electron and determines the shape of the molecular station.
- Electrons occupy various molecular stations according to their increasing energy arrangement.
- Pauli's principle and Hund's rule also apply to molecules and each electron has a spin of (+1)/2 or (-1)/2.

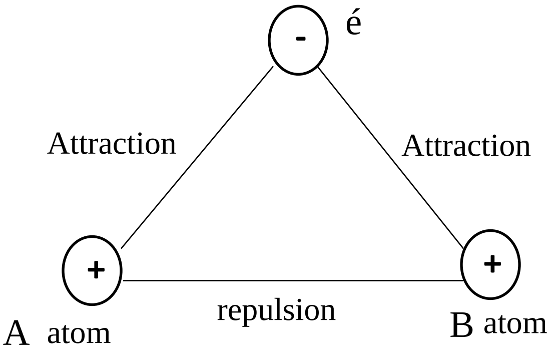
The study of chemical bonding in quantum theory goes back to the study of the properties of molecular stations and their energy levels.

4.1.1. Single-electron molecular orbitals :

a. Linear Combination of Atomic Orbitals (LCAO) (Linear Combinations of Atomic Orbitals) :

According to wave mechanics, the atomic orbitals can be expressed by wave functions (ψ's) which represent the amplitude of the electron waves. These are obtained from the solution of Schrodinger wave equation. However, since it cannot be solved for any system containing more than one electron, molecular orbitals which are one electron wave functions for molecules are difficult to obtained directly from the solution of Schrodinger wave equation. To overcome this problem, an approximate method known as **linear combination of atomic orbitals (LCAO)** has been adopted.

Let us apply this method to the homonuclear diatomic hydrogen molecule. Consider the simplest bond that can be studied is a bond between two hydrogen atoms, one of which has lost an electron (H_2^+) :



Schrödinger's equation is written as :

$$-\frac{h^2}{8\pi^2 m}\Delta\psi + (E_{Pr} + E_{pa})\psi = \mathrm{E}\,\psi$$

m: Electron mass

E_{Pr}: The potential energy of repulsion between the two nuclei.

E_{pa}: The potential energy of an electron subjected to the force of attraction by the two nuclei.

In the case of an isolated hydrogen atom, the electron is described by the atomic station ψ, while in the case of the molecular ion H_2^+, the electron is described by the wave function ∅, which is a molecular station. The function Ø is described by the LCAO method as a linear union of the atomic terminals ψ_A and ψ_B of hydrogen atoms A and B.

$$Ø = C_A\psi_A + C_B\psi_B$$

ψ_A and ψ_B are atomic terminals and the coefficients C_A and C_B are two unknown real numbers that can be calculated.

The solutions obtained are:

$$Ø^+ = \frac{1}{\sqrt{2(1+s)}}(\psi_A + \psi_B) \qquad \text{Symmetrical function}$$

$$Ø^- = \frac{1}{\sqrt{2(1-s)}}(\psi_A - \psi_B) \qquad \text{Asymmetric function (with antisymmetry).}$$

$Ø^+$ and $Ø^-$ are molecular orbitals.

S represents the extent of overlap between stations ψ_A and ψ_B and is known as the overlap integral, which measures the sum of the common points between the two stations. The larger the overlap between the two stations, the higher the value of S.

b. Physical interpretation of the two molecular wave functions :

- ✓ **Function $Ø^+$** : Let's compare $Ø^{+2}$ and $(\psi_A{}^2 + \psi_B{}^2)$: (Figure A)

$Ø^{+2}$ Is greater than $(\psi_A{}^2 + \psi_B{}^2)$, this means that the probability of an electron being between the two nuclei is greater. The station $Ø^+$ is orbitale liante.

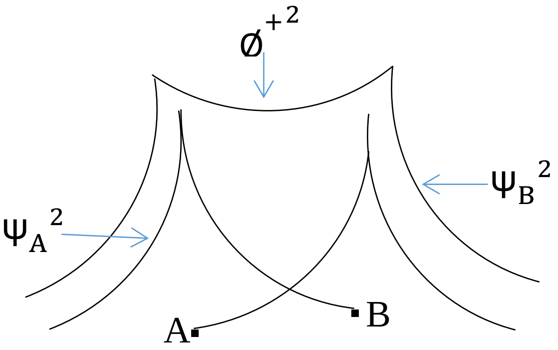


Figure A

- ✓ **Function $\emptyset^{-}$** : Let's compare $\emptyset^{-2}$ and $\left(\psi_A{}^2 + \psi_B{}^2\right)$: (Figure B)

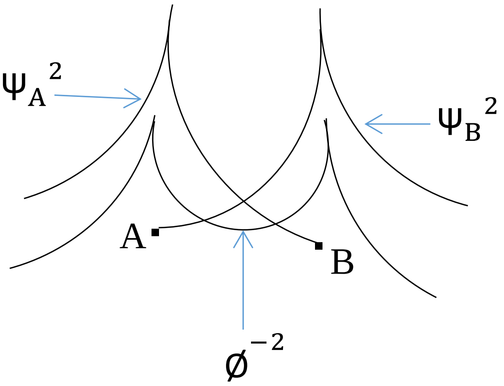


Figure B

We note that the probability of an electron being between the two nuclei is weak. The orbital $\emptyset^{-}$ is orbitale antiliante.

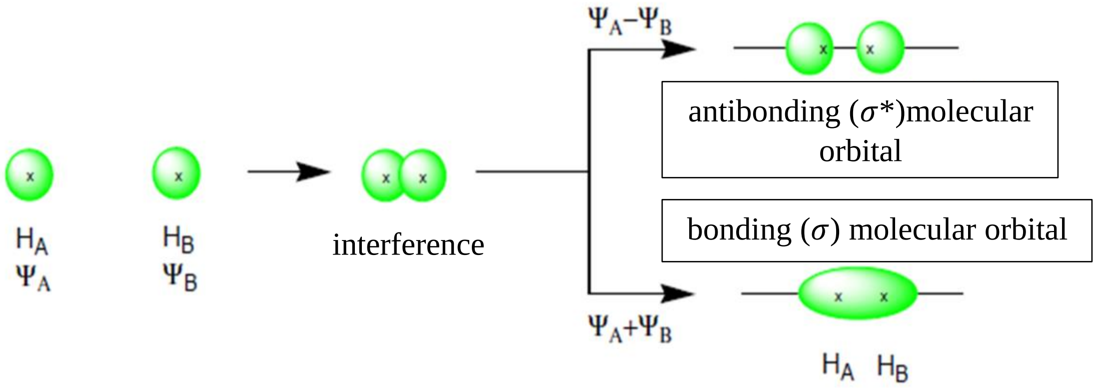
The solution $\emptyset^{+}$ corresponds to the existence of H_2^+ in a stable state, and from it the condition for the formation of the bond here is achieved between the two nuclei.

Conclusion :

Qualitatively, the formation of molecular orbitals can be understood in terms of the constructive or destructive interference of the electron waves of the combining atoms. In the formation of bonding molecular orbital, the two electron waves of the bonding atoms reinforce each other due to constructive interference while in the formation of antibonding molecular orbital, the electron waves cancel each other due to destructive interference. As a result, the electron density in a bonding molecular orbital is located between the nuclei of the bonded atoms because of which the repulsion between the nuclei is very less while in case of an antibonding molecular orbital, most of the electron density is located away from the space between the nuclei, there is a nodal plane (on which the electron density is zero) between the nuclei and hence the repulsion between the nuclei is high. Electrons placed in a bonding molecular orbital tend to hold the nuclei together and stabilize a molecule. Therefore, a bonding molecular orbital always possesses lower energy than either of the atomic orbitals that have combined to form it. In contrast, the electrons placed in the antibonding molecular orbital destabilize the molecule. This is because the mutual repulsion of the electrons in this orbital is more than the attraction between the electrons and the nuclei, which causes a net increase in energy.

In may be noted that the energy of the antibonding orbital is raised above the energy of the parent atomic orbitals that have combined and the energy f the bonding orbital has been lowered than the parent orbitals. The total energy of two molecular orbitals, however, remains the same as that of two original atomic orbitals.

c. Geometric form of molecular orbitals $Ø^{+}$ and $Ø^{-}$:



d. Energy of molecular orbitals :

It was found that the electron is more stable in a partially binding molecular orbital than in an atomic orbital.

It was also found that the energy of the anti-binding molecular orbital is greater than the energy of the atomic orbitals that form it.

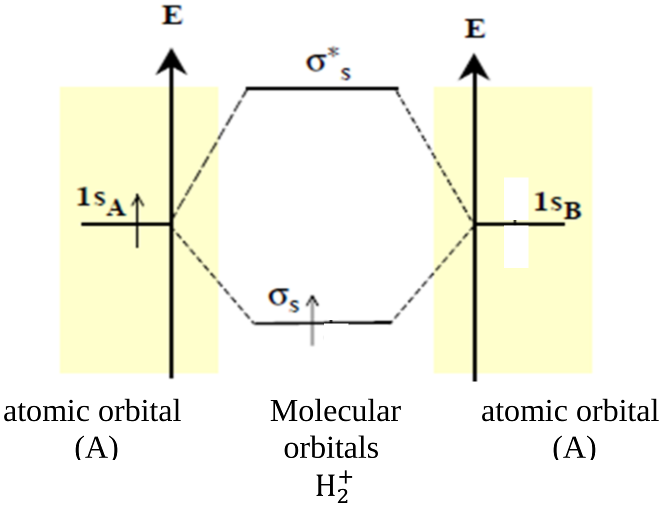


Figure 41 : Formation of bonding (σ) and antibonding (σ*) molecular orbitals by the linear combinition of atomic orbitals ψ_A and ψ_B centered on two atoms A and B respectively.

4.1.2. Multi-electron molecular orbitals :

The results obtained during the study of the H_2^+ ion can be generalized to molecules carrying several electrons.

a. Molecular orbitals σ and π :

P and d orbitals such as S orbitals are capable of forming molecular orbitals. We distinguish according to symmetry :

- **Molecular orbitals σ :**

It is obtained by axial interference of two atomic orbitals (axial overlap), the bond σ is a stable bond.

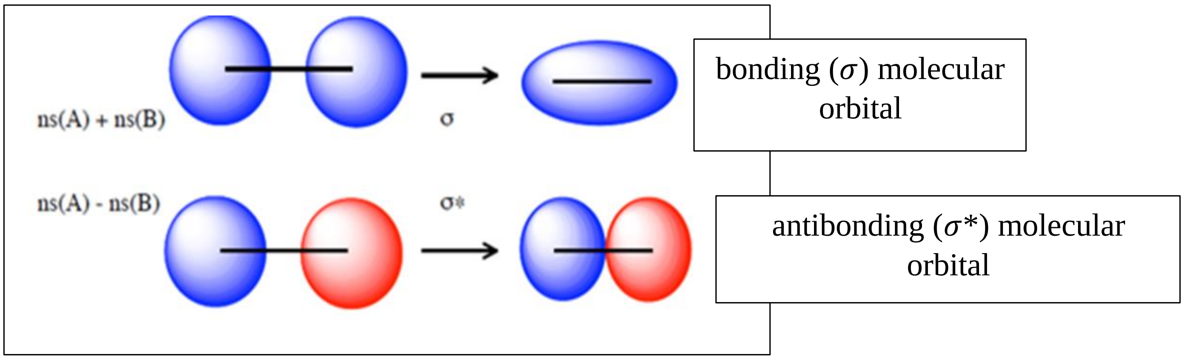
- **Molecular stations π :**

It is obtained by lateral interference of two atomic orbitals (Side overlap).

b. form of molecular orbitals :

Determined by the type of overlapping atomic orbitals.

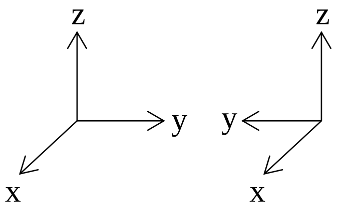
b.1. S orbital interference with S orbital :



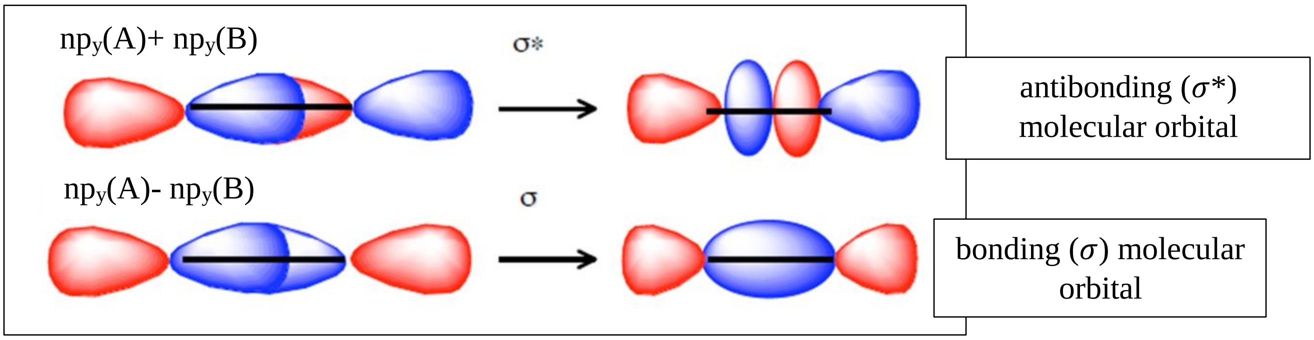
The overlap of S orbitals is always axial to give orbitals of type σ.

b.2. Interference of the p orbital with the p orbital :

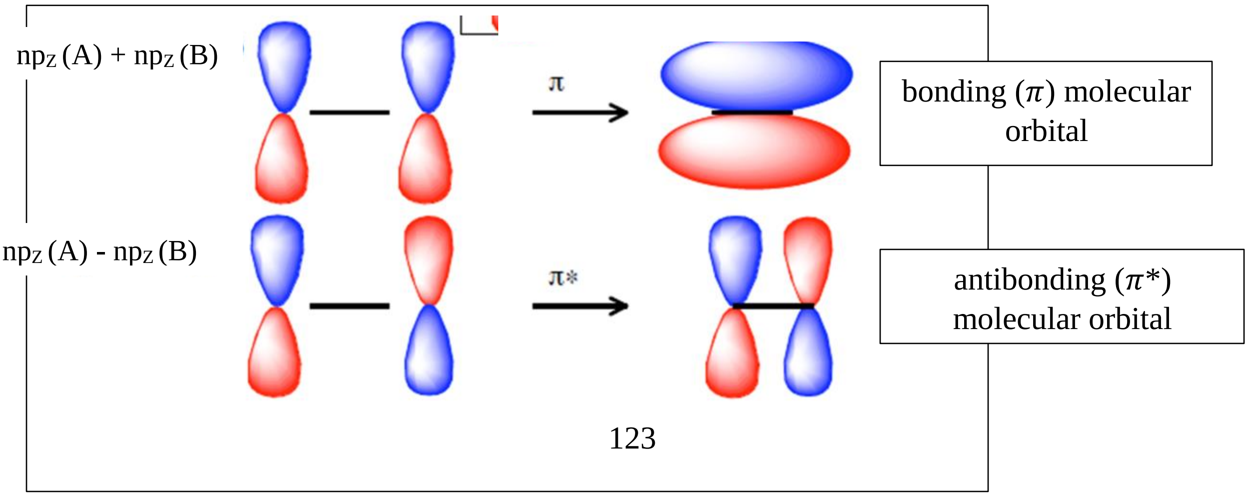
Let us choose the following set of axes for atoms A and B.



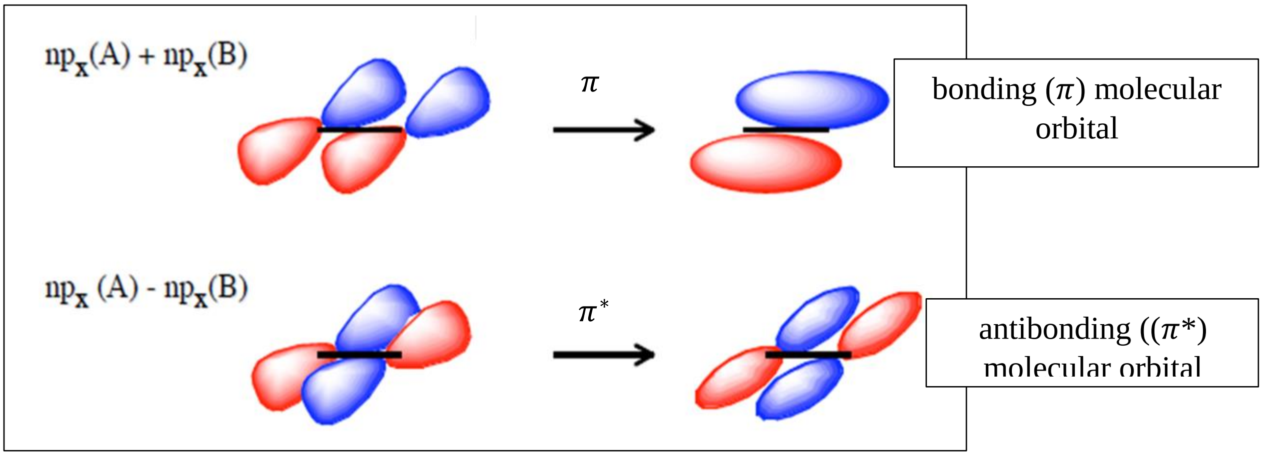
✓ **Interference of the py orbital with the py orbital.**



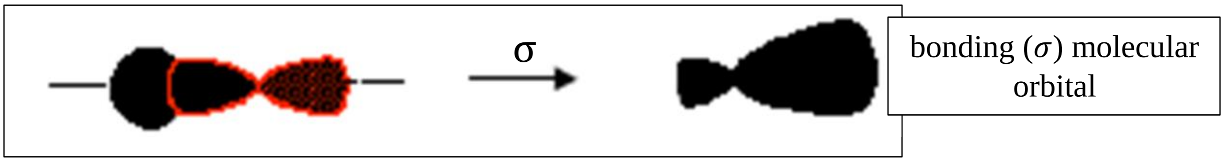
✓ **P_Z orbital interference with P_Z orbital :**

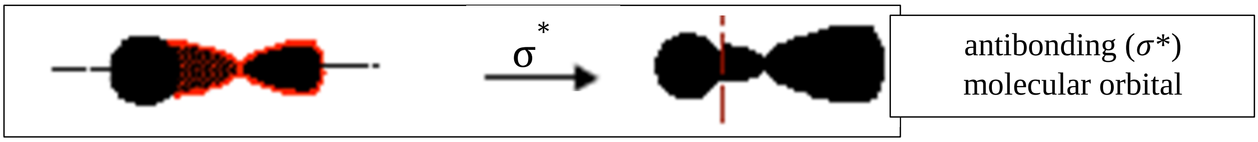


- ✓ **P_x orbital interference with P_x orbital :**



- ✓ **S orbital interference with P_y orbital :**





c. Energy of molecular orbitals :

c.1. A_2 type molecule :

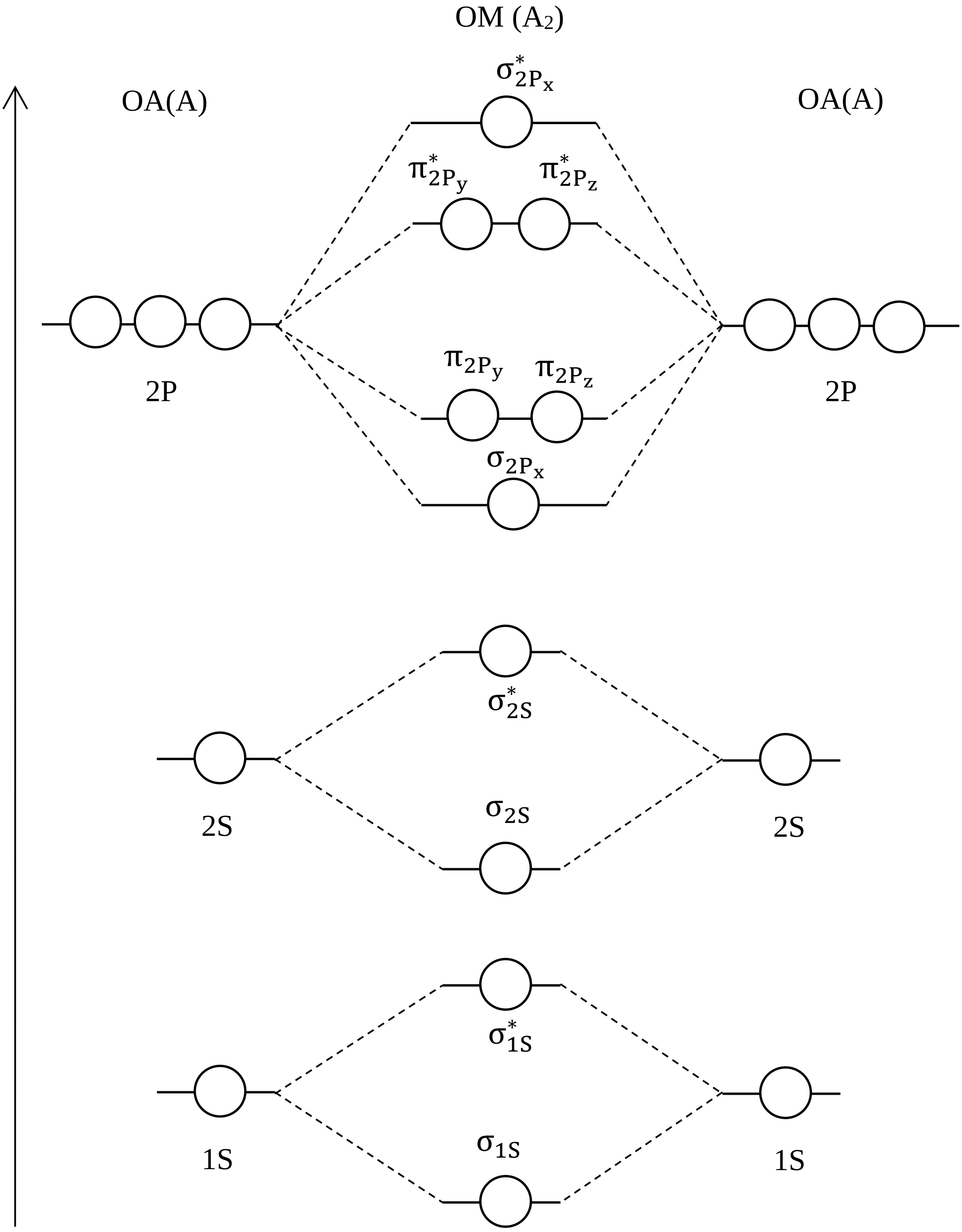


Figure 42 : Energy diagram of the molecular orbitals of $\mathbf{A_2}$ molecule

The order of energy levels in general is :

$$\sigma_{1s} < \sigma_{1s}{}^{*} < \sigma_{2s} < \sigma_{2s}{}^{*} < \sigma_{2px} < \pi_{2py} = \pi_{2pz} < \pi_{2y}{}^{*} = \pi_{2z}{}^{*} < \sigma_{2px}{}^{*}$$

Note :

In some molecules called light molecules, which generally have fewer than or equal to 14 electrons, it is observed that the energy of the σ_{2px} orbital is greater than the energy of the π_{2py} and π_{2py} orbitals.

The order of energy levels is :

$$\sigma_{1s} < \sigma_{1s}^{*} < \sigma_{2s} < \sigma_{2s}^{*} < \pi_{2py} = \pi_{2pz} < \sigma_{2px} < \pi_{2y}^{*} = \pi_{2z}^{*} < \sigma_{2px}^{*}$$

Filling molecular orbitals follows the same rules as atomic orbitals.

c.2. AB type molecule (B is more electronegative than A):

Atom B is more electronegative than A, B is placed to the right of the diagram, represented by atomic orbitals that have less energy than A.

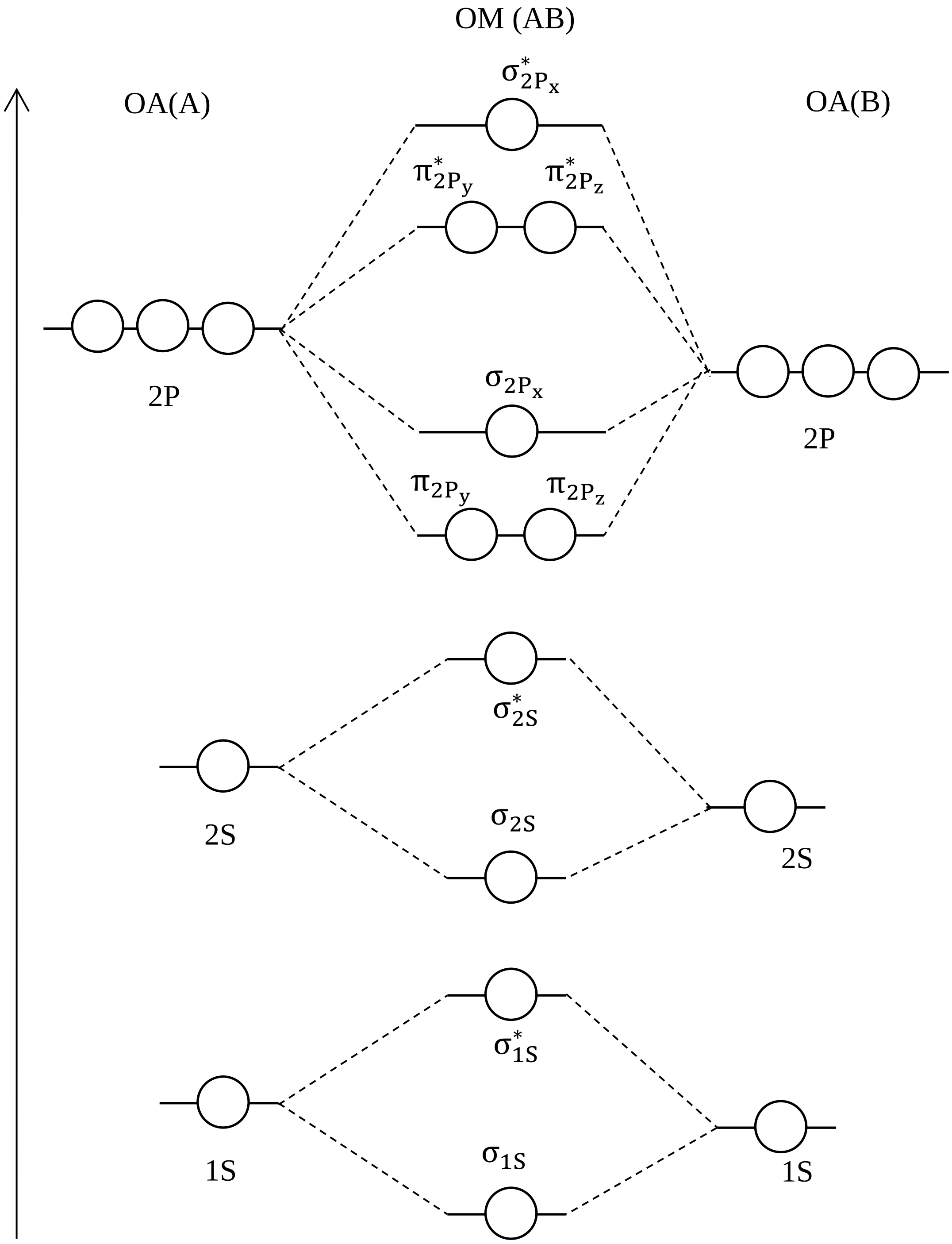


Figure 43 : Energy diagram of the molecular orbitals of molecule **AB**

The order of energy levels is similar to that of the light molecule **A_2**:

$$\sigma_{1s} < \sigma_{1s}{}^{*} < \sigma_{2s} < \sigma_{2s}{}^{*} < \pi_{2py} = \pi_{2pz} < \sigma_{2px} < \pi_{2y}{}^{*} = \pi_{2z}{}^{*} < \sigma_{2px}{}^{*}$$

d. Electronic formula of molecules :

It is writing the molecular stations horizontally, arranging them according to the increase in energy, and placing each station in parentheses. Above the parenthesis, we put the number of electrons in the orbital.

Example of an **O_2** molecule :

$$O_2 : (б_{1S})^2\ (б_{1S}^*)^2\ (б_{2S})^2\ (б_{2S}^*)^2(б_{2px})^2(\pi_{2py})^2(\pi_{2pz})^2(\overset{*}{\pi}_{2py})^1(\overset{*}{\pi}_{2pz})^1(б_{2px}^*)^0$$

e. Bond order :

$$\text{Bond Order} = \frac{(\text{Number of electrons in bonding MOs}) - (\text{number of electrons in antibonding MOs})}{2}$$

The higher the bond order, the greater the stability.

f. Magnetic properties of molecules :

f.1. Paramagnetism (Attracted to Magnetic Field) :

Paramagnetism refers to the magnetic state of an atom with one or more unpaired electrons. The unpaired electrons are attracted by a magnetic field due to the electrons' magnetic dipole moments. Hund's Rule states that electrons must occupy every orbital singly before any orbital is doubly occupied. This may leave the atom with many unpaired electrons. Because unpaired electrons can spin in either direction, they display magnetic moments in any direction. This capability allows paramagnetic atoms to be attracted to magnetic fields. Diatomic oxygen, O_2 is a good example of paramagnetism (described via molecular orbital theory).

f.2. Diamagnetism (Repelled by Magnetic Field) :

molecular oxygen (O_2) is paramagnetic and is attracted to the magnet. In contrast, molecular nitrogen (N_2) has no unpaired electrons and is diamagnetic ; it is unaffected by the magnet. Diamagnetic substances are characterized by paired electrons, e.g., no unpaired electrons. According to the Pauli Exclusion Principle which states that no two electrons may occupy the same quantum state at the same time, the electron spins are oriented in opposite directions. This causes the magnetic fields of the electrons to cancel out ; thus there is no net magnetic moment, and the atom cannot be attracted into a magnetic field. In fact, diamagnetic substances are weakly repelled by a magnetic field.

5. Geometric forms of molecules :

Despite the success achieved by the hypothesis of linear unions of atomic orbitals in clarifying the magnetic properties of molecules and determining the energy of molecular orbitals, it failed to determine the geometric forms of most molecules.

To determine the shapes of molecules, we must become acquainted with the Lewis electron dot structure. Although the Lewis theory does not determine the shapes of molecules, it is the first step in predicting shapes of molecules. The Lewis structure helps us identify the bond pairs and the lone pairs. Then, with the Lewis structure, we apply the valence-shell electron-pair repulsion (VSPER) theory to determine the molecular geometry and the electron-group geometry.

To identify and have a complete description of the three-dimensional shape of a molecule, we need to know also learn about state the bond angle as well. Lewis Electron Dot Structures play crucial role in determining the geometry of molecules because it helps us identify the valence electrons. To learn how to draw a Lewis electron dot structure click the link above.

5.1. Valence-Shell Electron-Pair Repulsion Theory :

Now that we have a background in the Lewis electron dot structure we can use it to locate the the valence electrons of the center atom. The **valence-shell electron-pair repulsion (VSEPR) theory** states that electron pairs repel each other whether or not they are in bond pairs or in lone pairs. Thus, electron pairs will spread themselves as far from each other as possible to minimize repulsion. VSEPR focuses not only on electron pairs, but it also focus on electron groups as a whole. An **electron group** can be an electron pair, a lone pair, a single unpaired electron, a double bond or a triple bond on the center atom. Using the VSEPR theory, the electron bond pairs and lone pairs on the center atom will help us predict the shape of a molecule.

The shape of a molecule is determined by the location of the nuclei and its electrons. The electrons and the nuclei settle into positions that minimize repulsion and maximize attraction. Thus, the molecule's shape reflects its equilibrium state in which it has the lowest possible energy in the system. Although VSEPR theory predicts the distribution of the electrons, we have to take in consideration of the actual determinant of the molecular shape. We separate this into two categories, the **electron-group geometry** and the **molecular geometry**.

Electron-group geometry is determined by the number of electron groups.

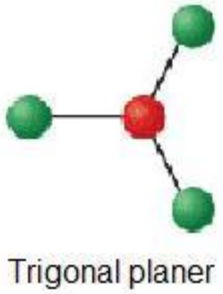
Number of electron groups	**Name of electron group geometry**
222222222222222222222222222222222222222	Linear
3	trigonal-planar
4	Tetrahedral
5	trigonal-bipyramidal
6	Octahedral

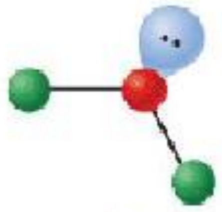
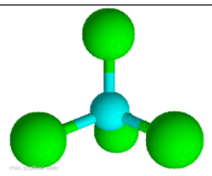
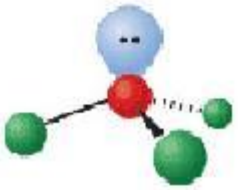
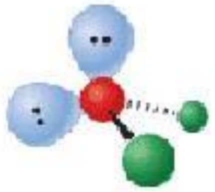
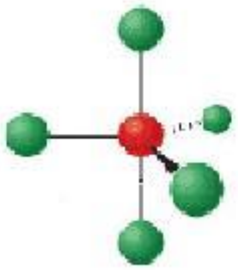
Molecular geometry, on the other hand, depends on not only on the number of electron groups, but also on the number of lone pairs. When the electron groups are all bond pairs, they are named exactly like the electron-group geometry. See the chart below for more information on how they are named depending on the number of lone pairs the molecule has.

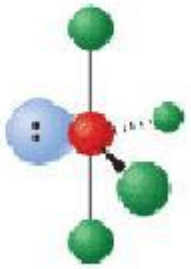
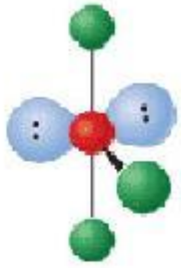
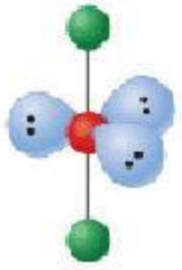
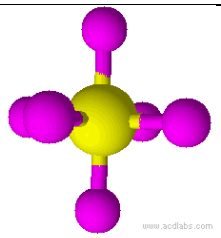
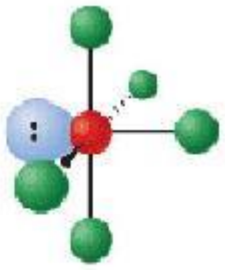
- **VSEPR Notation :**

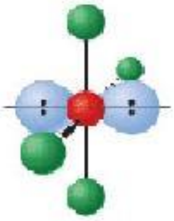
As stated above, molecular geometry and electron-group geometry are the same when there are no lone pairs. The VSEPR notation for these molecules are $AX_{n.}$ "A" represents the central atom and n represents the number of bonds with the central atom. When lone pairs are present, the letter E_x is added. The x represents the number of lone pairs present in the molecule. For example, a molecule with two bond pairs and two lone pairs would have this notation : $AX_2E_{2.}$

Geometry of Molecules Chart

Number of Electron Groups	**Electron-Group Geometry**	**Number of Lone Pairs**	**VSEPR Notation**	**Molecular Geometry**	**Ideal Bond Angles**	**Examples**
2	Linear	1	AX_2		180°	BeH_2
3	trigonal-planar	0	AX_3		120°	CO_3^{2-}

		1	AX_2E	 Bent	120°	O_3
4	Tetrahedral	0	AX_4	 Tetrahedral	109.5°	$S0_4^{2-}$
		1	AX_3E	 Trigonal Pyramidal	109.5°	H_3O^+
		2	AX_2E_2	 Bent	109.5°	H_2O
5	trigonal-bipyramidal	0	AX_5	 Trigonal-bipyramidal	90°, 120°	PF_5

		1	AX$_4$E^b	 Seesaw	90°, 120°	TeCl$_4$
		2	AX$_3$E$_2$	 T-shaped	90°	ClF$_3$
		3	AX$_2$E$_3$	 Linear	180°	I$_3^-$
6	Octahedral	0	AX$_6$	 octahedral	90°	PF$_6^-$
		1	AX$_5$E	 Square Pyramidal	90°	SbCl$_5^{2-}$

		2	AX_4E_2	 Square Planer	90°	ICl_4^-

5.2. Hybridization :

There are various types of hybridization involving s, p, and d orbitals. The different types of hybridization are as under.

5.3.Types of Hybridization :

- **sp hybridization :**

This type of hybridization involves the mixing of one *s* and one *p* orbital resulting in the formation of two equivalent sp hybrid orbitals. The suitable orbitals for *sp* hybridization are s and *pz*, if the hybrid orbitals are to lie along the *z*-axis. Each *sp* hybrid orbitals has 50% *s*-character and 50% *p*-character. Such a molecule in which the central atom is *sp*-hybridized and linked directly to two other central atoms possesses liner geometry. This type of hybridization is also known as diagonal hybridization.

The tow *sp* hybrids point in the opposite direction along the *z*-axis with projecting positive lobes and very small negative lobes, which provides more effective overlapping resulting in the formation of stronger bonds.

Example of molecule having sp hybridization :

$BeCl_2$: The ground state electronic configuration of Be is $1s^2 2s^2$. In the exited state one of the 2*s*-electrons is promoted to vacant 2p orbital to account for its divalency. One 2*s* and one 2*p*-orbitals get hybridized to form two *sp* hybridized orbitals. These two *sp* hybrid orbitals are oriented in opposite direction forming an angle of 180. Each of the sp hybridized orbital overlaps with the 2*p*-orbital of chlorine axially and form two Be-Cl sigma bonds. This is shown below figure.

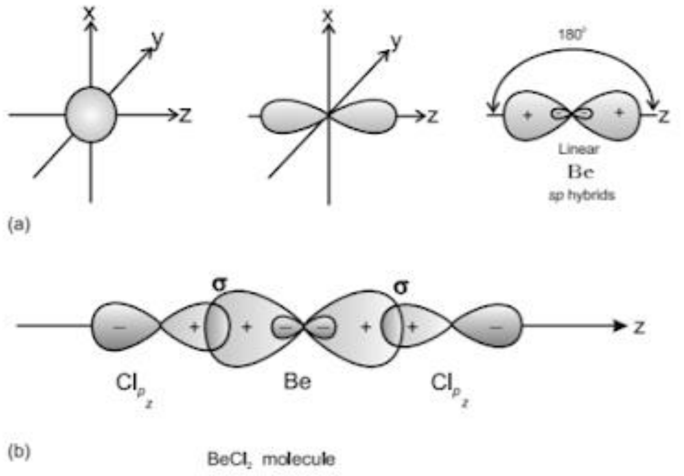


Figure 44 : a) Formation of sp hybrids from s and p orbitals
b) Formation of the linear BeCl$_2$ molecule

- **Sp^2 hybridization :**

In this hybridization there is involvement of one s and two p-orbitals in order to form three equivalent *sp*^{2} hybridized orbitals. For example, in BCl$_3$ molecule, the ground state electronic configuration of central boron atom is $1s^2 2s^2 2p^1$. In the excited state, one of the 2*s* electrons is promoted to vacant 2*p* orbitals as a result boron has three unpaired electrons. These three orbitals (one 2*s* and two 2*p*) hybridise to form three sp^2 hybrid orbitals. The three hybrid orbitals so formed are oriented in a trigonal planar arrangement and overlap with 2*p* orbitals of chlorine to form three B-Cl bonds. Therefore, in BCl$_3$ the geometry is trigonal planar with CIBCl bond of 120.

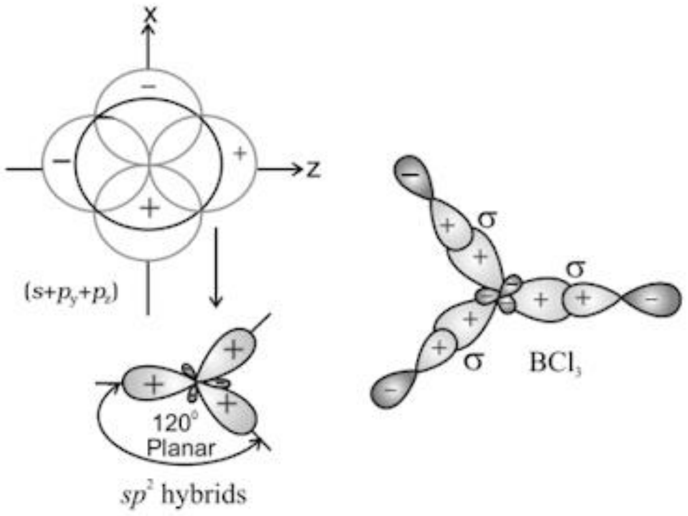


Figure 45 : Formation of sp^2 hybrids and the BCl$_3$ molcule

- **Sp^3 hybridization :**

This type of hybridization can be explained by taking the example of CH_4 molecule in which three is mixing of one s-orbital and three *p*-orbitals of the valence shell to form four sp^3 hybrid orbital of equivalent energies and shape. There is 25% s-character and 75% p-character in each sp^3 hybrid orbital. The four sp^3 hybrid orbitals so formed are directed towards the four corners of the tetrahedron. The angle between sp^3 hybrid orbital is 109.5 as shown below.

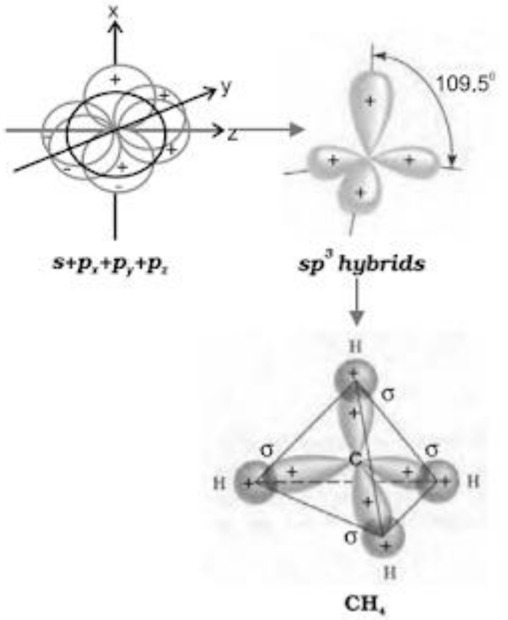


Figure 46 : Formation of sp^3 hybrids by the combinition of s, p_x, p_y and p_z atomic orbitals of carbon and the formation of CH_4 molecule

The structure of NH_3 and H_2O molecules can also be explained with the help of sp^3 hybridization. In NH_3, the valence shell (outer) electronic configuration of nitrogen in the grounds state is $2s^2\ 2p^1_x\ 2p^1_y\ 2p^1_z$ having three unpaired electrons in the sp^3 hybrid orbitals and a lone pair of electrons is present in the fourth one. These three hybrid orbitals overlap with 1*s* orbitals of hydrogen atoms to form three N-H sigma bonds. As we know that the force of repulsion between a lone pair and a bond pair is more than the force of repulsion between two bond pairs of electrons. The molecule thus gets distorted and the bond angle is reduced to 107 from 109.5. The geometry of such a molecule will be pyramidal as shown below.

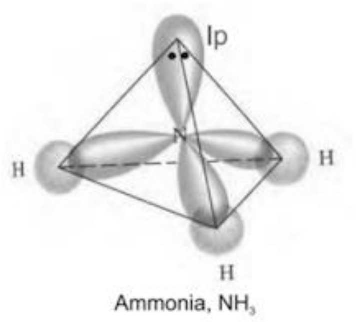


Figure 47 : Formation of NH_3 moecule

In the case of H_2O molecule, the four oxygen orbitals (one 2*s* and three 2*p*) undergo sp^3 hybridization forming four sp^3 hybrid orbitals out of which two contain one electron each and the other two contain a pair of electrons. These four sp^3 hybrid orbitals acquire a tetrahedral geometry, with two corners occupied by hydrogen atoms while the other two by the lone pairs. The bond angle in this case is reduced to 104.5 from 109.5 and the molecule thus acquires a V-shape or angular geometry.

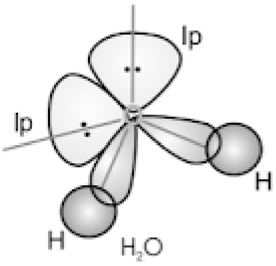


Figure 48 : Formation of H_2O moecule

Practical exercises :

Exercise 1 :

1. Provide the Lewis representation for the following atoms and ions :
   ${}_4Be$, ${}_2He$, ${}_{13}Al$, ${}_8O$, ${}_{17}Cl$, ${}_{10}Ne$, ${}_7N$, ${}_{16}S$, ${}_{17}Cl^-$, ${}_{26}Fe^{2+}$.
2. Provide the Lewis representation for the following molecules :
   Cl_2, CO_2, HCl, HCN, C_2H_2, H_2SO_4.

Exercise 2 :

Calculate the dipole moment for the following two molecules :

Given :

$\mu CH = 0.4\ D$, $\mu CO = 3.1\ D$

Exercise 3 :

Consider the N_2 molecule :

1. Provide the Lewis representation for this molecule.
2. Draw the energy levels (energy diagram) for this molecule.
3. Calculate the bond order.

Exercise 4 :

What is the hybridization type of the carbon atoms in the following molecules ?

CH_4, HCN, CH_2O, CO_2, C_4H_8.

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