CHAPTER 4.

ELECTRONIC STRUCTURE OF THE ATOM

Chapter contents

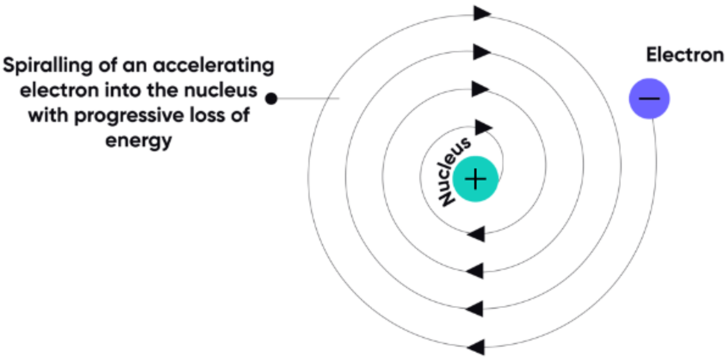
- **Wave-particle duality,**
- **Interaction between light and matter,**
- **Bohr’s atomic model: hydrogen atom,**
- **The hydrogen atom in wave mechanics,**
- **Poly electronic atoms in wave mechanics**

I- Introduction

Rutherford's atomic model failed to explain the stability of electrons in a circular path.

Drawbacks of the Rutherford model

1. This was not according to the classical theory of electromagnetism proposed by Maxwell: Every accelerated charged particle must emit radiation in the form of electromagnetic waves and lose its total energy. Since the energy of electrons keeps on decreasing, the radius of the circular orbits should also decrease, and ultimately the electron should fall into the nucleus. But it never happens.



2. It could not explain the line spectrum of the H-atom. According to this model, the spectrum of an atom must be continuous, whereas practically it is a line spectrum.

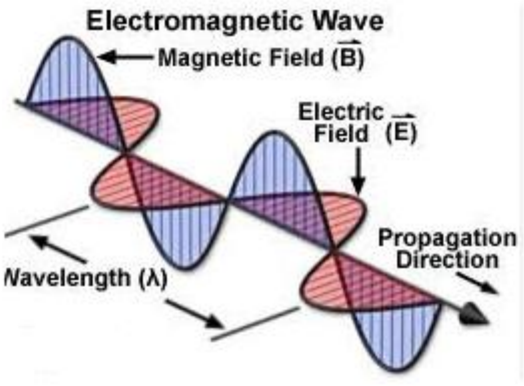
3. It did not explain how the electrons are distributed around the nucleus and what the energies of these electrons are.

II- Wave-particle duality

The main conclusion from both Planck's and Einstein's work was that the behavior of light and other forms of electromagnetic radiation is more complex than had been formerly believed. In addition to behaving as waves, light energy can also behave as small particles. First, we need to understand what electromagnetic radiation is.

1- Electromagnetic radiation

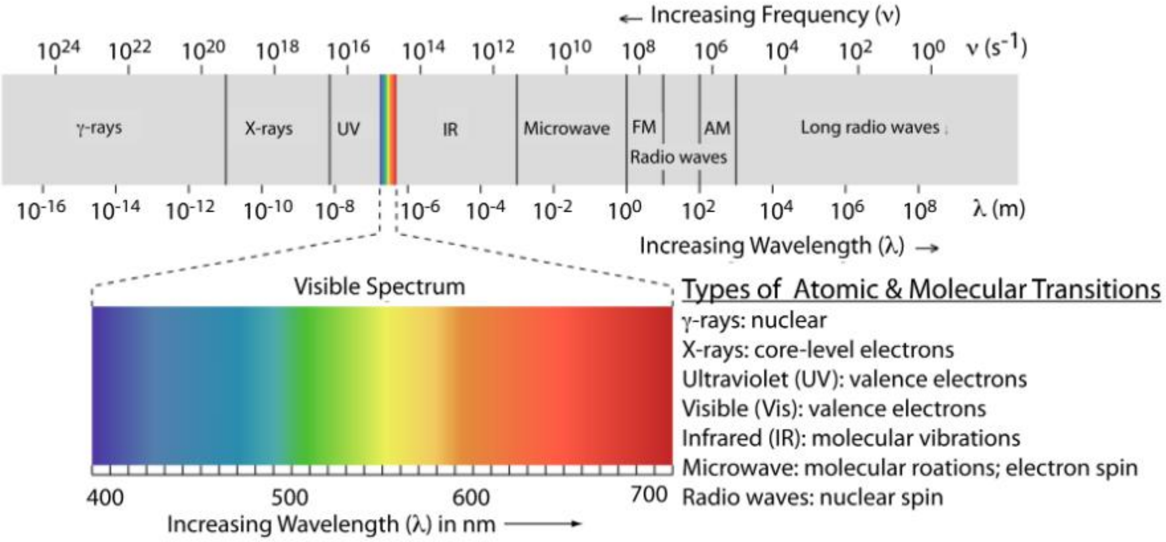
It consists of oscillating electric and magnetic fields, perpendicular to each other, that propagate in a vacuum at the speed of light **$C = 3 \times 10^8$ m/s**. An electromagnetic wave is characterized by **wavelength, λ (Å)**, which is the distance between successive maxima.



Wavelength is inversely related to **frequency, ∂**, which refers to the number of wave cycles per second. The higher the frequency of the signal, the shorter the wavelength. The relationship between wavelength and frequency is:

$$\partial = \frac{C(m/s)}{\lambda(m)}\,(S^{-1})$$

Electromagnetic radiation is divide into different regions (**the electromagnetic spectrum**) based on the type of atomic or molecular transition that gives rise to the absorption or emission of photons.



Types of Atomic & Molecular Transitions

γ-rays: nuclear
X-rays: core-level electrons
Ultraviolet (UV): valence electrons
Visible (Vis): valence electrons
Infrared (IR): molecular vibrations
Microwave: molecular roations; electron spin
Radio waves: nuclear spin

For ultraviolet and visible electromagnetic radiation, the wavelength is typically expressed in nanometers (1 nm = 10^{-9} m), while for infrared radiation, it is given in micrometers (1µm=10^{-6} m).

- Another useful unit is the **wavenumber**, $\bar{\partial}$, which is the reciprocal of wavelength :

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

2- Quantum theory (Planck; the Nobel Prize in Physics in 1918)

We have described light in terms of wave behavior. Under certain conditions, it is also possible to describe light as composed of *particles*, or **photons.**

Max Planck in **1900**, marked the assumption that each photon of light has an individual amount (**a quantum**) of energy in the same way that matter does and was therefore ***quantifiable.*** The amount of energy possessed by a photon depends on the frequency of the light. Planck wrote a mathematical equation involving a figure to represent these individual units of energy, which he called ***quanta***.

$$\boxed{E = h\,\partial}$$

Where ∂ is the frequency of the light and **h** is Planck's constant :

$$\boxed{h = 6{,}62\times 10^{-34}\,\mathrm{j.s}}$$

Exercise 1

The wavelengths of ultraviolet light of frequency $2.73 \times 10^{16}\ s^{-1}$ and of yellow light of frequency $5.26 \times 10^{14}\ s^{-1}$. Calculate the energy, in joules, of an individual photon of each. Compare these photons by calculating the ratio of their energies.

This example shows that a photon of ultraviolet light has more energy than a photon of yellow light (visible region). This is one reason why ultraviolet (UV) light damages your skin much more rapidly than visible light.

1- In case of light

The now-famous equation, proposed in 1905 by Albert Einstein (the 1921 Nobel Prize in Physics winner), is part of his special theory of relativity. He extended Planck's idea that light behaves as though it were composed of ***photons***, each with a mass m_0 and a particular amount of energy:

$$E = m_0\, c^2$$

Since $E = h\partial$ then $h\partial = m_0c^2$ $\Rightarrow$ $h\frac{c}{\lambda} = m_0c^2$

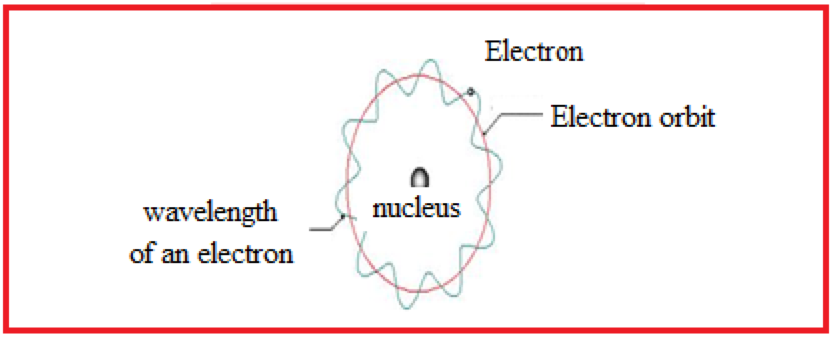
So it's possible to derive a relationship between mass and wavelength:

$$\boxed{\lambda = \frac{h}{m_0 c}}$$

2- In case of matter

In **1924**, **Louis de Broglie** proposed that there is no fundamental difference in the behavior of energy and matter; on the atomic and subatomic level either may behave as if made of either particles or waves. This theory became known as the principle of *wave-particle duality*:

De Broglie suggested that a similar equation might be applied to an electron by replacing the speed of light (*c*) by the speed of the electron (*v*).



The resultant de Broglie equation thus allows calculation of a "wavelength" of an electron or of any other particle or object of mass ***m*** moving at velocity ***v***:

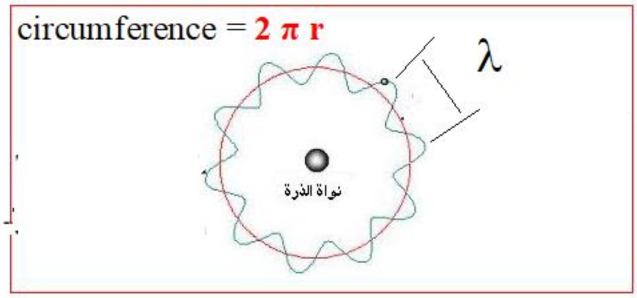
$$\boxed{\lambda = \frac{h}{mv}}$$

Example 2

The mass of an electron is 9.11×10^{-31} kg, and the velocity *v* of an electron in a hydrogen atom is 2.2×10^{6} m/s (about 1% of the speed of light). What is the wavelength of this electron?

In **1913**, **Niels Bohr** assumed that electrons orbiting the nucleus could exist in only certain stable orbits of specific energies and with a corresponding stable wavelength.

Since the perimeter of the circle or circumference = $2\pi r$ and it is surrounded by a natural number n of wavelength λ. So:



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

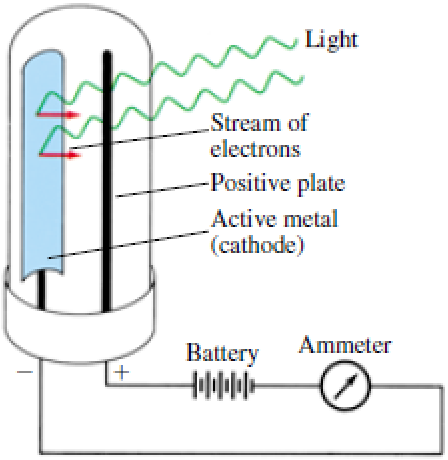
This equation is called **Bohr's quantum condition**.

III- Interaction between light and matter

1- The Photoelectric Effect

In **1905**, the German-American physicist **Albert Einstein** used the theory to solve another mystery in physics, the photoelectric effect, a phenomenon in which electrons are ejected from the surface of certain metals exposed to light at least a certain minimum frequency, called the **threshold frequency** ∂_0.

The apparatus for the photoelectric effect shown the negative electrode in the evacuated tube is made of a pure metal such as cesium. When light of a sufficiently high energy strikes the metal, electrons are knocked off its surface. They then travel to the positive electrode and form a current flowing through the circuit.



The important observations were:

1. Electrons can be ejected only if the light is of sufficiently short wavelength and frequency more than the threshold frequency $\partial_0 < \partial_1$ (has sufficiently high energy), no matter how long or how brightly the light shines. The wavelength limit varies for different metals.

2. The current (the number of electrons emitted per second) increases with increasing *brightness* (intensity) of the light. The current, however, does not depend on the color of the light, as long as the wavelength is short enough (has high enough energy).

when a photon falls on the surface of a metal, the entire photon's energy **E** is transferred to the electron. A part of this **energy E_0** (**work function or the binding energy of electrons**) is used to remove the electron from the metal atom's grasp and the rest is given to the ejected electron as **kinetic energy Ec**.

$$\boxed{E = E_C + E_0} \quad \Rightarrow \quad \boxed{E - E_0 = E_C = 1/2\, mv^2}$$

where E_C is the kinetic energy of the ejected electron and E_0 is called the **work function**.

At the threshold frequency, ∂_0 electrons are just ejected and do not have any kinetic energy. Below this frequency, $\partial_0 > \partial_1$ there is no **electron emission**. Thus, the energy of a photon with this frequency must be the work function of the metal.

The more intense beam of light consists of a larger number of photons; consequently, it ejects more electrons from the metal's surface than the weaker beam of light. Thus, the more intense the light, the greater the number of electrons emitted by the target metal; the higher the frequency of the light, the greater the kinetic energy of the ejected electrons.

Example 3

a- What is the energy in joules and electron volts of a photon of 420-nm violet light?

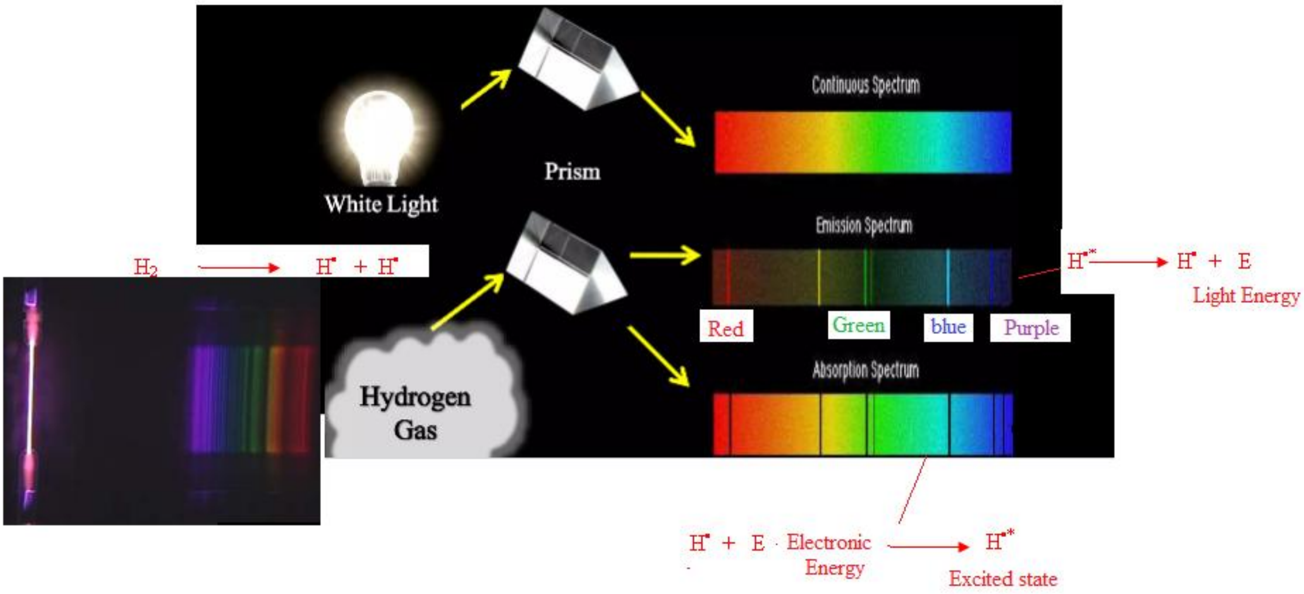
b- What is the maximum kinetic energy of electrons ejected from calcium by 420-nm violet light, given that the binding energy (or work function) of electrons for calcium metal is 2.71 eV?

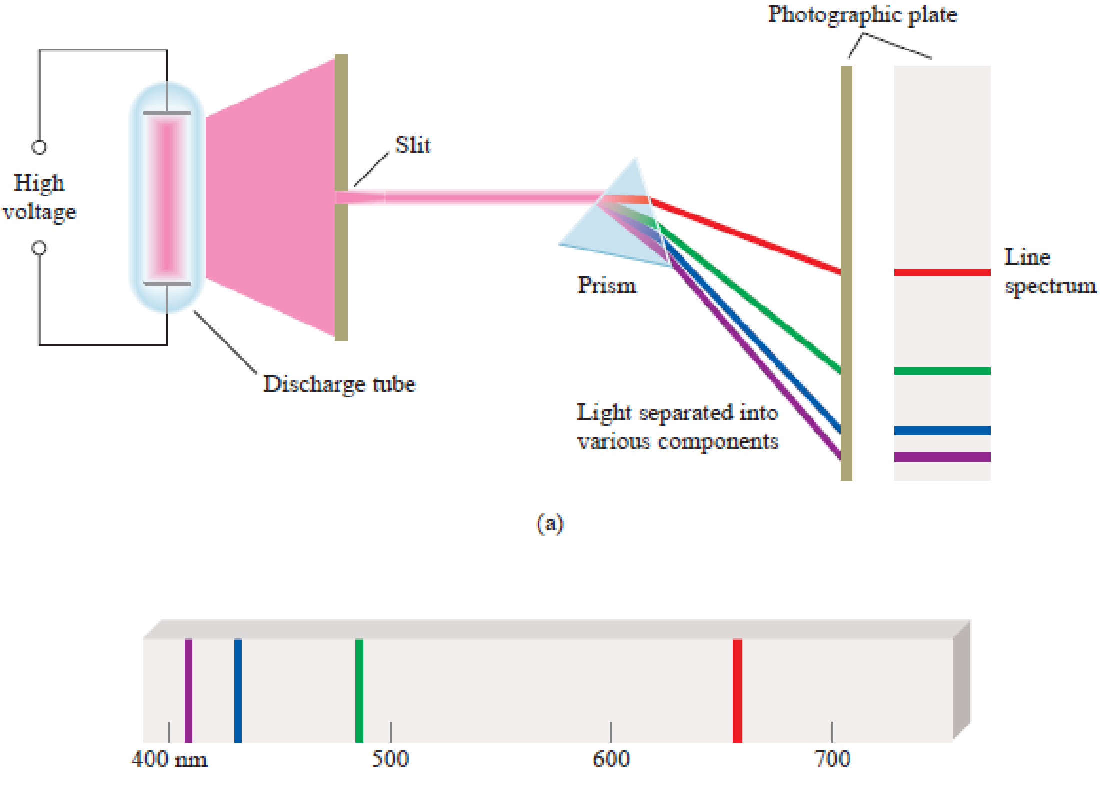
c- Calculate the velocity of the electrons ejected from calcium by 420-nm violet light.

d- Calculate the number of photons emitted per minute from 100W blue light bulb ($\lambda = 420$ nm)

2- The spectrum of hydrogen atoms.

When an electric current is passed through hydrogen gas at very low pressures, several series of lines in the spectrum of hydrogen are produced. Many scientists have studied these lines intensely.





(a)

(b)

3- The line spectrum of the hydrogen

In the late nineteenth century, **Johann Balmer** (1825–1898) and **Johannes Rydberg** (1854–1919) showed that the wavelengths of the various lines in the hydrogen spectrum can be related by a mathematical equation:

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

Where R_H, the Rydberg constant, has the value:

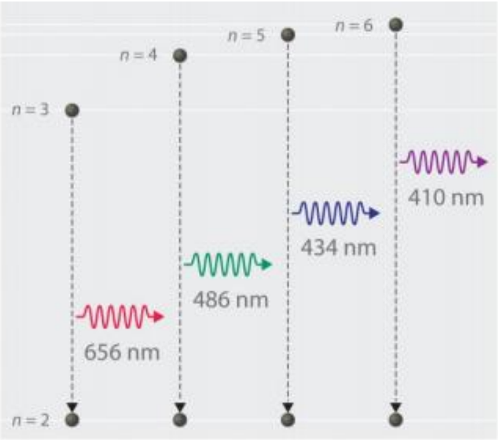
$$\boxed{R_H = 1{,}09677\times 10^5\ \mathrm{cm}^{-1}}$$

The number n is an integer called the **principal quantum number**; it has the values n= 1, 2, 3, ..

The general formula for the calculation of wave number $\bar{\partial}$ of hydrogen spectral line emissions due to the transition of an electron from one orbit **n_1** to another orbit **n_2** is given by:

$$\boxed{\bar{\partial} = R_H\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)\ n_2 > n_1}$$

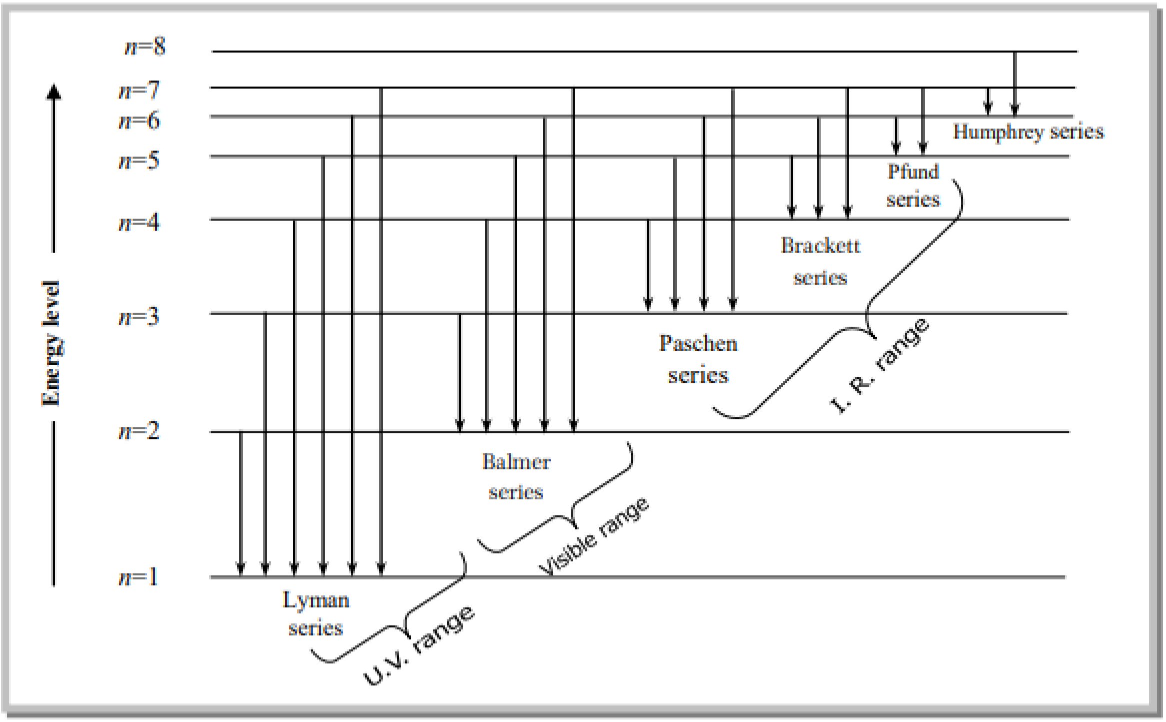
n_1 denotes the series, while n_2 denotes a line within the serie.



The Balmer series is basically the part of the hydrogen emission spectrum responsible for the excitation of an electron from the second shell to any other shell. Similarly, other transitions also have their own series names. Some of them are listed below.

Table. The Various Series in Atomic Hydrogen Emission Spectrum.

Series	n_f	n_i	Spectrum Region
Lyman	**1**	2, 3, 4....	**Ultraviolet**
Balmer	**2**	3, 4, 5....	**Visible**
Paschen	**3**	4, 5, 6....	**Infrared**
Brackett	**4**	5, 6, 7....	**NeerInfrared**
Pfund	**5**	6, 7, 8....	**Far Infared**



The general formula for the calculation of wavenumber $\bar{\partial}$ of hydrogen-like atoms spectral line emissions is given by:

$$\bar{\partial} = \mathbf{R_H Z^2} \left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \quad n_2 > n_1$$

Not that, **hydrogen-like atoms** are any atom or ion that only have **one electron**. Examples all alkali metals such as **Rb and Cs**, singly ionized alkaline earth metals such as **Ca$^+$ and Sr$^+$** and other ions such as **He$^+$, Li^{2+}, and Be^{3+}** and isotopes of any of the above.

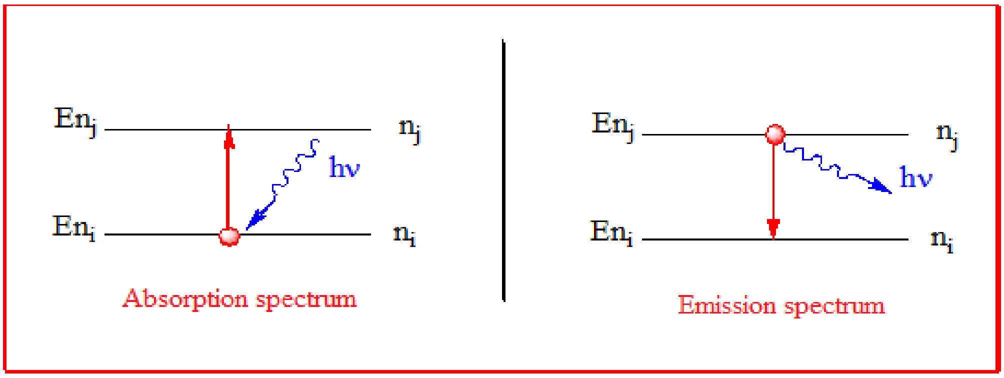
Exemple 5

1- Calculate the wavenumber of first line of Balmer series of hydrogen atom. What is the wavenumber of first line of Balmer series of ion Li^{2+}?

2- If the limit wavelength of the emitted spectral line for hydrogen atom is 187.5×10^{-9} m. what is the spectral series?

3- Emission energy

Light is emitted when the electron undergoes a transition from an orbit with **a higher value of n** (at a higher energy) to an orbit with **a lower value of n** (at lower energy) and versa.



Absorption spectrum

Emission spectrum

The **energy gap** between these levels corresponds to light in the visible portion of the electromagnetic spectrum and it is given by:

$$\Delta E = E_{final} - E_{initial}$$

In another side,

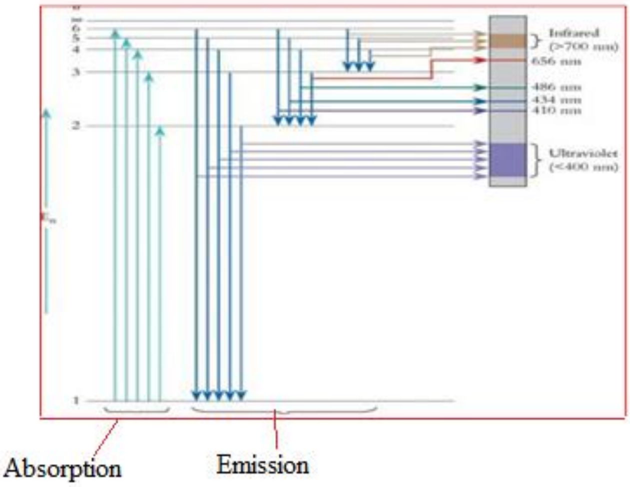
$$\Delta E = h\partial \quad \text{and} \quad \partial = \frac{c}{\lambda} = c\,\bar{\partial} \quad \Rightarrow \quad \Delta E = h\,C\,\bar{\partial}$$

Substituting $\bar{\partial}$ for its formula gives:

$$\boxed{\Delta E = h\,C\,R_H\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)}$$

Example

Calculate the energy gap when an electron is removed from an H-atom in Lyman series.



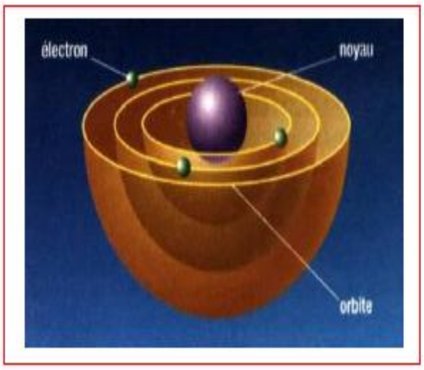
IV- Bohr’s atomic model: hydrogen atom

Bohr set down the following postulates to account for:

- The stability of the hydrogen atom (that the atom exists and its electron does not continuously radiate energy and spiral into the nucleus)
- The line spectrum of the atom.

1. Bohr’sPostulates

- Bohr proposed that in an atom electron is revolving around the nucleus in a definite circular path called **orbits**. These orbits are called ‘**stationary orbits**’ and each orbit or shell possesses fixed energy.
- Energy-level Postulate: An electron can have only *specific energy values in an atom*, which are called its energy levels. Therefore, the atom itself can have only specific total energy values. Thus, the electron in the lower energy state is called the **ground state**.



- The energy levels are represented by an integer called quantum numbers where n = 1, 2, 3…. These integers indicate **principal quantum numbers.** Various energy levels are designed as K(n=1), L(n=2), M(n=3) …. etc.
- The electron's angular momentum is quantized in its orbitals. So, electrons can move only those permissible orbits that should be an integral multiple of $\frac{h}{2\pi}$ where h is the Planck's constant. Thus, the Bohr's quantum condition wrote.

(Bohr's quantum condition)

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

Where, m = mass of the electron, r = radius of the electronic orbit, v = velocity of the electron in its orbit.

- Transitions Between Energy Levels: An electron in an atom can change energy only by going from one energy level to another. By so doing, the electron undergoes a ***transition***.

$$\boxed{\Delta E = E_{final} - E_{initial} = h\partial = hC\bar{\partial}}$$

- The electron gains energy when it jumps from a lower energy level to a higher energy level and the electron loses its energy as it jumps from the higher energy to a lower energy level.

2. Advantages of Bohr's theory

Bohr's theory satisfactorily explains the spectra of species having one electron, viz. hydrogen and H-like atoms and it gave the characteristics of electron in his orbit.

2.1- Calculation of energy of electron in Bohr's orbit

Bohr showed that the energies that an electron in hydrogen atom can occupy are given by :

$$\boxed{\underbrace{E_t}_{\text{Total Energy}} = \underbrace{E_c}_{\text{Kinetic Energy}} + \underbrace{E_p}_{\text{Potential Energy}}}$$

The force of attraction between the nucleus and the electron, F_{ce}, is equal to the centrifugal force, F_c, of the moving electron:

$$\boxed{k = \frac{1}{4\pi\varepsilon_0} = \begin{cases} 9 \times 10^9 (MKSA) \\ 1\ (CGS) \end{cases}}$$

$$\left|\overrightarrow{F_{Ce}}\right| = \left|\overrightarrow{F_c}\right| \begin{cases} \boxed{\left|\vec{F}_{ce}\right| = \dfrac{KZ|qq'|}{r^2}} \\ \text{And} \\ \boxed{\left|\overrightarrow{F_c}\right| = \dfrac{m_e v^2}{r}} \end{cases}$$

Where, **q_1** and **q_2** are the charges of nucleus and of electron, respectively. r is the distance between the nucleus and the electron. $\boldsymbol{\varepsilon_0}$ is the permittivity constant: = 8.85 x 10^{-12} $C^2/(N \cdot m^2)$.

For an electron:

$$\left|\overrightarrow{F_{Ce}}\right| = \left|\overrightarrow{F_c}\right| \quad \Rightarrow \quad \frac{Ke^2}{r^2} = \frac{mv^2}{r} \quad \Rightarrow \quad \boxed{mv^2 = \frac{Ke^2}{r}}$$

Since $E_C = ½\ mv^2$ $\Rightarrow$ $\boxed{E_c = \frac{1}{2}\frac{ke^2}{r}}$

In another side, the force acting on the electron is calculated as: $F_c = \frac{dE_p}{dr}$; where dE_p is the variation in the potential energy and dr is the variation in radius of the electronic orbit.

$$\int_0^{E_P} dE_p = \int_{\infty}^{r} F_c . dr = \int_{\infty}^{r} \frac{Ke^2}{r^2}\, dr \quad \overset{\square}{\Rightarrow} \quad \boxed{E_p = -\frac{ke^2}{r}}$$

Substituting E_c and E_p for their formula in E_t gives:

$$\boxed{E_{t=} \frac{-KZe^2}{2r}}$$

2.2- Calculation of radius of Bohr's orbit

$$mv^2 = \frac{KZe^2}{r} \qquad\qquad m^2v^2 = \frac{mKZe^2}{r} \qquad (1)$$

And from Bohr's quantum condition, we write:

$$mvr = \frac{nh}{2\pi} \qquad \Rightarrow \qquad m^2v^2 = \frac{n^2h^2}{4\pi^2r^2} \qquad (2)$$

Substituting of *K*, gives us:

$$\boxed{r = \frac{h^2\varepsilon_0}{\pi m e^2}\frac{n^2}{Z}}$$

Where, *n* =Orbit number, *m* = 9.1×10^{-31}Kg, e =1.6×10^{-19}c, *Z* =Atomic number of element,ε_0 = 0.884×10^{-11} $c^2/N.m^2$, h=6.62×10^{-34}j.s.

After putting the values of *m*, *e*, ε_0, *h*, we get.

$$\boxed{r_n = a_0\frac{n^2}{Z}}$$

Thus, a_0 is the radius of the first orbit of hydrogen atom. Where

$$\boxed{a_0 = 0.53\ \text{Å}}$$

Substituting of r and kin the energy formula, gives us:

$$\boxed{E_{t=}\frac{-me^4Z^2}{8\varepsilon_0^2h^2n^2}}$$

In ground state energy of atom is minimum and for 1st orbit of H-atom, n=1.

$$\boxed{E_1=-13.54\ ev}$$

Putting the value of E_1, we get :

$$\boxed{E_n = E_1\frac{Z^2}{n^2}}$$

Exercise 6

1- The frequency of the shortest wavelength transition in Balmer series of atomic hydrogen is 8.227 $\times 10^{14}$ s^{-1}. Calculate R_H, the Rydberg constant.

2- Calculate the energy associated with the first orbit of He^+. What is the radius of this orbit?

2.3- Calculation of velocity of electron

$$mvr = \frac{nh}{2\pi} \quad \Rightarrow \quad v = \frac{nh}{2\pi mr}$$

Substituting of r, gives us

$$\boxed{v = \frac{h}{2\pi m a_0}\frac{Z}{n}}$$

v_1 is the velocity of hydrogen atom:

$$\boxed{V_1 = 2{,}18 \times 10^6 m/}$$

Substituting r, gives us:

$$\boxed{V_n = V_1 \frac{Z}{n}}$$

2.4- Ionization energy

Also called the **first ionization energy, E_i,** is the energy required to remove an electron from **its stable orbit to infinity ∞**.

$$\boxed{E_i = E_\infty - E_n}$$

$$E_n = E_1 \frac{Z^2}{n^2} \quad \text{and} \quad E_\infty = 0 \quad \Rightarrow \quad \boxed{E_i = -E_n = E_1 \frac{Z^2}{n^2}}$$

Exercise 7

- Light radiation of wavelength 10 nm (uv rays) can ionize a H-like atom in its ground state.
  1- Calculate the atomic number.
  2- What is the radius of this orbit in the 1st excited state of this atom?
  3- Calculate the force of attraction between the nucleus and the electron in this orbit.
- Calculate the velocity of electron in the second Bohr orbit of excited state of H atom. What is the wavelength associated to this electron ?

V- The hydrogen atom in wave mechanics

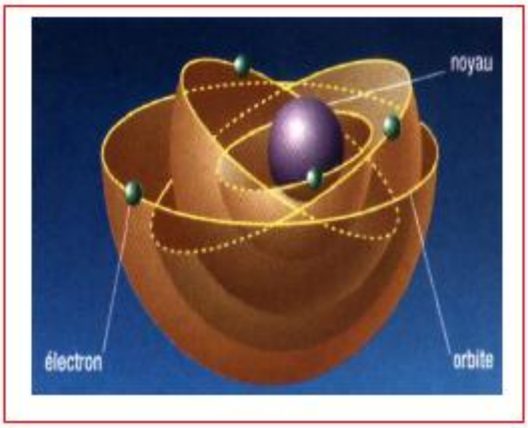
Bohr's theory firmly established the concept of atomic energy levels. It was unsuccessful, however, in accounting for the details of atomic structure. Further understanding of atomic structure required other theoretical developments.

1- Limitations of Bohr's Model of an Atom

- Bohr Theory could not explain the line spectra of atoms containing more than one electron.
- This theory could not explain the presence of multiple spectral lines.
- This theory could not explain the splitting of spectral lines in magnetic field (Zeeman Effect) and in electric field (Stark effect). The intensity of these spectral lines was also not explained by the Bohr atomic model.
- This theory was unable to explain of dual nature of matter as explained on the basis of De Broglie's concept.
- This theory could not explain uncertainty principle.
- No conclusion was given for the concept of quantization of energy.

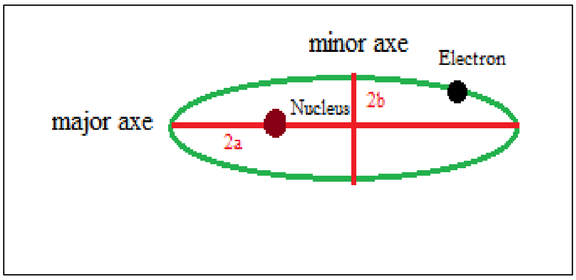
2- Bohr – Sommerfeld's model

In **1915**, **Arnold Sommerfeld** introduced a new atomic model to explain the fine spectrum of hydrogen atom. He gave concept that electron revolve round the nucleus in ***elliptical orbit***. Circular orbits are formed in special conditions only when major axis and minor axis of orbit are equal.



For circular orbit, the angular momentum=$\frac{nh}{2\pi}$where *n*= principal quantum number only one component. For elliptical orbit, another quantum number k, where the relation between n and k is :

$$e = \frac{b}{a} = \frac{k}{n}$$

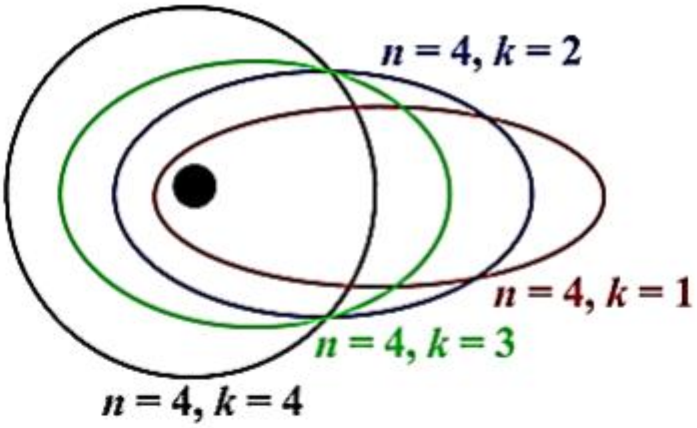


Thus Sommerfield showed that Bohr's each major level was composed of several sub-levels or subshells withe a new **quantum number** **ℓ**called the **orbital quantum number**, where

$k = \ell + 1$

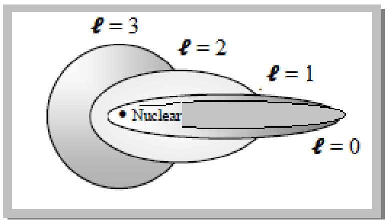
Since $0 \le e \le 1 \quad \Rightarrow \quad 0 \le \frac{k}{n} \le 1 \quad \Rightarrow \quad 0 \le \frac{\ell+1}{n} \le 1$

So, $\boxed{\mathbf{0 \le \ell \le n-1}}$



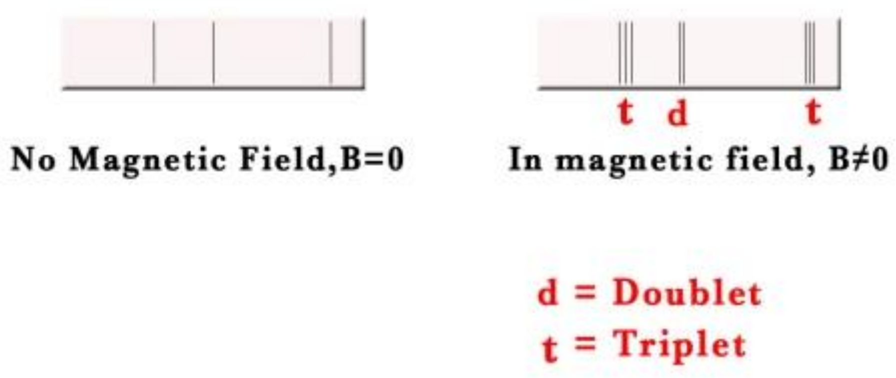
For, n = 4 ;

ℓ = 0 ; **4s** sub shell	e = 1/4 ellipse more flatter
ℓ=1 ; **4p** sub shell	e = 2/4 ellipse flatter
ℓ=2 ; **4d** sub shell	e = 3/4 ellipse less flatter
ℓ=3 ; **4f** sub shell	e = 4/4circular

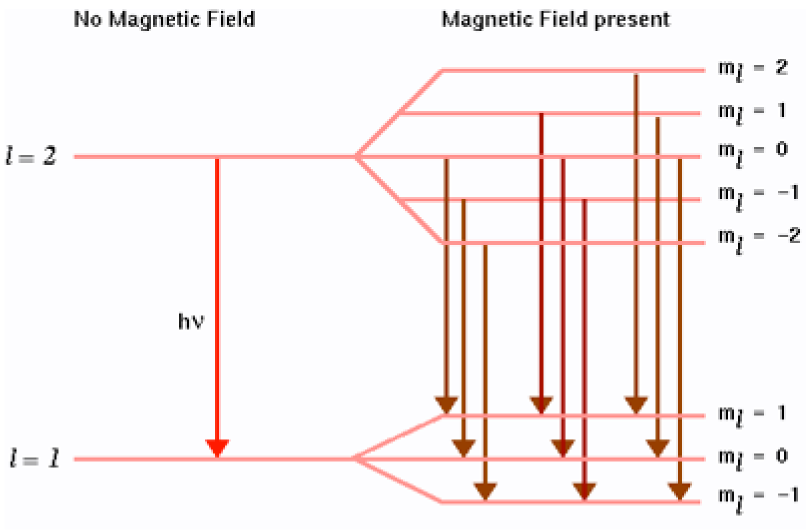


3- Magnetic quantum numbers m (Noble prize in 1902)

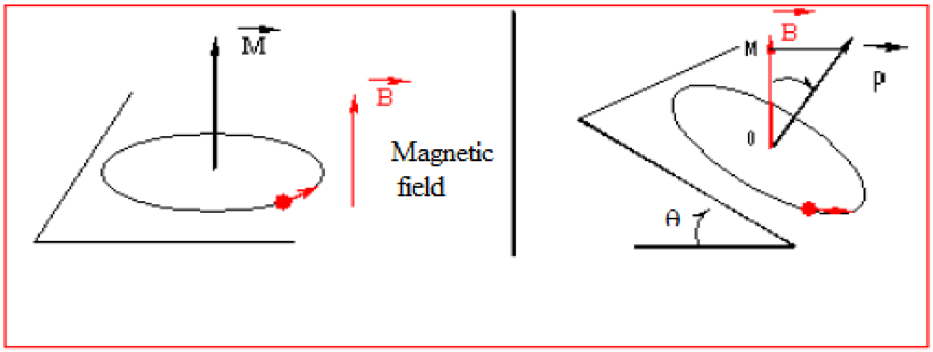
It was proposed by **Zeeman** and denoted by 'm'. It gives the number of permitted orientation of subshells. It tells about the splitting of spectral lines **into doublets or triplets** in the magnetic field i.e. this quantum number proved the Zeeman effect.



Degenerate orbitals: Orbitals having the same energy are known as degenerate orbitals.



The origin of Zeeman Effect is the following. In an atomic energy state, an electron orbits around the nucleus of the atom and has a magnetic dipole moment $\|\overrightarrow{OM}\|$associated with its angular momentum p. In a magnetic field, it acquires an additional energy just as a bar magnet does and consequently the original energy level is shifted. The energy shift may be positive, zero, or even negative, depending on the angle between the electron magnetic dipole moment and the field.



$$\boxed{\|\overrightarrow{OM}\| = p\cos\theta}$$

$$\|\overrightarrow{OM}\| = \frac{mh}{2\pi} \quad \Rightarrow\Rightarrow \quad \frac{mh}{2\pi} = p\cos\theta \qquad \frac{mh}{2\pi} = \frac{\ell h}{2\pi}\cos\theta$$

$$\boxed{\mathbf{Cos}\ \theta = \frac{m}{\ell}}$$

$$-1 \leq \cos\theta \leq +1 \quad \Rightarrow \quad -1 \leq \frac{m}{\ell} \leq +1 \quad \Rightarrow \quad \boxed{-\ell \leq m \leq +\ell}$$

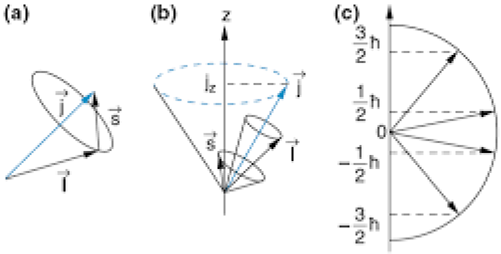


Fig.5.23 (a) Coupling of l and s and their precession around the space-fixed vector $j = l + s$ without external field. (b) Precession of j in an external magnetic field B_z. (c) Possible orientations of j with components $j_z = m\hbar$

4- The Spin Quantum Number(s)

In **1921**, **Otto Stern and Walter Gerlach**, conducted an experiment to study the magnetic properties of a single electron. They shot a beam of silver atoms through a slit and passed this beam through a non-uniform magnetic field. They choose Silver metal to conduct the experiment because it contains a single electron in its outermost shell 5S (ℓ =0, m =0),so technically it would not interact with any external magnetic field. Also, silver is easily detectable on a photographic plate. Instead, they saw that the field split the beam into two separate parts!

The only possible reason for this observation was that the electron had two different orientations of the magnetic moment. Even after making these observations, Otto Stern and Walter Gerlach, could not conceive the idea of electron spins themselves. It was in **1925**, that **Samuel A. Goudsmit and George E. Uhlenbeck** conceptualized the idea of **electron spins**! They proposed that the electron doesn't just revolve around the nucleus but also spins around itself. This was the birth of the fourth quantum number: **the spin quantum number(s)** :

$$\boxed{S = \pm\frac{1}{2}}$$

5- Heisenberg's uncertainty principle

One of the important consequences of the dual nature of an electron is the uncertainty principle, developed by ***Warner Heisenberg***.

According to uncertainty principle "It is impossible to specify at any given moment both the position and momentum (velocity) of an electron". Mathematically it is represented as,

$$\boxed{\Delta Q\ .\Delta x\ \geq \frac{h}{4\pi}}$$

Where,Δx is uncertainty position of the particle, Δp= mΔv uncertainty in the momentum of the particle.

So equation becomes, $\Delta x\ .m\ \Delta v \geq \frac{h}{4\pi}$ or $\Delta x\ .\ \Delta v \geq \frac{h}{4\pi m}$

The sign≥ means that the product ofΔx andΔp (or of Δx and Δv) can be greater than, or equal to but never smaller than$\frac{h}{4\pi m}$. If Δx is made small,Δp increases and vice versa.

In terms of uncertainty in energy, ΔE, and uncertainty in time Δt, this principle is written as:

$$\Delta E\ .\Delta t \geq \frac{h}{4\pi}$$

Heisenberg's uncertainty principle cannot apply to a stationary electron because its velocity is 0, and its position can be measured accurately.

Exercise

- Calculate the uncertainty (in meters) in the position of a 120 g baseball thrown at a velocity of 45 m/s if the uncertainty in the velocity is 2%.
- The mass m of an electron is 9.11×10^{-31} kg and the velocity v of an electron in a hydrogen atom is 2.2×10^{6} m/s. If we assume that the velocity is known to within 10%, or 0.2×10^{6} m/s. calculate the uncertainty in the electron's position in a hydrogen atom.

VI-Poly electronic atoms in wave mechanics

Bohr made a significant contribution to our understanding of atoms. But his theory did not provide a complete description of electronic behavior in atoms and this approach could not account for the emission spectra of atoms containing more than one electron, such as atoms of helium and lithium.

In **1926**the Austrian physicist **Erwin Schrödinger**, using a complicated mathematical technique, formulated an equation that describes the behavior and energies of submicroscopic particles in general. It is important to know, however, that the equation incorporates both particle behavior, in terms of mass m, and wave behavior, in terms of a ***wave function*** Ψ.

- Ψ depends on the location in space of the system which has no direct physical meaning.
- The **probability of finding** the electron in a certain region in space is proportional to the square of the wave function, $\boldsymbol{\Psi^2}$.
- According to wave theory, the intensity of light is proportional to the Ψ^2.
- The most likely place to find an electron is where the intensity is greatest, that is, where the value of Ψ^2 is greatest.
- A wave function for an electron in an atom is called an **atomic orbital**; this atomic orbital describes a region of space in which there is a high probability of finding the electron.

Orbit and orbital are not synonymous:

- An orbit, as proposed by Bohr, is a circular path around the nucleus in which an electron moves. A precise description of this path of the electron is impossible according to the Heisenberg uncertainty principle. Bohr orbits, therefore, have no real meaning and their existence can never be demonstrated experimentally.
- An atomic orbital, on the other hand, is a quantum mechanical concept and refers to the one-electron wave function ψ in an atom. It is characterized by three quantum numbers (n, l and m) and its value depends upon the coordinates of the electron.

1- Klechkowski rules (Aufbau principle)

The filling of energy levels and sub-levels is produced in accordance with **Vsevolod. M. Klechkowski** rules which are based on the two solutions of the E. Schroedinger equation the principal n and the orbital ℓ quantum numbers.

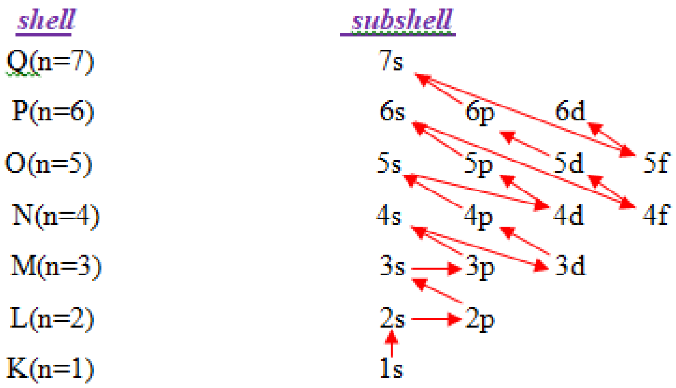
- Each orbital in an atom is specified by a set of three quantum numbers (n, ℓ, m) and each electron is designated by a set of four quantum numbers (n, l, m and s).
- The maximum number of an electron in an orbit is $2n^2$
- The maximum number of electrons in subshell = $2(2\ell+1)$

S -subshell →2 electrons
p -subshell →6 electrons
d -subshell →10 electrons
f -subshell →14 electrons

- The energy of any electron depends on the value of ***n*** and **ℓ** because total energy = **($n + \ell$)**. The electron enters that sub-orbit whose (n + ℓ) value or the value of energy is less.
- For subshells with the same value of (n + ℓ), electrons are assigned first to the subshell with lower n.

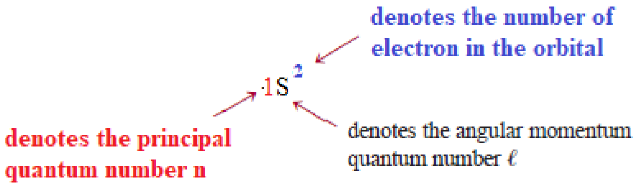
$0 \leq \ell \leq n-1$

n	***ℓ***	**n+*ℓ***	subshell
1	0	1	1S
2	0	2	2S
2	1	3	2P
3	0		3S
3	1	4	3P
4	0		4S
3	2	5	3d
4	1		4P
5	0		5S
4	2	6	4d
5	1		5P
6	0		6S
4	3	7	4f
5	2		5d
6	1		6P
7	0		7S



1- Electron Configuration

The electron configuration of an atom refers to how electrons are distributed among the various atomic orbitals, which is essential for understanding electronic behavior. Recall that the number of electrons in an atom is equal to its atomic number Z.



Two general rules help us to predict electron configurations:

- Electrons are assigned to orbitals in order of increasing value of ($n + \ell$).
- For subshells with the same value of ($n + \ell$), electrons are assigned first to the subshell with lower n.

Exemple: **$_8$O:** $1s^2\ 2s^2\ 2p^4$

Note that we often write the configurations in a **shorthand version** by giving the symbol of the **noble gas** in the previous row to indicate electrons in filled shells, and then specifying only those electrons in unfilled shells.

Exemple :

Na: $\overbrace{1s^2\ 2s^2\ 2p^6}^{\text{Neon configuration}}\ 3s^1$ or [Ne] $3s^1$

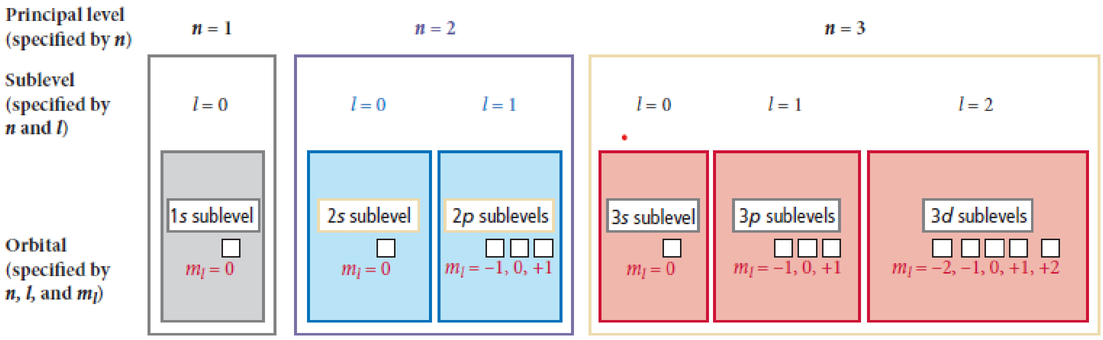
Mg: $1s^2\ 2s^2\ 2p^6\ 3s^2$ or [Ne] $3s^2$

Noble gas, is extremely stable and no reactions of it are known. Noble gases are: **Helium ($_2$He), neon ($_{10}$Ne), argon ($_{18}$Ar), krypton ($_{36}$Kr), xenon ($_{54}$Xe), and radon ($_{86}$Rn).**

2- The Atom Orbitals diagram

The atomic orbital is represented with **a quantum box**. An electron in an orbital is shown by **an arrow**. The arrow points up when *S* = +½ and down when *S* = -½. Each quantum box holds a maximum of twice as many electrons as the number of orbitals in the subshell.

The following diagram illustrates all the orbitals, each represented by a small square, in the first three principal energy levels.



3- The Pauli exclusion principle

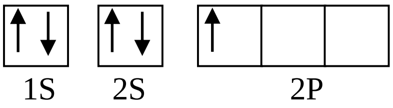
Wolfgang Pauli, Nobel Prize **1945**, states that *no two electrons in the same atom can have identical values for all four of their quantum numbers*. What this means is that no more than **two** electrons can occupy the same orbital, and that two electrons in the same orbital must have **opposite spins**.

If one electron in an atom has the quantum numbers *n* = 1, *l* =0, *m*= 0, and *S*= +1/2, no other electron can have these same quantum numbers.

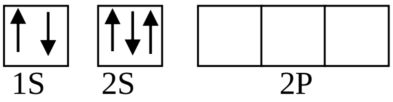
Example

Which of the following orbital diagrams or electron configurations are possible and which are impossible, according to the Pauli exclusion principle? Explain.

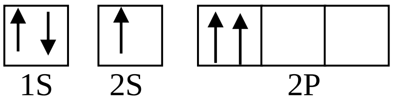
a-



b-



c-

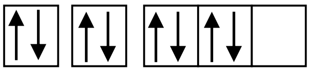


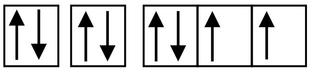
4- Hund's Rule

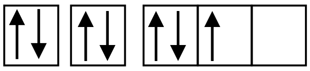
In about 1927, **Friedrich Hund** discovered an empirical rule determining the lowest energy arrangement of electrons in a subshell. Hund's rule states that *the lowest-energy arrangement of electrons in a subshell is obtained by putting electrons into separate orbitals of the subshell with the same spin before pairing electrons*.

Exemple

1- Which of the following arrangements of electrons are possible and which are impossible?

a-


b-


c-


2- What is the electron configuration and orbital diagram for a phosphorus atom? What are the four quantum numbers for the last electron added?

5- Electron Configurations of Ions

We have seen that ions are formed when atoms **gain or lose electrons**.

A cation (positively charged ion) forms when one or more electrons are removed from a parent atom. For main group elements, the electrons that were added last are the first electrons removed.

An anion (negatively charged ion) forms when one or more electrons are added to a parent atom. The added electrons fill in the order predicted by the Aufbau principle.

Example: Predicting Electron Configurations of an Ion

What is the electron configuration and orbital diagram of:

a. Na^+
b. P^{3-}
c. Al^{2+}
d. Fe^{2+}
e. Sm^{3+}

First, write out the electron configuration and formation for each parent atom. Next, determine whether an electron is gained or lost. Remember electrons are negatively charged, so ions with a positive charge have *lost* an electron. For main group elements, the last orbital gains or loses the electron. For transition metals, the last *s* orbital loses an electron before the *d* orbitals.