

Chapter IV :

Atomic Spectrometry and *Bohr* 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 (Figure 2). 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.

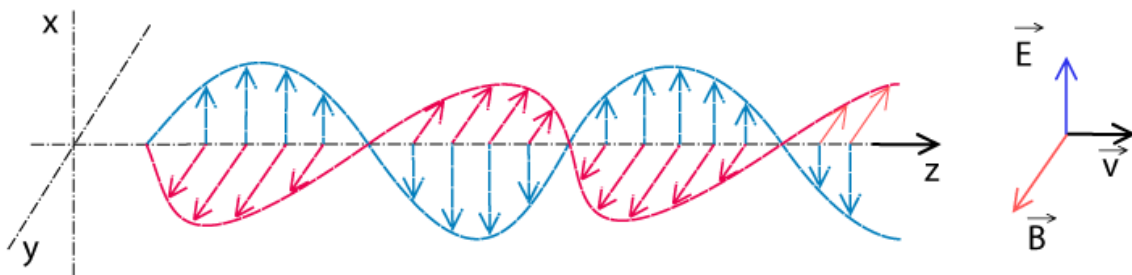
As discussed in our Atomic Theory II module, at the end of 1913 Niels Bohr facilitated the leap to a new paradigm of atomic theory – quantum mechanics. Bohr's new idea that electrons could only be found in specified, quantized orbits was revolutionary (Bohr, 1913). As is consistent with all new scientific 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.

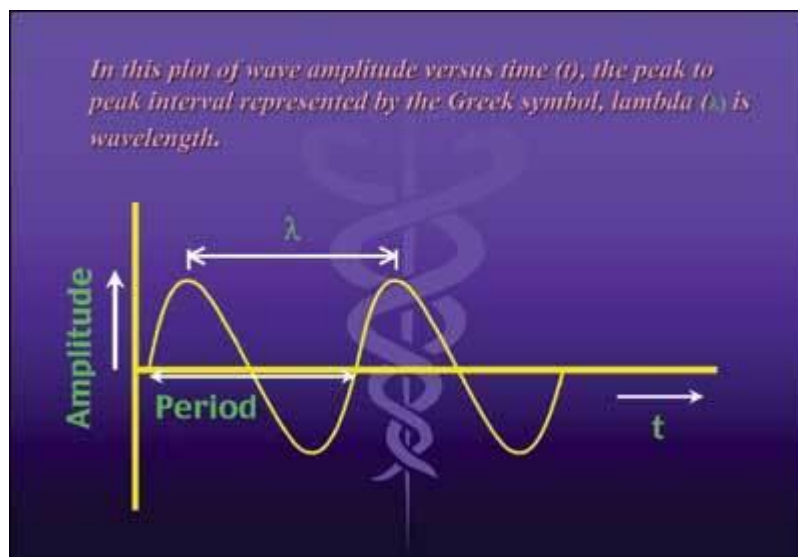
2- wave nature of light :

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

ELECTROMAGNETIC WAVE PROPAGATION



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



This waveform movement is known as:

- **Wavelength (λ):** distance between corresponding points of two consecutive [waves](#). “Corresponding points” refers to two points or particles in the same phase
- **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.
- **Frequency (ν):** The frequency of a wave is the number of waves that pass by each second, and is measured in Hertz (Hz).

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

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

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

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

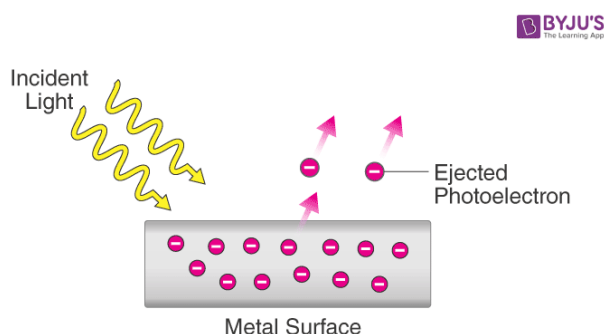
The wave theory of light failed to explain some physical phenomena, such as the distribution of energy emanating from a very hot (reddish) body and the photoelectric effect:

a- 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: $E=h\nu$, h, the constant of Planck, equal to $6,62 \cdot 10^{-34} \text{J}\cdot\text{s}$ and ν the frequency of light (photon).

b- 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.



• 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](#).

$$E = h\nu = hc/\lambda$$

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.

$$\Phi = h\nu_0 = hc/\lambda_0$$

- **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:

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

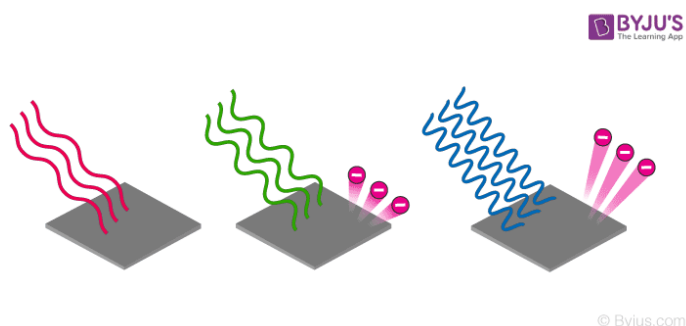
$$\Rightarrow h\nu = h\nu_0 + \frac{1}{2}m_e v^2$$

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.

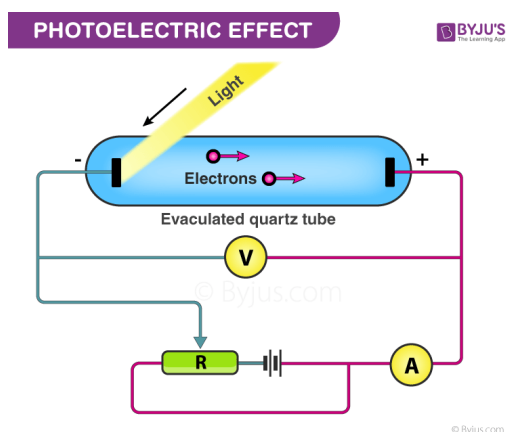


We note through the photo :

- 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**



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. Plate 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.

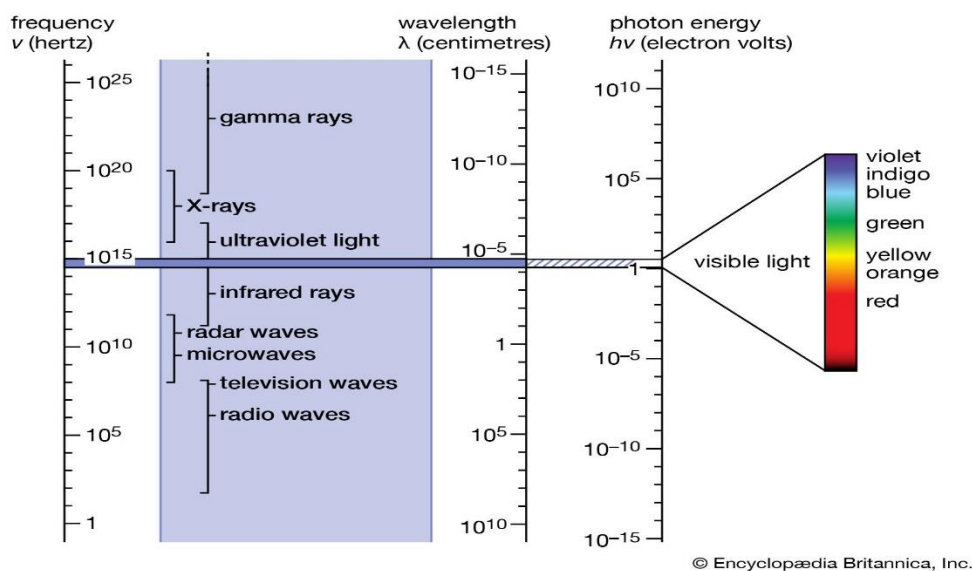
Characteristics of the Photoelectric Effect

- 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:

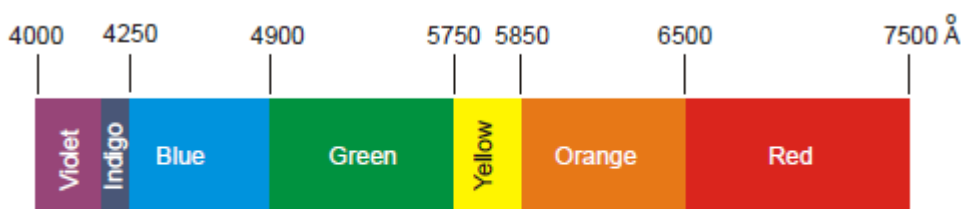
Electromagnetic spectrum, the entire distribution of electromagnetic radiation according to frequency or wavelength. Although all electromagnetic waves travel at the speed of light in a vacuum, they do so at a wide range of frequencies, wavelengths, and photon energies. The electromagnetic spectrum comprises 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.



5. Atomic Spectra

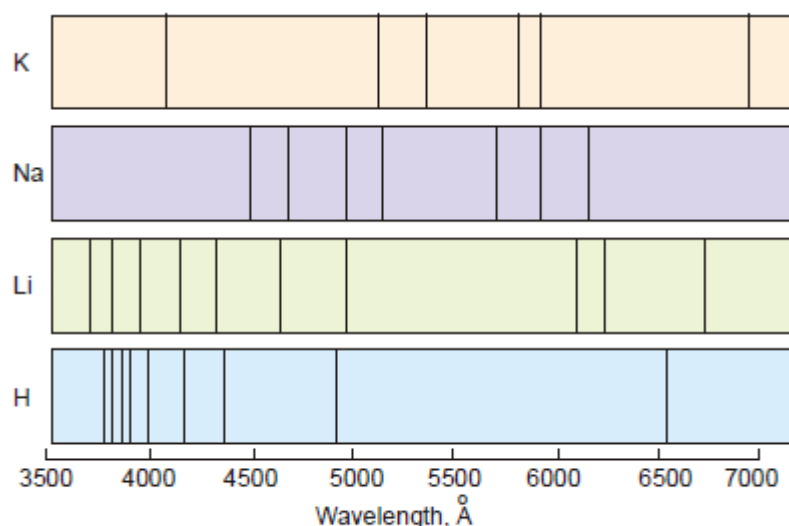
□ When an element in the vapour or the gaseous state is heated in a flame or a discharge tube, the atoms are excited (energised) and emit light radiations of a characteristic colour. The colour of light produced indicates the wavelength of the radiation emitted.



Wavelength range of colour bands in Å 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 photographic plate), 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.



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.

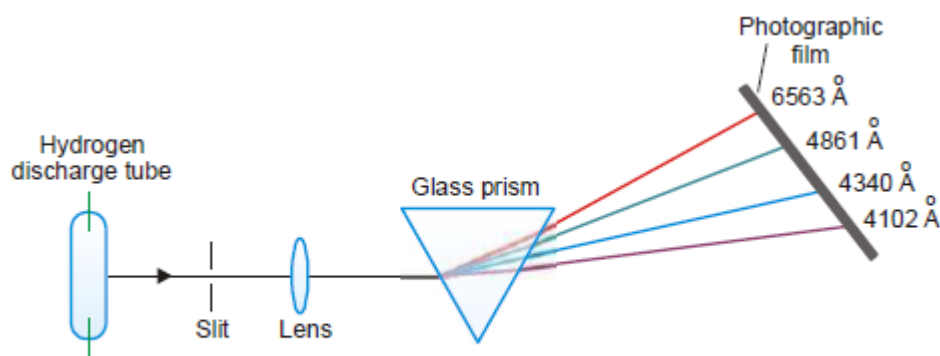
□ Today spectral analysis has become a powerful method for the detection of elements even though present in extremely small amounts.

□ 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.

a. 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.



The 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.

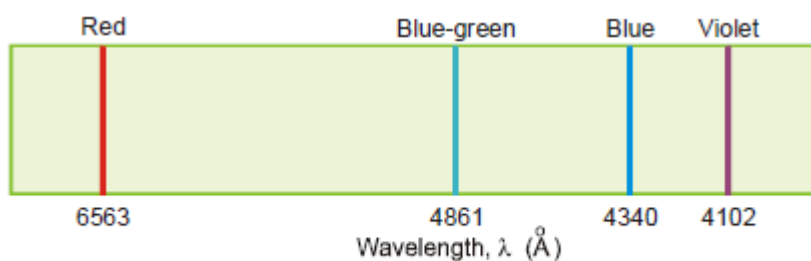
□ The above series of four lines in the visible spectrum of hydrogen was named as the Balmer Series. By carefully studying the wavelengths of the observed lines, Balmer was able empirically to give an equation which related the wavelengths (λ) of the observed lines.

□ 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 $109,677 \text{ cm}^{-1}$.

$n = 3, 4, 5, 6$ 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.



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

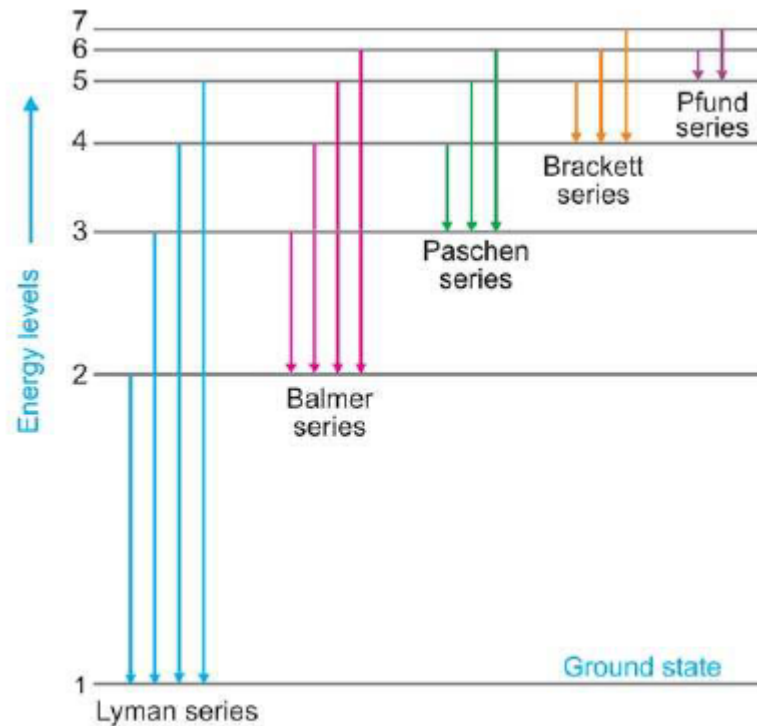
□ Balmer equation had no theoretical basis at all. Nobody had any idea how it worked so accurately in finding the wavelengths of the spectral lines of hydrogen atom. However, in 1913 Bohr put forward his theory which immediately explained the observed hydrogen atom spectrum.

b. 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.

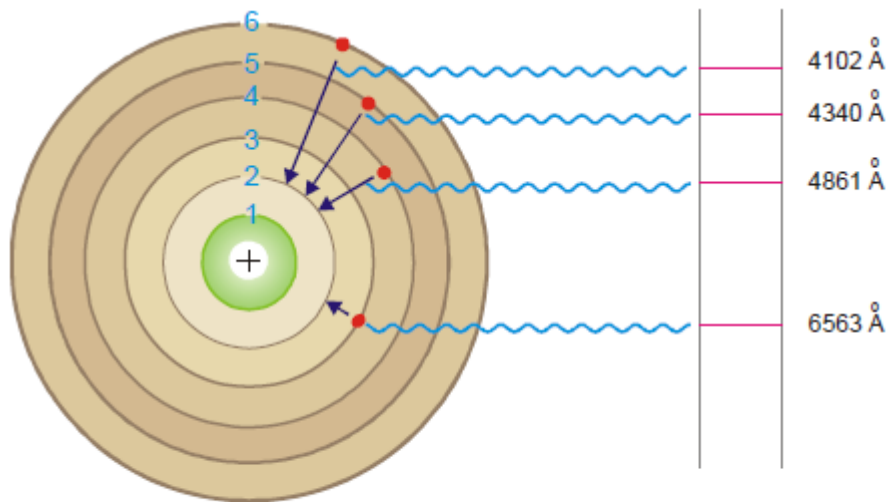
□ Lyman series is obtained when the electron returns to the ground state i.e., $n = 1$ from higher energy levels ($n_2 = 2, 3, 4, 5$, etc.). Similarly, Balmer, Paschen, Brackett and Pfund series are produced when the electron returns to the second, third, fourth and fifth energy levels respectively as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



Hydrogen spectral series on a Bohr atom energy diagram.

Spectral series vary according to n_1 values:

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



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

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

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

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

$$\Delta E = E_{n_2} - E_{n_1} = \frac{2\pi^2 m e^4}{h^2} \left[\frac{1}{n_1^2} - \frac{1}{n_2^2} \right] \quad \text{①}$$

According to Planck's equation:

$$\Delta E = h\nu = \frac{hc}{\lambda} \quad \text{②}$$

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

$$\begin{aligned} \frac{hc}{\lambda} &= \frac{2\pi^2 e^4 m}{h^2} \left[\frac{1}{n_1^2} - \frac{1}{n_2^2} \right] \\ \frac{1}{\lambda} &= \frac{2\pi^2 e^4 m}{h^3 c} \left[\frac{1}{n_1^2} - \frac{1}{n_2^2} \right] \\ &= R \left[\frac{1}{n_1^2} - \frac{1}{n_2^2} \right] \end{aligned} \quad (3)$$

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 $109,679 \text{ cm}^{-1}$ and agrees closely with the value of Rydberg constant in the original empirical Balmer's equation ($109,677 \text{ cm}^{-1}$).

- **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 in number of electrons and varies in number of Z protons such as: ${}^4_2\text{He}^+$, ${}^6_3\text{Li}^{+2}$, ${}^9_4\text{Be}^{3+}$

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:

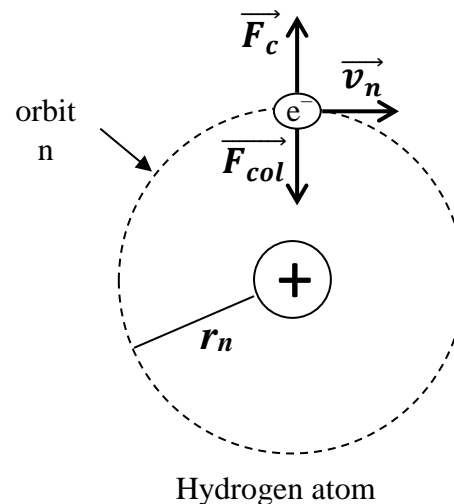
$$h\nu = E_i - E_f$$

(E_i is the energy of the initial state and E_f is the energy of the final state. Also, $E_i > E_f$).

• Determination of the radius of Bor 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 \vec{F}_{col} and the centrifugal force \vec{F}_c as shown in the figure:

$$\begin{aligned}\vec{F}_c &= \vec{F}_{col} \text{ et } F_c = F_{col} \\ \text{où } F_c &= \frac{m v^2}{r} \text{ et } F_{col} = \frac{K Z e^2}{r^2} \\ \Rightarrow \frac{m v^2}{r} &= \frac{K Z e^2}{r^2} \\ \Rightarrow m v^2 &= \frac{K Z e^2}{r} \\ \Rightarrow m^2 v^2 &= \frac{K Z e^2 m}{r} \dots \dots (1)\end{aligned}$$



By Postulate II for bohr :

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

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

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

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

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

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

Compensation in the equation (3):

$$\Rightarrow r_n = \frac{n^2}{Z} (r_1) \text{ o\`u } r_1 = 0,53 \text{ \AA}$$

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

- For hydrogen $Z = 1$, 1_1H :

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

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

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

For helium $Z = 2$, ${}^4_2He^+$:

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

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

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

- **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:

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

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

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

Compensation in the equation (4):

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

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 $Z \neq 1$.

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

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

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

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

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

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

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

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

- **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

$$E_T = E_p + E_c$$

$$E_c = \frac{1}{2} m v^2 \quad \text{و} \quad E_p = - \frac{K Z e^2}{r}$$

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:

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

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

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

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

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

Compensation in the equation (6):

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

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

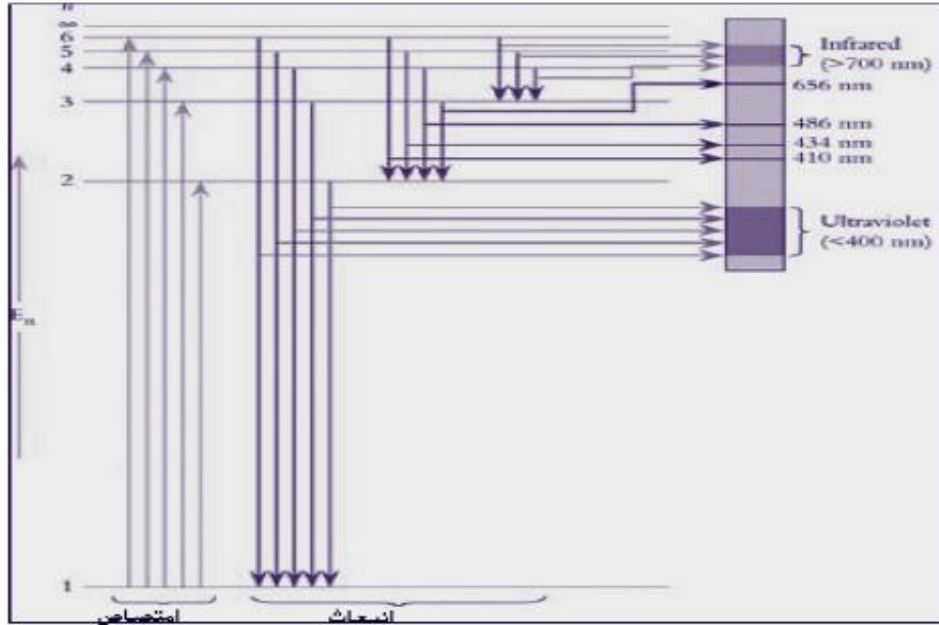
$$n = 1 \Rightarrow E_1 = \frac{1^2}{1^2} (-13,6) = -13,6 \text{ ev}$$

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

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

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

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



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 “ m_e ” is electron mass, “ e ” is the charge of the electron, h -bar, “ 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:

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

Where,

R_H is the Rydberg constant ($1,09737 \cdot 10^7 \text{ m}^{-1}$)

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 :

$$\Delta E = h\nu = h\frac{c}{\lambda} = hc\bar{\nu} \Rightarrow \Delta E = hCZ^2R_H\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

7- 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:

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

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

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

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

- **Final line :**

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

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

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

$$\lambda_{\min} = \frac{n_1^2}{Z^2R_H}$$

8- 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 :

$$E_i = E_\infty - E_1$$

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

Ionization energy is always positive

9. 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.

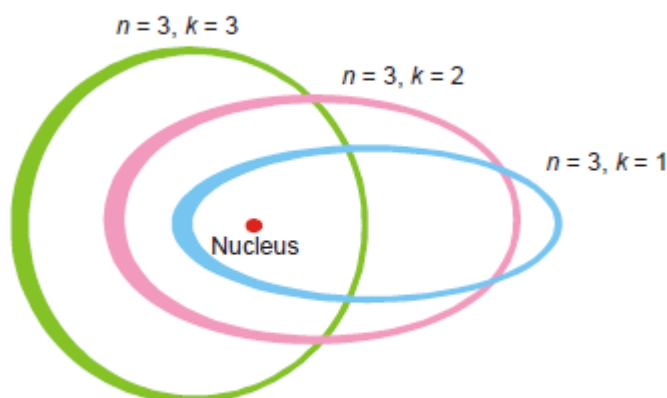
☐ Sommerfeld modified Bohr's theory as follows. Bohr considered electron orbits as circular but Sommerfeld postulated the presence of elliptic orbits also.

☐ 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 $(h/2\pi)$ 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:

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



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.

10. 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

- **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. $n=1,2,3,4\dots$

- **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 ($n-1$):

$$l=0,1,2,3,4\dots,(n-1)$$

- **The Magnetic Quantum Number (m_l)**

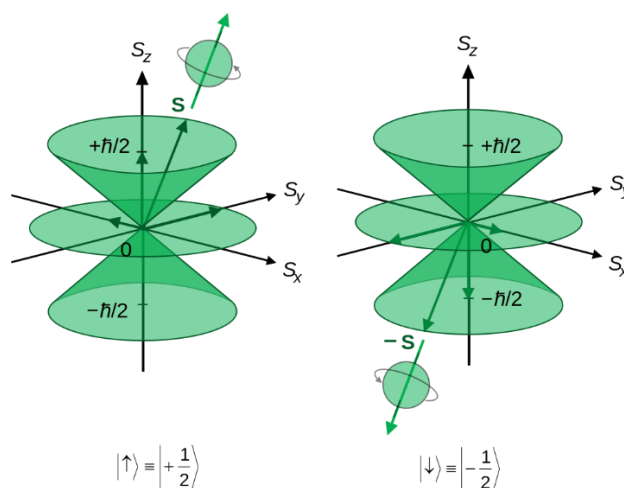
The magnetic quantum number m_l determines the number of orbitals and their orientation within a subshell. Consequently, its value depends on the orbital angular momentum quantum number l . Given a certain l , m_l is an interval ranging from $-l$ to $+l$, so it can be zero, a negative integer, or a positive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

$$m_l = -l, (-l+1), (-l+2), \dots, -2, -1, 0, 1, 2, \dots, (l-1), (l-2), +l$$

- **The Electron Spin Quantum Number (m_s)**

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 \uparrow , or $-1/2$, represented by \downarrow . 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.](#))

$$m_s = \pm 1/2$$



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

1- introduction

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.

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)

The 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.

$$E=hv, \quad v = \frac{c}{\lambda}$$

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.

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

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:

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

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 \AA . Determine the uncertainty in the speed of protons using Heisenberg's uncertainty principle.

Solution:

Mathematically, the Heisenberg uncertainty principle is:

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

According to the question,

$$\Delta x = 0.05 \text{ \AA}$$

Applying Heisenberg's Uncertainty principle,

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

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

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

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

$$\Delta v = 2,31 \cdot 10^7 \text{ m/s}$$

The uncertainty in the speed of protons using Heisenberg's uncertainty principle is $2,31 \cdot 10^7 \text{ m/s}$

Conclusion

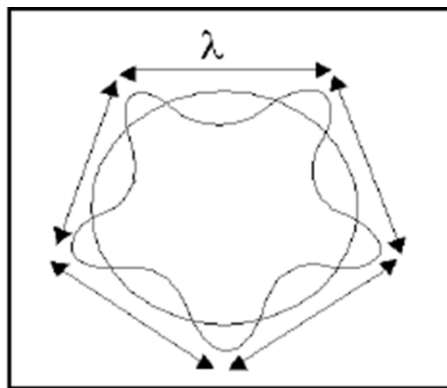
Heisenberg's uncertainty principle states that it is impossible to determine the position and momentum of any particle at the same time with absolute accuracy. The principle was stated by the German physicist and philosopher, Werner Heisenberg in 1927, and is of great significance in quantum physics. The principle is based on the wave-particle duality i.e., 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 (Schrödinger, 1926). 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 (Equation 1). 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.



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

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

By offsetting De Broglie's wavelength phrase we get:

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

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

a- 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.

b- 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:

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

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

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

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

Compensation in the equation(1) :

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

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:

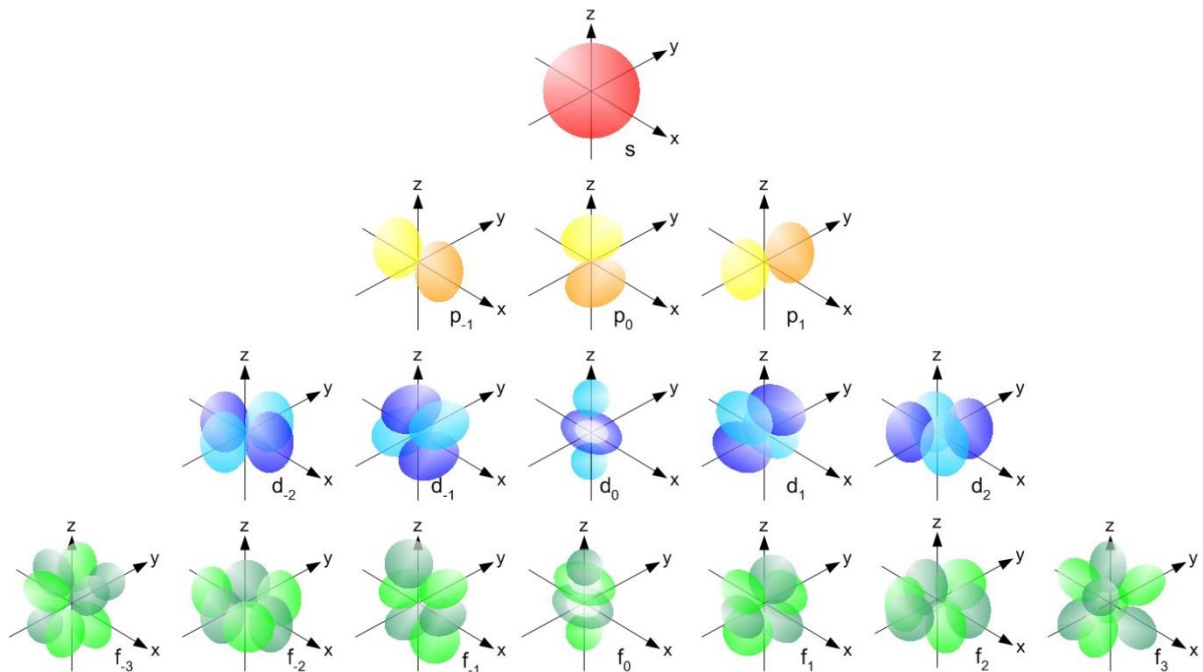
$$dP = \psi^2 dV$$

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, but there are three additional considerations, detailed below, that must also be understood. Without these, we would have an incomplete picture of our non-relativistic understanding of electrons in atoms.

- **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).



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*).