Chapter 3: Electronic Structure of the Atom

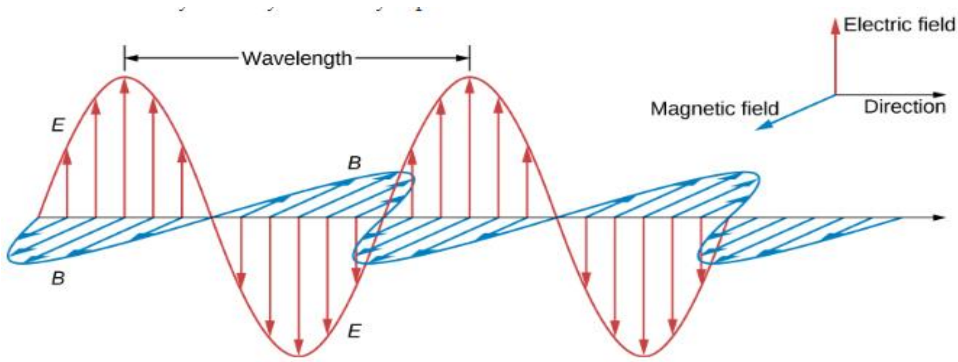
After the discovery of the three constituent particles of the atom, scientists continued their efforts to understand the structure of the atom and the distribution of electrons within it, especially after Rutherford's model failed to explain it.

1- Wave-particle properties of light

Throughout the ages, scientists have held differing views on the nature of light. Some believed that light consisted of tiny particles moving at incredible speeds (Newton, Einstein, Planck, etc.), while others saw light as waves (Maxwell, Young, Hertz, etc.). However, it was the scientist De Broglie who demonstrated that light exhibits a dual nature, which became known as wave-particle duality.

1-1- The Wave Nature of Light

Light is an electromagnetic wave, an oscillation or wave of electromagnetic energy that propagates through space at a speed of 3.10^8 m/s. Electromagnetic waves are generated by heating atoms, causing the electrons to vibrate. This vibrating motion of electrons creates a changing electric field, which in turn generates a magnetic field in the adjacent region. This magnetic field, in turn, generates an electric field in the neighboring region, and so the disturbance propagates from one point to another through the alternating changes in the electric and magnetic fields.



The propagation of the electromagnetic wave.

Each wave is characterized by its wavelength λ (lambda) (which is the distance between two consecutive peaks or troughs) and frequency $\nu(nu)$ (which is the number of waves passing through a point per second).

$$\begin{cases} \nu = \dfrac{c}{\lambda} \\ \dfrac{1}{\lambda} = \dfrac{\nu}{c} = \bar{\nu} \end{cases}$$

c: Speed of light

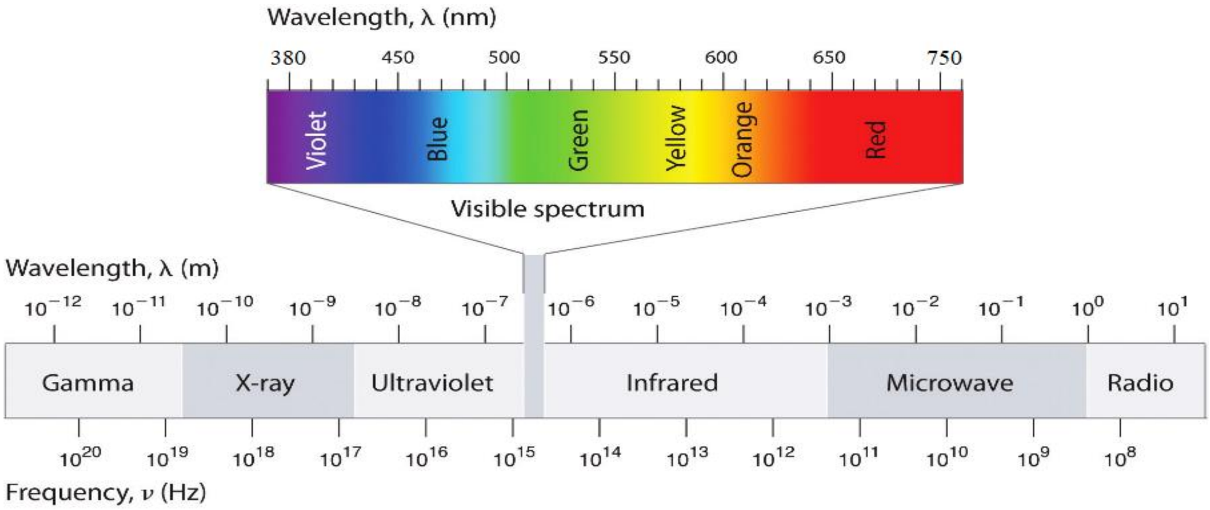
ν: Frequency (in $S^{-1} \equiv Hz$)

$\bar{\nu}$: Wavenumber

Initially, Maxwell's theory of electromagnetic waves was validated through experimental observations, including phenomena such as refraction, reflection, interference. However, many unresolved issues remained for physicists because Maxwell's idea of light as purely electromagnetic waves couldn't explain several other important phenomena.

Electromagnetic spectrum

Electromagnetic waves encompass a wide range of wavelengths and frequencies. They are collectively referred to as the electromagnetic spectrum, with the visible spectrum representing a small portion of this spectrum.



Spectral regions	Wavelength (nm)
Ultraviolet radiation	10-380
Visible light	380-780
Infrared radiation	780-300000

1-2- The particle nature of light

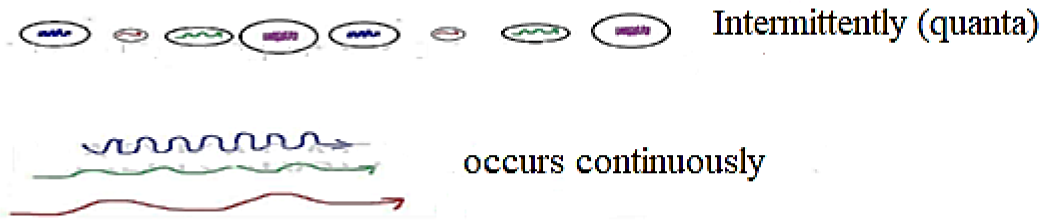
Classical physics failed to explain issues related to atomic and molecular phenomena, among the most important of which are:

1- Blackbody Radiation:

A blackbody is a body that absorbs all incident radiation of varying wavelengths (a perfect absorber) and then re-emits it perfectly. Scientists observed that the emission of radiation from hot bodies varies with the temperature of the body. Even though hot bodies are considered to be blackbodies, emitting radiation across all wavelengths, it was found that they do not emit all wavelengths with the same intensity. The wavelength associated with the maximum intensity is the dominant color of the light emitted from the body.

The wave theory of light was unable to explain the decrease in intensity of blackbody radiation and its approach to zero with a decrease in wavelength and an increase in frequency. This is because it considered light as electromagnetic waves emitted by objects in the form of a continuous stream of energy. If the wavelength of radiation decreases, the frequency increases, leading to an increase in energy and radiation intensity. This contradicts the results of practical experiments.

In the year 1900, Max Planck proposed a solution to explain this phenomenon. He assumed that electromagnetic waves are not emitted continuously but rather in discrete quantities called "quanta," which later became known as photons. The quantum is considered the smallest specific amount of energy that can be exchanged between objects at a certain frequency, and the energy of the quantum is related to the frequency of radiation.



The accompanying equation is:

$$E = h\nu$$

Where E represents the energy of emitted quanta, ν denotes the frequency of radiation, and the constant h is known as Planck's constant, where $h = 6.62 \times 10^{-34}$ J.s.

The total energy of radiation (for a given number n of photons are whole number) is:

$$E_n = nh\nu$$

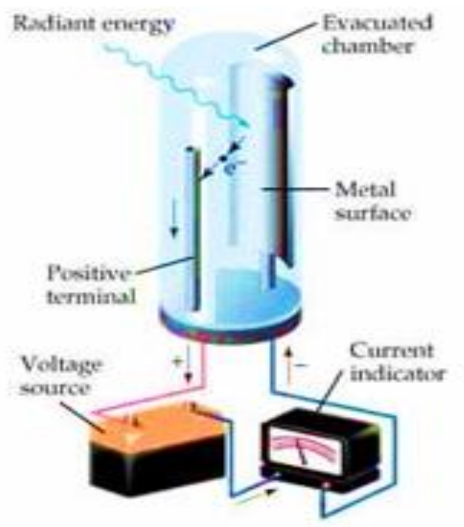
(The energy is quantized, just like charge.)

2- Photoelectric effect

The photoelectric effect was discovered by scientist Hertz in 1887. It is a phenomenon where electrons are emitted from the surfaces of metals when light with a certain wavelength falls on them.

A photoelectric cell consists of a metal plate inside a vacuum glass tube. The metal plate is called the emitter, and the wire is called the collector, with a positive charge connected to an electrical circuit containing a generator. When the tube is completely shielded from light, no current flows in the circuit.

When a beam of light falls on the emitter, electrons are released from its surface and move toward the collector connected to the positive pole of the generator. The collector accumulates the electrons and returns them to the emitter after passing them through the circuit. The emitted electrons are called photoelectrons, and the current generated is known as the photoelectric current.



photoelectric cell

The wave theory failed to explain the phenomenon of the photoelectric effect because it perceived that the emission of photoelectrons depended on the intensity of incident light and not on its frequency. It anticipated:

1. Electrons continuously absorbing energy from electromagnetic waves. An increase in the intensity of incident light was expected to result in a higher rate of electron energy absorption, thus giving them

greater kinetic energy. There was assumed to be no relationship between the frequency of the incident light and the kinetic energy of the liberated electrons. However, experiments revealed that the kinetic energy of electrons depends on the frequency of the incident light and is not influenced by its intensity.

2. Electrons require some time to absorb sufficient energy to be liberated from the metal, especially when exposed to dim light (low intensity). This is because energy absorption was thought to occur continuously until enough energy was acquired for liberation. Contrarily, experiments demonstrated that electrons are emitted immediately upon the arrival of light on the metal.

3. When high-intensity light falls on a metal, it was expected to release electrons regardless of the frequency of the incident light. Nevertheless, experiments showed that electrons are only liberated from the metal when the frequency of the incident light exceeds a certain threshold value known as the threshold frequency, regardless of how intense the light is.

Einstein was able, in 1905, to explain the photoelectric effect by relying on Planck's energy quantization principle (which earned him the Nobel Prize in Physics). Einstein's postulates for explaining the photoelectric effect are as follows:

1. Einstein considered that a beam of light consists of bundles or quanta of energy called photons, each carrying a specific amount of energy, denoted by ($E = hv$). Increasing the intensity of light increases the number of photons, and each photon collides with one electron, giving it all of its energy.

2. For each metal, there is a minimum energy required to release an electron from its surface, known as the threshold energy, E_0, where:

$$E_0 = h.\, v_0$$

3. If the energy of the incident photon is less than the threshold energy ($E < E_0$), no electrons are emitted from the surface, regardless of the intensity of the incident light or the duration of exposure.

4. If the energy of the incident photon equals the threshold energy ($E = E_0$), then this photon can barely liberate an electron from the metal surface. In this case, the frequency of the photon is referred to as the critical frequency or the threshold frequency (v_0).

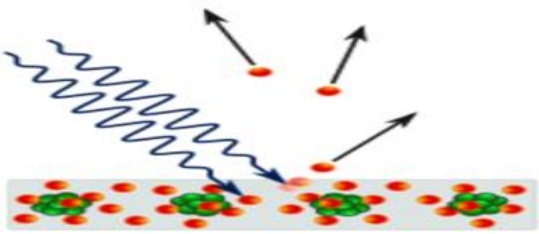
If the energy of the incident photon is greater than the threshold energy, the energy difference appears in the form of kinetic energy (Ec) gained by the emitted electron ($\mathbf{E_c = ½\, mv^2}$). Consequently, the electron moves with a higher velocity, and this kinetic energy increases with an increase in frequency, where:

$$\mathbf{Ec + E = E_0}$$

$$\mathbf{hv = hv_0 + ½\, mv^2}$$

$$\mathbf{h(v - v_0) = ½\, mv^2}$$

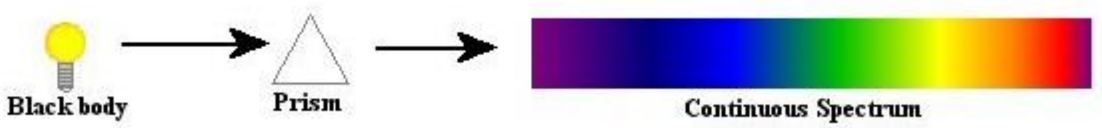
The liberated electrons vary in their kinetic energy depending on their location. Electrons near the surface that do not collide with metal atoms before liberation have a greater amount of kinetic energy.



3- Atomic Spectra

3-1- Continuous Spectrum (Emission Spectrum)

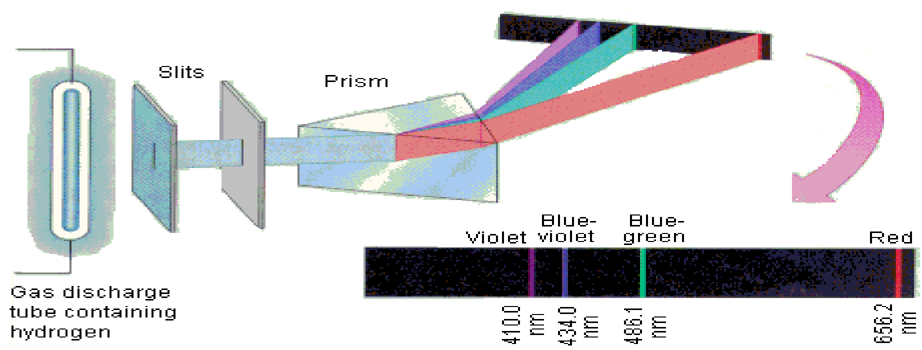
It is obtained from the analysis of light from a regular electric lamp or sunlight, and there are no distinct boundaries between its colors. It encompasses all the wavelengths within the visible range (400-700 nm). It is emitted by incandescent solid bodies to the point of white heat or by hot, high-density liquids, or gases under very high pressure. Examples include the spectrum produced by the filament of an electric lamp and also from a piece of iron when heated to white incandescence.



3-2- Discrete Atomic Spectrum

The Line Emission Spectrum

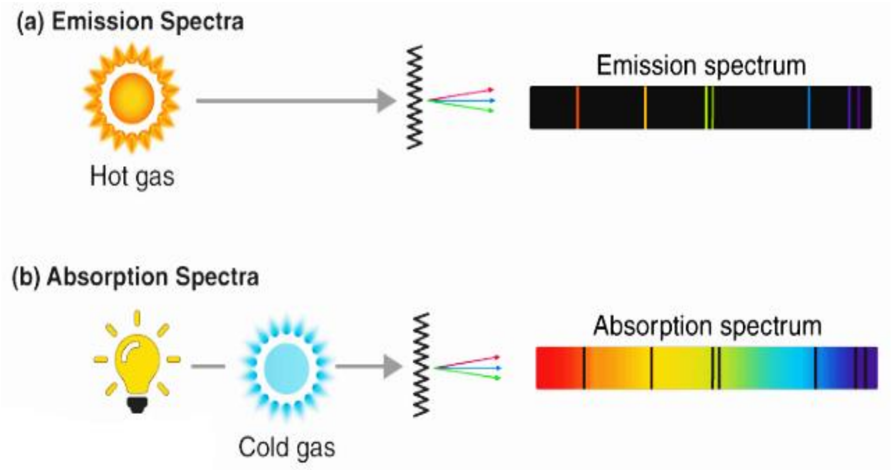
When analyzing the light emitted by excited atoms of an element in the gaseous state through a spectroscope and receiving the resulting rays on a screen, it produces what is known as the discrete atomic spectrum or the line emission spectrum. This spectrum consists of distinct, spaced-out colored lines, each with specific wavelengths, separated by dark regions. However, some spectral lines appear in the non-visible region of the electromagnetic spectrum, which is why the collection of lines that appear in the visible and non-visible regions is referred to as the atomic spectrum.



If we replace the hydrogen lamp with another lamp, such as a neon or sodium lamp, the spectrum changes, and different colored lines appear at different positions. This means that each element has its own unique spectrum that distinguishes it from others.

Absorption Spectrum

The absorption spectrum is produced when white light is passed through the vapor of one of the elements, resulting in distinct, spaced-out dark lines appearing in the same positions where the colored lines appear in the emission spectrum.



In the study of hydrogen by scientists, it was observed that four colored lines appeared in the visible light region. It was possible to measure the wavelengths of these lines, and the scientist Balmer noticed a mathematical relationship among these numbers. In 1885, he formulated an empirical mathematical relationship that gives the wavelengths of the visible spectrum lines of hydrogen.

$$\bar{\nu} = \frac{1}{\lambda} = R_H(\frac{1}{2^2} - \frac{1}{n^2})$$

n= (3,4,5,6…………….)

Then, the physicist Rydberg in 1890 arrived at the general relationship for all series:

$$\bar{\nu} = \frac{1}{\lambda} = R_H(\frac{1}{n_1^2} - \frac{1}{n_2^2})/ \quad n_2 > n_1$$

$$\nu = \frac{c}{\lambda} = c.R_H(\frac{1}{n_1^2} - \frac{1}{n_2^2})/$$

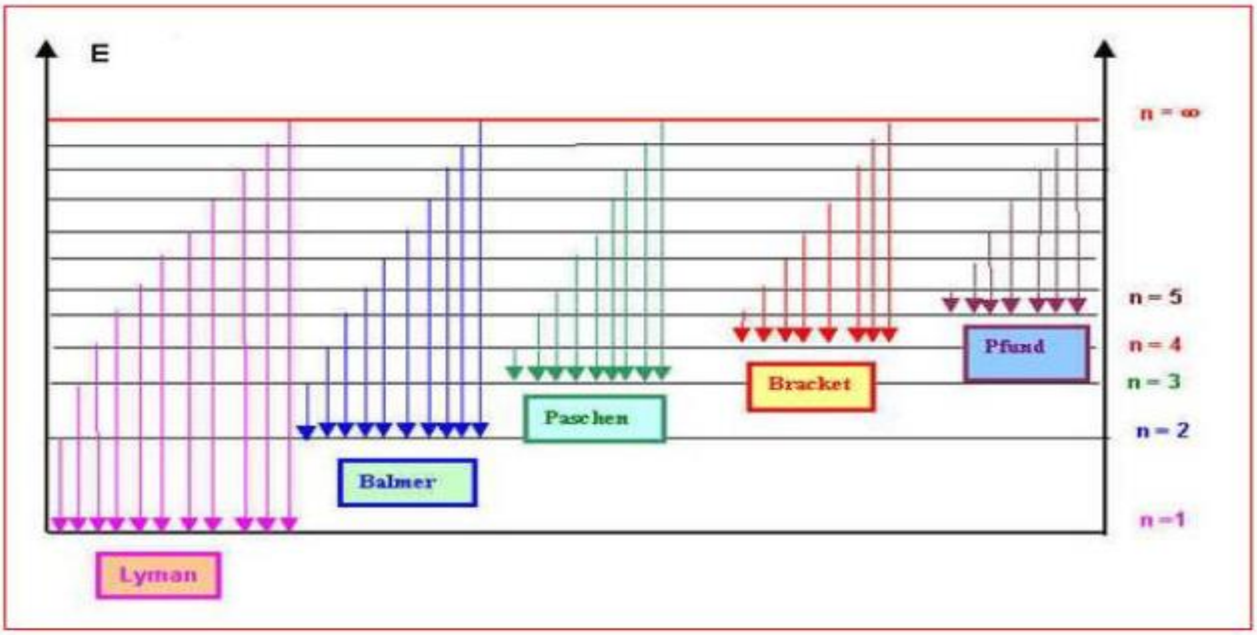
R_H: Rydberg constant for hydrogen R_H=109677.7cm^{-1}

The discovery of other spectral line series for the hydrogen atom continued, and all of them obeyed the same previously mentioned relationship.

n_2	n_1	spectral region	series	the year
2,3,4,…………..∞	1	ultraviolet radiation	Lyman	1916
3,4,5,…………… ∞	2	visible light	Balmer	1885
4,5,6,…………… ∞	3	infrared radiation	Paschen	1908
5,6,7………… ∞	4	infrared radiation	Brackett	1922
6,7………… ∞	5	infrared radiation	Pfund	1924

7,8…………… ∞	6	infrared radiation	Humphreys	1953
8,9…………… ∞	7	infrared radiation	Hansen- strong	1973

We can summarize the various transitions of the hydrogen atom electron in the following diagram:



The energy diagram for the different spectral series of hydrogen

1-3- Wave-Particle Duality (Louis de Broglie)

The wave model of light successfully explained the phenomena of interference, reflection, and diffraction, while the particle model successfully explained the phenomena of the photoelectric effect and blackbody radiation. This led to a contradiction and ambiguity in the nature of light it is a wave or a particle. This ambiguity persisted until 1924 when the scientist Louis de Broglie introduced his idea about the dual nature of matter. In this idea, he clarified that light has a dual nature: it behaves like a wave under certain conditions (in agreement with Huygens' theory), and like a particle or photon under other conditions (in agreement with Newton's theory).

By applying quantum theory to the case of photons:

$$\begin{cases} E = h.\nu \quad According\ to\ Planck. \\ E = m.c^2 \quad According\ to\ Einstein. \end{cases}$$

$$\Rightarrow h.\frac{c}{\lambda} = m.c^2$$

$$\Rightarrow \lambda = \frac{h}{m.c}$$

From this equation, we can observe that the wavelength, which is a property of waves, can be expressed in terms of momentum, which is a property of particles. This implies that photons or radiation exhibit a dual wave-particle behavior: they possess wavelengths and exhibit wave-like properties such as interference and diffraction, while also behaving as particles with momentum, as seen in phenomena like the photoelectric effect. The specific behavior depends on the type of interaction.

De Broglie proposed to generalize this relationship to include material particles. In other words, there exist waves that accompany the motion of material particles, known as de Broglie waves:

$$\lambda = \frac{h}{m.\vartheta}$$

λ: represents the wavelength associated with the material particle (m).

m: is the mass of the particle (kg).

h: is Planck's constant (J·s).

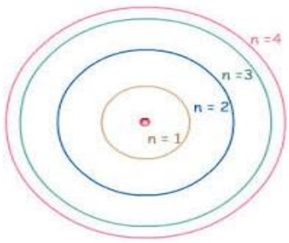
ϑ : represents the velocity of the particle (m/s).

2- Bohr's Model of the Hydrogen Atom

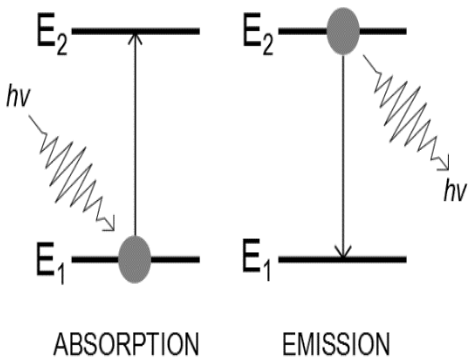
Despite the accuracy of the Rydberg formula in describing experimental results, the origin of this constant and the significance of these integer numbers were not understood until 1913 when Niels Bohr introduced a theoretical explanation for atomic spectra. His theory was a combination of Planck's and Einstein's ideas (where each photon gives all its energy to one electron) and Rutherford's atomic model. Bohr studied the spectrum of the hydrogen atom, as it is the simplest atom with the simplest spectrum.

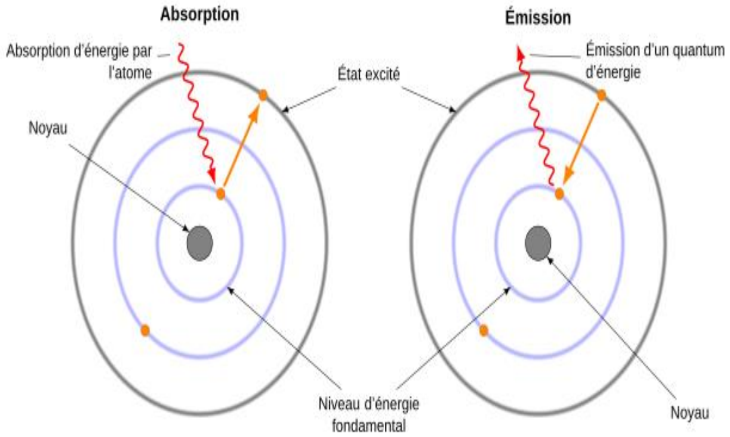
Bohr's model can be summarized by the following assumptions:

1. Electrons orbit the nucleus in fixed circular orbits, similar to Rutherford's model, without losing energy. These orbits are known as Bohr's energy levels or energy shells. Each energy level is represented by an integer "n" which takes on positive integer values: n = 1, 2, 3,... ∞.



2. The electron neither emits nor absorbs energy as long as it orbits in the same energy level around the nucleus.
3. When an electron transitions from one allowed energy state E_2 to another allowed energy state E_1, where E_1 is less than E_2, the energy difference is converted into electromagnetic radiation with a frequency ν.





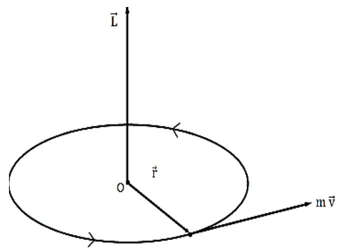
When an electron transitions from a lower energy level to a higher energy level, it absorbs energy. The energy of the photon emitted or absorbed during this transition can be calculated using the following equation:

$$E_{\text{photon}} = |\Delta E| = |E_f - E_i| = h\nu$$

$$\Delta E > 0 \;\; emission$$

$$\Delta E < 0 \; absorption$$

4-The electron's angular momentum, L, during this transition is quantized as:



$L_n = P.r_n = m.\,\vartheta_n.r_n = n\,h\,/\,2\pi$

Where:

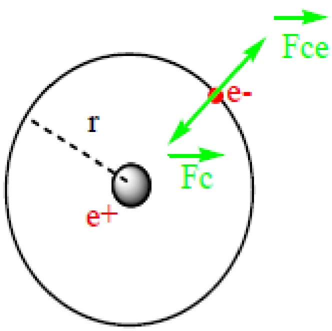
L_n is the angular momentum of the electron and ϑ_n is the speed of the electron in this orbit.

Calculating the radius of Bohr's orbits

For an electron to remain in orbit around the nucleus without falling onto it, the sum of the forces acting on it must be zero. The forces affecting the electron in its orbit include:

Coulombic Attraction $\vec{F}_1$:

$$|\vec{F}_1| = K\frac{|qq'|}{r^2}$$



$$k = \frac{1}{4\pi\varepsilon_0} = \begin{cases} 9\times10^9 \text{ (MKSA)} \\ 1 \quad \text{(CGS)} \end{cases}$$

$$F_1 = K\frac{e^2}{r^2}$$

$$F_c = \frac{m_e . \vartheta^2}{r}$$

$$F_1 = F_c \Rightarrow K\frac{e^2}{r^2} = \frac{m_e . \vartheta^2}{r}$$

$$r = \frac{K . e^2}{m_e \vartheta^2} \dots \dots \dots \dots (1)$$

Susceptibility of Vacuum" is referred to as ε_0.

From Bohr's Hypothesis number 4:

$$m_e \vartheta \quad r = n\,h / 2\pi \quad \Rightarrow \vartheta = \frac{nh}{2\pi m_e r}$$

$$\Rightarrow r = \frac{K . e^2 . 4\pi^2 . m_e^2 . r^2}{m_e . n^2 . h^2}$$

$$\Rightarrow r = \frac{n^2 . h^2}{4 . \pi^2 K . m_e . e^2} \dots \dots (2)$$

From this relationship, we can calculate the radius of each orbit in Bohr's orbits. When n=1, we find :

$$r_1 = \frac{h^2}{4 . \pi^2 K . m_e . e^2} = \frac{(6.626 \times 10^{-34})^2}{4 . \pi^2 . 9 . 10^9 . 9.1 \times 10^{-31} (1.6 \times 10^{-19})^2}$$

$$r_1 = a_0 = 0.529 . 10^{-10} m = 0.53 Å$$

$$r_n = a_0 . n^2 = 0.53 . n^2 Å$$

Calculating the kinetic energy of the electron

$$F_1 = F_c$$

$$K\frac{e^2}{r^2} = \frac{m_e . \vartheta^2}{r} \Rightarrow m_e . \vartheta^2 = K\frac{e^2}{r}$$

$$E_c = \frac{1}{2} m_e . \vartheta^2 \Rightarrow E_c = \frac{1}{2}\frac{K . e^2}{r}$$

Calculating the potential energy of the electron

$$\int_0^{E_p} E_p = \int_\infty^r F_c . dr = \int_\infty^r \frac{Ke^2}{r^2} dr \quad \Rightarrow \quad E_p = -\frac{ke^2}{r}$$

Calculating the total energy of the electron

$$E_t = -\frac{1}{2}\frac{K.e^2}{r} = -\frac{K.4.\pi^2 K.m_e.e^2}{2.n^2.h^2}$$

$$E_t = -\frac{2.\pi^2 K^2.m_e.e^4}{n^2.h^2}$$

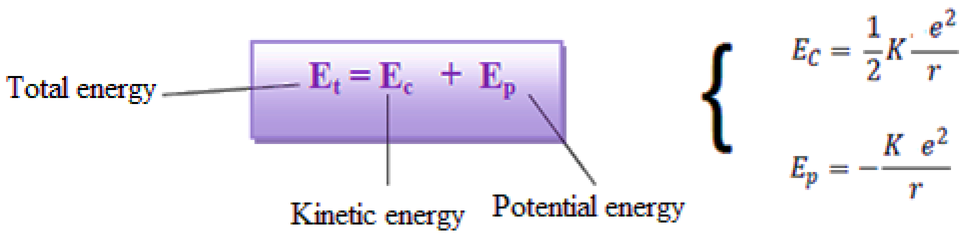
From this, we conclude that the energy is quantized. When n=1, we find:

Ground state (n=1): E_1= -13.6 eV

Excited state (n=2): $E_2 = -\frac{13.6}{2^2}$ eV

Excited state (n=3): $E_3 = -\frac{13.6}{3^2}$eV

n=∞ $\Longrightarrow E_\infty = 0\ ev$



Therefore, $E_n = -\frac{A}{n^2} = \frac{E_H}{n^2}$

Calculating the electron's velocity:

From hypothesis 4:

$$m_e \vartheta \quad r = n\ h / 2\pi$$

$$\Rightarrow \vartheta = \frac{nh}{2\pi m_e r} = \frac{n.h.4\pi^2.K.m_e.e^2}{2\pi.m_e n^2.h^2} = \frac{2\pi.K.e^2}{n.h}$$

When n=1, we find :

$$\vartheta_1 = \frac{2\pi.K.e^2}{n.h} = \frac{2\pi.9.10^9.(1.6\times 10^{-19})^2}{6.626\times 10^{-34}} = 2.18\times 10^6 m/s$$

Therefore, $\vartheta_n = \frac{\vartheta_1}{n}$

The relationship between the wavelength and energy levels

When an electron transitions from energy level n_1 to energy level n_2, where $n_2 > n_1$, it absorbs energy as follows:

$$E_{photon} = |\Delta E| = E_{n_2} - E_{n_1} = h\nu$$

$$\Rightarrow \nu = \frac{1}{h}(E_{n_2} - E_{n_1}) = \frac{1}{h}(-\frac{2.\pi^2K^2.m_e.e^4}{n_2^2.h^2} + \frac{2.\pi^2K^2.m_e.e^4}{n_1^2.h^2})$$

$$\nu = \frac{2.\pi^2K^2.m_e.e^4}{h^3}(\frac{1}{n_1^2} - \frac{1}{n_2^2})$$

$$\begin{cases} \nu = \frac{c}{\lambda} \\ \frac{1}{\lambda} = \bar{\nu} \end{cases}$$

$$\bar{\nu} = \frac{\nu}{c} = \frac{2.\pi^2K^2.m_e.e^4}{c.h^3}(\frac{1}{n_1^2} - \frac{1}{n_2^2})$$

By comparing this relationship with the Balmer's formula:

$$\bar{\nu} = R_H(\frac{1}{2^2} - \frac{1}{n^2})$$

$$R_H = \frac{2.\pi^2K^2.m_e.e^4}{c.h^3} = \frac{2.\pi^2(9.10^9)^2.9.1 \times 10^{-31}(1.6 \times 10^{-19})^4}{3.10^8.(6.626 \times 10^{-34})^3}$$

$$R_H = 1.09557 \times 10^7\ m^{-1}$$

This value shows a significant agreement with the experimental value:

$$R'_H = 109677.7\ cm^{-1} = 1.096777 \times 10^7\ m^{-1}$$

The ionization energy of the hydrogen atom

Is the energy required to lift the electron from the ground state to infinity, i.e., to transform an electrically neutral atom into a charged one after electron loss.

$$E_i = \Delta E = E_\infty - E_1 = E_3 = E_3 = -\frac{13.6}{\infty^2} + \frac{13.6}{1} = 13.6\ ev$$

3- Applying Bohr's theory to hydrogen-like ions

Which are ions that have lost all electrons except for one in the outermost orbit but have atomic numbers greater than one (e.g., Be^{3+}, Li^{2+}, He^{+}). Bohr's postulates remain valid for hydrogen-like ions with only change only:

$$F_1 = K\frac{Z.e^2}{r^2}, \quad E_p = -\frac{K.Z.e^2}{r}$$

The total energy of hydrogen-like ions is given by: $E_n = -\frac{Z^2A}{n^2} = \frac{Z^2E_H}{n^2}$

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

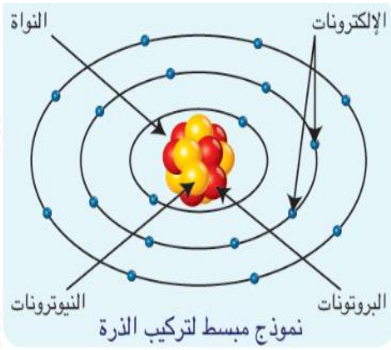
$$\bar{\nu} = Z^2.R_H(\frac{1}{n_1^2} - \frac{1}{n_2^2})$$

$$\vartheta_n = \vartheta_1.\frac{Z}{n}$$

4-Limitations of the Bohr Model

Despite the successes achieved by the Bohr model in explaining the spectra of hydrogen and similar ions, it failed to explain the spectra of more complex, multi-electron atoms, which were considerably more intricate. The model also treated electrons as purely material bodies, whereas it is now understood that electrons exhibit wave-like properties. Additionally, it assumed that the position and velocity of an electron could be determined simultaneously, which is practically impossible. Therefore, research turned towards developing a theory that could better describe the behavior of electrons in atoms, leading to the development of the wave-mechanical or modern atomic theory.

Bohr proposed the following model for the atom:



Exercise:

The spectrum of a hydrogen atom contains a violet line with a wavelength of 411 nm. Calculate the corresponding frequency and energy of the photon. What is the corresponding electronic transition for this line, knowing that n_1=2?