The People's Democratic Republic of Algeria

Ministry of Higher Education and Scientific Research

Martyr Hamma Lakhdar University - El Oued

Faculty of Exact Sciences

Department of Physics

Lectures on Spectroscopy

Intended for 2nd year physics students

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Preamble

These lectures, entitled **Spectroscopy**, are a set of lessons directed to second-year students of the L-M-D system, Physics specialty. The content of these lessons was prepared in accordance with the official program and was presented in a simple manner that allows the student to easily understand and grasp issues related to understanding wave-particle duality, atomic spectroscopy, and induced reactions.

It is divided into six chapters. The first chapter is entitled Wave-Particle Duality, to familiarize the student with the concept of the black body radiation, the photoelectric effect, the Compton effect, and de Broglie waves. The second chapter gives information related to the planetary model of the atom, followed by the third chapter, which deals with atomic spectroscopy, which it covers the topic of ionization potential, excited state of the atom, atomic spectra, Ritz principle and Heisenberg uncertainty principle. The fourth chapter is entitled: Atoms with multiple electrons. The fifth chapter explains the absorption and stimulated emission (laser effect). Finally, the sixth chapter is an introduction to molecular physics, which deals with diamolecules. All of these chapters are supported by illustrative diagrams and practical examples.

Dr. Meftah Nassima

Contents

Chapter I:

Wave-Particle Duality

I-Introduction:

The journey of wave-particle duality began in the late 17th century when Sir **Isaac Newton** formulated his laws of motion and gravity, providing the foundation for classical mechanics. **Newton's laws** successfully described the motion of macroscopic objects, planets, and celestial bodies, but as scientists delved deeper into the microscopic world, they encountered phenomena that defied classical explanations.

In the early 19th century, **Thomas Young** conducted a groundbreaking experiment known as the double-slit experiment with light. By shining light through two closely spaced slits onto a screen, he observed an interference pattern, similar to what one would expect from waves. This experiment presented the first hints of light's wave-like nature. Fast forward to the mid-19th century, and **James Clerk Maxwell's equations** unified electricity and magnetism, predicting the existence of electromagnetic waves. This further solidified the wave theory of light and offered a comprehensive description of its propagation. However, the wave theory encountered significant challenges in explaining certain phenomena. One such phenomenon was the photoelectric effect, which puzzled scientists for decades. In 1905, **Albert Einstein** proposed that light could also behave as a stream of discrete particles, later known as photons, to explain the photoelectric effect. This revolutionary idea laid the groundwork for the wave-particle duality concept.

Shortly after Einstein's proposal, **French physicist Louis de Broglie** presented his doctoral thesis in 1924, which introduced the concept that particles, like electrons, could also exhibit wave-like properties. De Broglie suggested that if light could sometimes behave as particles (photons), then particles should, in

turn, exhibit wave-like behaviors, challenging the classical notion of particles as point-like objects.

To test de Broglie's hypothesis, experiments were conducted with electrons and other particles, leading to the famous double-slit experiment with electrons. Astonishingly, the results mirrored those observed with light, confirming the wave-like nature of particles at the quantum level.

Max Planck, Niels Bohr, Werner Heisenberg, Erwin Schrödinger, and other pioneering scientists further developed the theory of wave-particle duality, culminating in the formulation of quantum mechanics in the 1920s. Quantum mechanics provided a comprehensive framework for understanding the behavior of matter and radiation at the atomic and subatomic levels, reconciling wave-like and particle-like behaviors. Since its inception, the concept of wave-particle duality has sparked countless experiments and discussions, revealing the enigmatic and non-intuitive nature of the quantum world. This revolutionary concept continues to shape our understanding of the fundamental building blocks of the universe and has paved the way for numerous technological advancements in the fields of electronics, telecommunications, and quantum computing.

In this chapter, you will learn about the energy quantum, a concept that was introduced in 1900 by the German physicist Max Planck to explain blackbody radiation. We discuss how Albert Einstein extended Planck's concept to a quantum of light (a "photon") to explain the photoelectric effect. We also show how American physicist Arthur H. Compton used the photon concept in 1923 to explain wavelength shifts observed in X-rays. After a discussion of Bohr's model of hydrogen, we describe how matter waves were postulated in 1924 by Louis-

Victor de Broglie to justify Bohr's model and we examine the experiments conducted in 1923–1927 by Clinton Davisson and Lester Germer that confirmed the existence of de Broglie's matter waves.

II-Black body radiation (اشعاع الجسم الاسود):

The phenomenon of black body radiation is the first phenomenon that classical physics could not explain and one of the pillars of modern physics. To understand the phenomenon, the electromagnetic radiation spectrum must first be identified, as well as what is meant by the black body.

II -1- The electromagnetic radiation spectrum (الطيف الكهرومغناطيسي):

- **Radiation** is an electromagnetic waves consisting of vibrating perpendicular electric and magnetic fields (**Figure (I-1)**), with propagation direction is perpendicular to both fields and their speed is the speed of light (3.10^8 m/s).

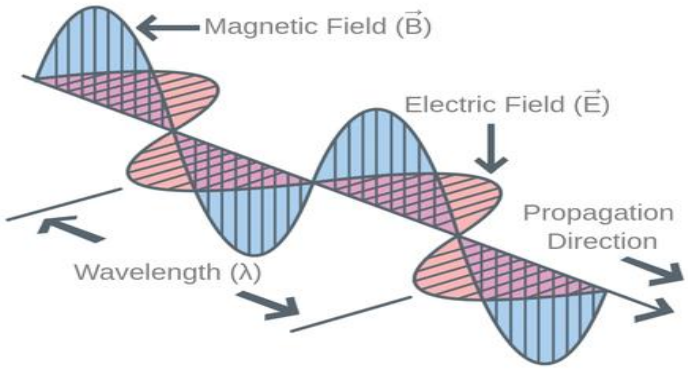


Figure (I-1): Electromagnetic wave structure.

Also, these waves travel in the material medium, as in a vacuum, and transfer energy with them. According to the classical theory, now these waves are characterized by reflection, refraction, interference and diffraction. Also, these waves agree in speed (v), but differ in frequency (ν) and wavelength (λ), Where:

$$v = \lambda * \nu \qquad (\mathbf{I-1})$$

- **The electromagnetic (EM) spectrum** includes all possible frequencies of electromagnetic radiation (**Figure (I-2)**). The electromagnetic spectrum extends

from low frequencies such as the frequencies used in radio, through medium frequencies such as the frequencies of visible light rays, to high frequencies such as X-rays, and ends with gamma rays.

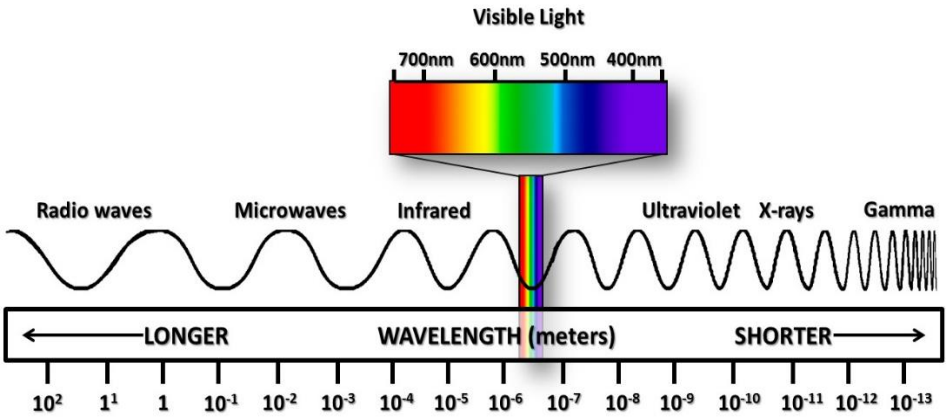


Figure (I-2): The electromagnetic radiation spectrum

II -2- Black body definition (تعريف الجسم الأسود):

A black body is an idealized physical object that absorbs **all incident electromagnetic radiation** (light) that falls onto it, regardless of the wavelength or frequency. It is called a "black" body because **it perfectly absorbs all radiation** without reflecting or transmitting any of it. Additionally, a black body is also an **ideal emitter** of radiation. Black bodies also emit radiation, based on their temperature.

In practice, true black bodies do not exist, as real-world objects typically reflect or transmit some amount of radiation. We can construct a close perception of a black body in the form of a small hole in the wall of a closed container known as a cavity radiator, as shown in Figure (I-3). The inner walls of a cavity cooler are so rough and blackened that any radiation entering through a small hole in the cavity wall becomes trapped inside the cavity. At thermodynamic equilibrium (at a temperature T), the cavity walls absorb as much radiation as they emit. Furthermore, inside the cavity, the radiation entering the hole is

balanced by the radiation coming out of it. The blackbody emission spectrum can be obtained by analyzing the light emitted from the crater. Electromagnetic waves emitted by a black body are called black body radiation. The black body is actually achieved through a small hole in the hollow radiator wall.

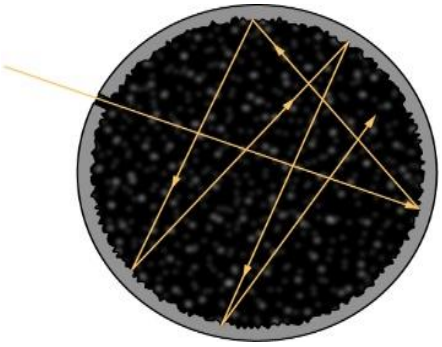


Figure (I-3): A hole in the wall of a hollow body.

So, anybody that has a temperature is either a glowing body or a non-luminous body.

1-**Incandescent bodies:** They are bodies that emit light and heat, such as the sun, lamp filament, and stars.

2-Non-glowing bodies: they emit thermal radiation, such as the Earth.

II-3- Black body radiation (اشعاع الجسم الاسود):

A fundamental concept in physics and thermodynamics, refers to the electromagnetic radiation emitted by an idealized object known as a black body. Electromagnetic radiation is emitted from all objects at any temperature at which it is present and is called **thermal radiation**. The amount of this heat radiation emitted by the body increases with an increase in temperature and decreases with a decrease in it. Also, objects exchange heat between them and the surrounding medium if the temperatures differ between them, so if the temperatures are equal, then in this case the body is in thermal equilibrium. The distribution of radiation emitted by the body at a certain temperature as a function of wavelength was a puzzling issue for scientists, as they did not find a

scientific explanation for the practical models that explain the relationship of radiation distribution with wavelength, and the classical theory was not able to find an explanation for it until the beginning of the twentieth century.

It was known that heat causes the molecules and atoms of a solid to vibrate. The scientist **Maxwell** said that these objects emit electromagnetic waves at the speed of light. That is, when a non-glowing body is heated, the energy resulting from the vibration of the particles of the particle is released in the form of electromagnetic waves of different wavelengths. According to Planck's law, which describes black body radiation, the spectral distribution of emitted radiation is solely dependent on the temperature of the black body as indicate **Planck curve (Figure (I-4))**.

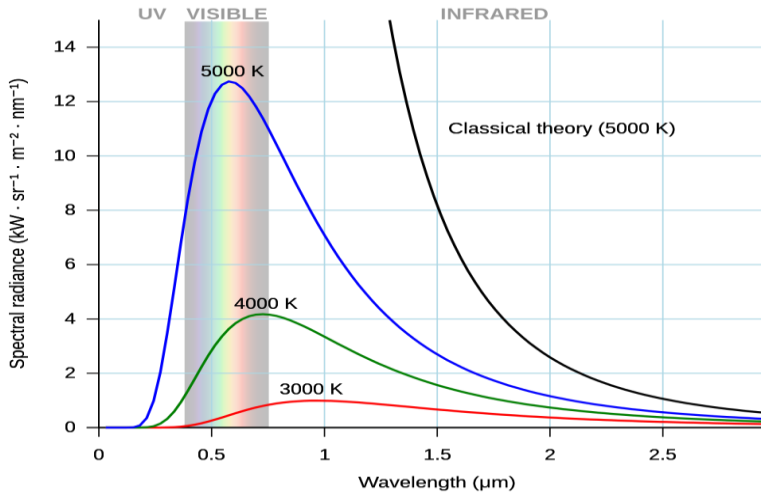


Figure (I-4): Two-dimensional plot of the spectrum of a blackbody with different temperatures.

This is a curve showing the relationship to **the distribution of the intensity of radiation** emitted by the black body **as a function** of **wavelength in nanometers**. The region marked from blue to red shows the visible part of the electromagnetic spectrum.

We ca seen from the above plot that:

The most intensely emitted radiation by an object has a wavelength λ that is inversely proportional to the temperature. Higher temperatures will emit intense radiation at shorter wavelengths, and the colour will shift to the blue spectrum. The spectrum of radiation has the following characteristics:

- ✓ The spectrum is continuous.
- ✓ The spectrum peak moves to shorter wavelengths as the temperature increases.
- ✓ The spectrum is 0 at 0 – this is the result of the quantisation of energy.
- ✓ The spectrum values at larger wavelengths are smaller.

II-4- Theories to explain blackbody radiation spectra (نظريات لتفسير طيف الجسم الاسود):

II-4-1-Wien's displacement law (قانون فين للإزاحة):

The peak of the wavelength distribution shifts to shorter wavelengths as the temperature increases as shown in the **Figure (I-5)**. This behavior is described by the following relationship, called Wien's displacement law:

$$\lambda_{max} T = 2.898 * 10^{-3} m.K \qquad (\mathbf{I-2})$$

Where λ_{max} is the wavelength at which the curve peaks and T is the absolute temperature of the surface of the object emitting the radiation.

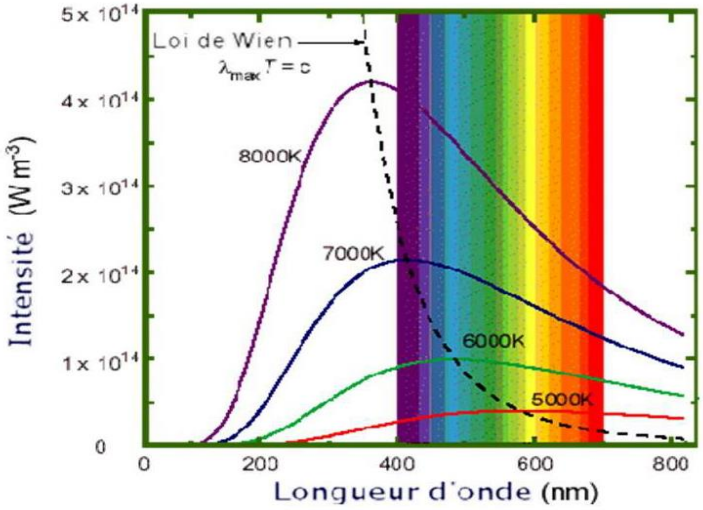


Figure (I-5): Wien's displacement law

The wavelength at the curve's peak is inversely proportional to the absolute temperature; that is, as the temperature increases, the peak is "displaced" to shorter wavelengths (Figure I-5).

Application:

A **hot body** glows with yellow radiation with a wavelength of 589nm.

-Calculate the body temperature.

Response: We have:

$$\lambda_{max}T = 2.898 * 10^{-3} \Rightarrow T = \frac{2.9.10^{-3}}{\lambda_{max}} = \frac{2.9.10^{-3}}{589.10^{-9}} = 4923.6K$$

So, the body temperature is $4923.6K$.

- Wien's displacement law mean that at room temperature, the object does not appear to glow because the peak is in the infrared region of the electromagnetic spectrum. At higher temperatures, it glows red because the peak is in the near infrared with some radiation at red end of the visible spectrum, and still at higher temperature, it glows white because the peak is in the visible so that all colors are emitted.

II-4-2- Stefan-Boltzmann's Law (قانون ستيفان-بولتزمان):

Stefan-Boltzmann's law states that the energy released by a black body per unit area (The area under the spectrum curve) is proportional to the fourth power of the body's degree of gravitational force (Figure (I-6)):

$$E(T) = \sigma \varepsilon A T^4 \qquad (\mathbf{I-3})$$

E(T): is the energy of the blackbody radiation per unit area.

σ: is called Stefan constant = 5.67×10^{-8} Watt/m^{2}K^4

A: is the surface area of the object in square meters.

ε: is the emissivity of the surface. For a back body, the emissivity is ε=1.

T: is the surface temperature in Kelvin.

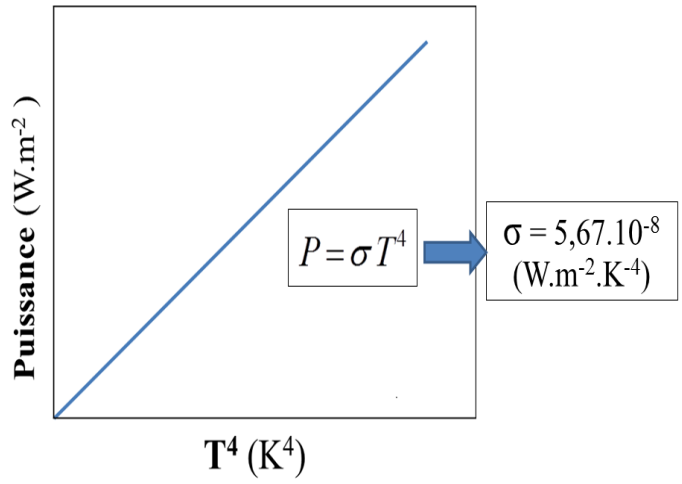


Figure (I-6): Plot reveals Stefan-Boltzmann's law

II-4-3- Rayleigh-Jeans law (قانون رايلي-جينز):

A successful theory for blackbody radiation must predict the shape of the curves in the figure (I-3), the temperature dependence expressed in **Stefan-Boltzmann's law**, and the shift of the peak with the temperature described by **Wien's law**. Early attempts to use **classical ideas** to explain the shapes of the curves in Figure (I-3) **failed**.

Let's consider one of these early attempts. To describe the distribution of energy from a black body, we define I(λ, T) dλ to be the intensity, or power per unit area, emitted in the wavelength interval dλ. The result of a calculation based on a classical theory of black body radiation known as the **Rayleigh-Jeans law** is:

$$I(\lambda, T) = \frac{2\pi c k_B T}{\lambda^4} \qquad (\mathbf{I-4})$$

An experimental plot of the back body radiation spectrum, together with the theoretical prediction of **Rayleigh-Jeans law,** is shown in figure (I-6). At long wavelengths, the **Rayleigh-Jeans law** is in reasonable agreement with experimental data, but at short wavelength, major disagreements are apparent.

Where k_B is Boltzmann's constant.

As λ approaches zero, the function I (λ, T) given by Equation (4) approaches infinity. Hence, according to classical theory, not only should short wavelengths predominate in a black body spectrum, but also the energy emitted by any black body should became infinite in the limit of zero wavelength. In contrast to this prediction, the experimental data plotted in figure (I-7) show that λ approaches zero, I (λ, T) also approaches zero. This mismatch of theory and experiment was so disconcerting that scientists called it ***the ultraviolet catastrophe.***

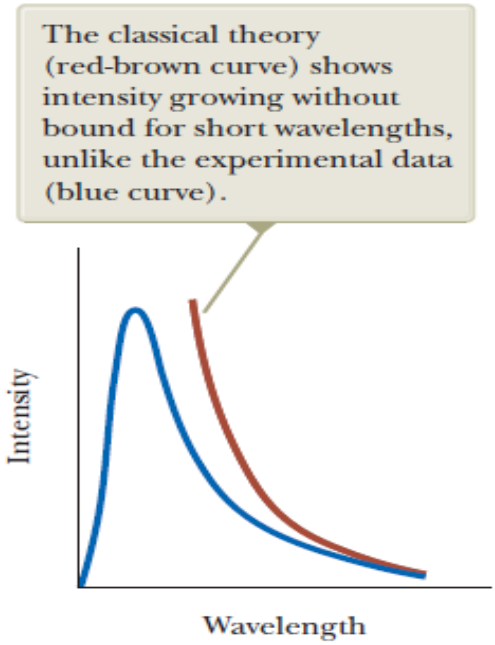


Figure (I-7): Comparison of the experimental results and the curve predicted by Rayleigh-Jeans law.

II-4-4- Planck hypothesis (فرضية بلانك):

In 1900, Max Planck developed a theory of black body radiation that leads to an equation for I (λ, T) that is in complete agreement with experimental results at all wavelengths. Planck assumed the cavity radiation came from atomic oscillators in the cavity walls in Figure (I-3). Planck made two bold assumptions concerning the nature of the oscillators in the cavity walls:

1- The energy of an oscillator can have only certain <u>discrete</u> value E_n:

$$E_n = nhf \qquad (\mathbf{I-5})$$

where n is a positive integer called a **quantum number**, f is the oscillator's frequency, and h is a parameter Planck introduced that is now called **Planck's constant**.

Because the energy of each oscillator can have only discrete values given by equation (5), we say the energy is **quantized**. Each discrete energy value corresponds to a different **quantum state**, represented by quantum **number n.** When the oscillator is in the **n=1** quantum state, its energy is ***hf ;*** when it is in the n=2 quantum state, its energy is ***2hf***; and so on,

2- The oscillators emit or absorb energy when making a transition from one quantum state to another. The entire energy difference between the initial and final states in the transition is emitted or absorbed as a single quantum of radiation.

So, an oscillator emits or absorbs energy only when it changes quantum states. If it remains in one quantum state, no energy is absorbed or emitted.

The key point in Planck's theory is the radical assumption of quantized energy states. This development marked birth of the quantum theory.

Example: A yellow lamp of 100 watts and with a wavelength of 5890Å.

-Calculate the number of quanta (photons) issued by the lamp per second.

Response: According to the following equation:

$$\boldsymbol{P = \frac{E}{t} = \frac{nh\nu}{t}}$$

Thus, the number of quantas issued by the lamp per second is:

$$\frac{n}{t} = \frac{P}{h\nu} = \frac{P\lambda}{hc} = \frac{100 \times 5890 \times 10^{-10}}{6.6 \times 10^{-34} \times 3 \times 10^{8}} = \boldsymbol{8.92 \times 10^{18} quanta/s}$$

II-4-4-1-Planck's formula for energy distribution (صيغة بلانك لتوزيع الطاقة):

Planck generated a theoretical expression for the wavelength distribution that agreed remarkably well with the experimental curves in Figure (I-3):

$$\boldsymbol{I(\lambda, T) = \frac{2\pi hc^2}{\lambda^5 (e^{hc/\lambda k_B T} - 1)}} \qquad \boldsymbol{(I-6)}$$

This function includes the parameter *h*, which Planck adjusted so that his curve matched the experimental data at all wavelengths. The value of this parameters is found to be independent of the material of which the black body is made and independent of the temperature; it is a fundamental constant of nature, the value of *h,* **Planck's constant** is:

$$\mathbf{h=6{,}626x10^{-34}\ J.\ s} \qquad (\mathbf{I-7})$$

- At long wavelengths, Equation (6) reduces to the **Rayleigh-Jeans law**, and at short wavelengths, it predicts an exponential decrease in T (λ, T) with decreasing wavelength, in agreement with experimental results. When Planck presents his theory. Most scientists did not consider the quantum concept to be realistic. They believed it was a mathematical trick that happened to predict the correct results. Hence, Planck and others continued to reach for a more rational explanation of black body radiation. Subsequent developments, however, showed that a theory based on the quantum concept had to be used to explain not only black body radiation but also a number of other phenomena at the atomic level.

III- Photoelectric effect (المفعول الكهروضوئي):

III-1-Photon:

A packet or bundle of energy is called a photon. The photon has an energy E as:

$$\boldsymbol{E=\frac{hc}{\lambda}} \qquad (\mathbf{I-8})$$

where h is the Planck's constant, ν is the frequency of the radiation or photon, c is the speed of light (e.m. wave) and λ is the wavelength.

III-2-Properties of photons:

i) A photon travels at a speed of light c in vacuum. (i.e. 3 x 10^{-8} m/s)

ii) It has zero rest mass. i.e. the photon cannot exist at rest.

iii) The kinetic mass of a photon is, $\boldsymbol{m} = \frac{\boldsymbol{E}}{\boldsymbol{c^2}} = \frac{\boldsymbol{h}}{\boldsymbol{c\lambda}}$

iv) The momentum of a photon is, $\boldsymbol{P} = \frac{\boldsymbol{E}}{\boldsymbol{c}} = \frac{\boldsymbol{h}}{\boldsymbol{\lambda}}$

v) Photons travel in a straight line.

vi) Energy of a photon depends upon frequency of the photon; so the energy of the photon does not change when photon travels from one medium to another.

vii) Wavelength of the photon changes in different media; so, velocity of a photon is different in different media.

viii) Photons are electrically neutral.

ix) Photons may show diffraction under given conditions.

x) Photons are not deviated by magnetic and electric fields.

III-3- Photoelectric effect:

Photoelectric effect is the process of **emitting the electrons** from a metal surface when the metal surface is exposed to an **electromagnetic radiation** of sufficiently high frequency (Figure (I-8)). For example, ultraviolet light is required in the case of ejection of electrons from an alkali metal.

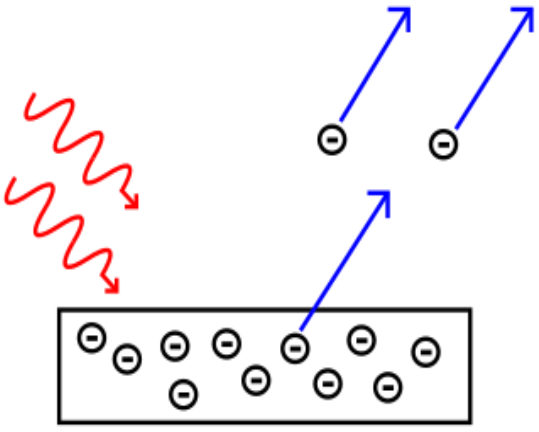


Figure (I-8): Photoelectric effect.

In 1887, the scientist Hertz noticed that when exposing a surface of a conductive material to an ultraviolet ray, electric sparks are generated more easily.

- ✓ However, the phenomenon needed a precise interpretation according to different concepts, which Hertz and all the followers of the classical school at the time failed to do.
- ✓ In 1905, Einstein presented a research paper that explained the practical results of the photoelectric phenomenon, stating that light energy exists in the form of **quantities of energy** called **photons**. His discovery led to a great revolution in quantum physics.
- ✓ The photoelectric effect requires the presence of photons of energy of about 1 MeV in elements with a large atomic number. The study of the photoelectric effect led to advances in understanding the quantum nature of light and electrons, and was instrumental in shaping the concept of wave-particle duality. It also sheds light on Max Planck's earlier discovery of the relationship between energy and frequency arising from energy quantization.

III-4- Photoemission mechanism (آلية الانبعاث الضوئي):

Photons have a **specific energy proportional** to **the frequency** of the light. In the photoemission process, if an electron in a material absorbs the energy of a single photon and its energy is greater than the **work coupling** (electron binding energy) of the material, the electron will be emitted. But if the energy of the photon is very low, the electron will not be able to

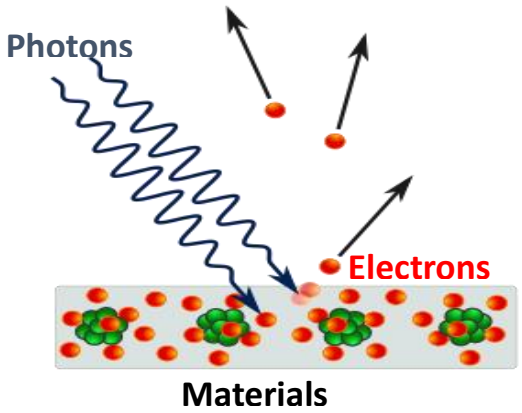


Figure (I-9): diagram describes the Photoemission mechanism.

break free from matter (Figure (I-9)). When the intensity of light increases, the number of photons emitted increases, and this leads to an increase in the number of emitted electrons, but it does not lead to an increase in the energy absorbed per electron. From this we conclude that the energy carried by the emitted electron does not depend on the intensity of the light falling on it, but only on the frequency (energy) of this light. This relates the energy of the incident photon to the energy of the emitted electron.

Electrons can absorb the energy of photons when exposed to a beam, but they usually follow the "all or nothing" principle. All photon energy is absorbed and used to free one electron from the atomic bond, otherwise the photon energy would be emitted again. If the energy of a photon is absorbed, part of the energy will free the electron from the atom, and the rest will work to increase the kinetic energy of the free electron.

III-5- Experimental observations of photoelectric emissions:

The photoelectric effect theory explained experimental observations of the emission of electrons from the surface of a material exposed to light.

For a particular metal, there is **a minimum frequency** where when the surface of the metal is exposed to a frequency lower than that as shown in Figure (I-10), there will be no photoelectrons emitted. This frequency is called **the threshold frequency**. When the frequency increased, and the number of incident photons

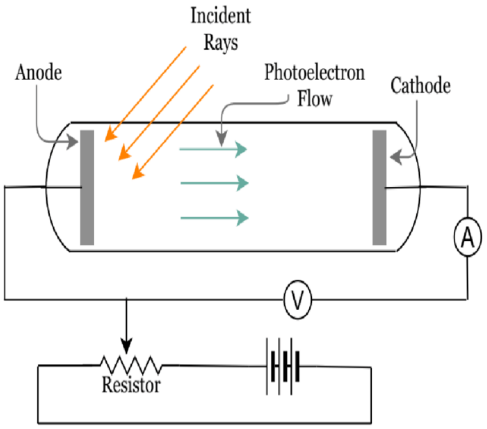


Figure (I-10): Experimental apparatus of photoelectric emissions

is kept constant, this will lead to an increase in the photon energy and thus an increase in **the kinetic energy of the emitted photoelectrons**, and thus an increase in the stopping voltage. The number of electrons also varies because the probability that each photon will cause an electron to be emitted is associated with the energy of the photon. Above the threshold frequency, the maximum kinetic energy of the electron depends on the frequency of the incident light, but it does not depend on the intensity of the incident light.

The number of emitted electrons is **directly proportional to the intensity of the incident light**, for a specific metal and at a specific frequency of the incident beam. Increasing the light intensity (while keeping the frequency constant) increases the value of the photocurrent, and the cut-off voltage remains constant. The time interval between the incidence of the beam and the emission of the electron is a very small period of time, approximately equivalent to less than 10^{-9} seconds. The direction of distribution of the emitted electrons reaches its maximum value in the direction of polarization (the direction of the electric field) of the incident light, if it is linearly polarized.

III-6- Mathematical description:

The maximum kinetic energy K_{max} of an emitted electron is given by:

$$\boldsymbol{K_{max} = hf - \varphi} \qquad \mathbf{(I-9)}$$

Where $\boldsymbol{h}$ is Planck's constant, $\boldsymbol{f}$ is the frequency of the incident photon, φ gives the minimum energy required to free an electron from the surface of a metal. The work association is:

$$\boldsymbol{\varphi = hf_0} \qquad \mathbf{(I-10)}$$

f_0 is the threshold frequency of the metal. Therefore, the maximum kinetic energy of an emitted electron is:

$$\boldsymbol{K_{max} = h(f - f_0)} \qquad \mathbf{(I-11)}$$

And since the kinetic energy is positive, then we have to get $f > f_0$ until the photoelectric effect appears.

III-7- Stopping potential (جهد الايقاف):

If a light source illuminates plate A, and another plate B collects the emitted electrons. We vary the voltage between "A" and "B" and measure the current flowing in the external circuit between the two plates.

- If the frequency and intensity of the incident light are constant, **the photocurrent will gradually increase** with **the positive voltage at the collector plate** until all the emitted photoelectrons are collected. At a certain point the photocurrent will reach saturation and then it will not increase even if the positive voltage increases. The saturation current depends on the intensity of the illumination, and does not depend on the wavelength.
- If we apply a negative voltage to the "B" plate and gradually raise it, the photoelectric current will decrease until it reaches zero, at a certain negative voltage on the "B" plate. The smallest negative voltage applied to the plate "B" such that it makes the photoelectric current become zero is called the **cut-off voltage**.

1- For a given frequency of incident radiation, the cut-off voltage depends on the intensity of the light.

2- For a certain frequency of incoming radiation, the cutoff voltage is related to the maximum kinetic energy of the photoelectron that has stopped reaching plate "s". If we consider m is the mass and v is the maximum velocity of the emitted photoelectron, then:

$$K_{max} = \frac{1}{2} m v_{max}^2 \qquad (\mathbf{I-12})$$

If q_e it is the charge of the electron and V_0 it is the stopping voltage, then the work done from the cutoff voltage is to stop the electron eV_0, so we get:

$$\frac{1}{2}mv_{max}^2 = q_eV_0 \qquad (\mathbf{I-13})$$

That is, the maximum speed of the emitted photoelectron is independent of the intensity of the incident light.

The stopping voltage changes linearly with the frequency of the light, but it also depends on the type of material. For any given material, there is a threshold frequency that must be exceeded, which is independent of the light intensity, for the emitted electron to be detected.

Application: A metallic surface is illuminated by UV light of wavelength λ=0.150μm. It emits electrons with a maximum kinetic energy of 4.8eV.

a) Calculate the extraction work W_0.

b) What is the nature of the metal?

Response:

a- The extraction work W_0 is:

$$W_0 = E - E_c = \frac{hc}{\lambda} = \frac{6.62\times10^{-34}\times3\times10^{8}}{0.15\times10^{-6}\times1.6\times10^{-19}} - 4.8 \Rightarrow W_0 = 2.6eV$$

b-Nature of the metal:

$$\lambda_0 = \frac{hc}{W_0} = \frac{6.62\times10^{-34}\times3\times10^{8}}{3.5\times1.6\times10^{-19}}$$

$$\boldsymbol{\lambda_0 = 3.5\times10^{-7} = 0.35\mu m}$$

The threshold wavelength corresponds to that of zinc; the metal is **zinc.**

IV- Compton effect (مفعول كمبتون)

IV-1- Introduction :

Compton effect is a phenomenon in which the scattering of a photon occurs as a result of its collision with a free charged particle such as an electron. It is a

quantum phenomenon that confirms the particle nature of electromagnetic radiation (photon), and this phenomenon cannot be explained by relying on classical physics. This phenomenon was named after the physicist who discovered it.

American physicist Arthur Holly Compton developed his theory by studying the effect of scattering of X-rays by electrons. Compton's theory of X-ray scattering gained its importance because it supported the particle nature of electromagnetic radiation that Albert Einstein assumed and relied upon in explaining the photoelectric phenomenon. Quantum mechanics contributed to finding an explanation for the scattering phenomenon that occurs to the photon when it collides with a free electron, while classical physics could not explain it.

➢ What happens in the Compton effect is what happens on the billiard table where a photon collides with a free electron. The free electron gains kinetic energy and the photon loses part or all of its energy. A photon's loss of energy is a decrease in its frequency, meaning an increase in its wavelength!

➢ Compton explained the particle properties of radiation through his scattering experiment. The experiment found an increase in the wavelength of the scattered radiation. He also discovered that the scattered photon had deviated from its initial angle (the angle of incidence) as shown in the Figure (I-11). This scattering is the result of

➢ **an elastic collision**, and we know that the collision is of **a particle nature**, and

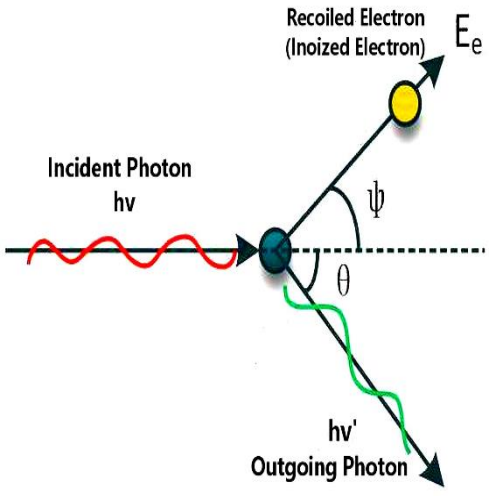


Figure (I-11): plot describes the Compton effect.

➢ here scientists were puzzled in explaining this collision based on the wave theory of radiation.

IV-2- An experiment demonstrating the Compton phenomenon:

When X-rays of wavelength λ_i fall on a free electron, the scattered X-rays colliding with the free electron have a different wavelength, say λ_f. Compton found through his experiments (Figure (I-12)) that there is always an increase in the wavelength of the scattered X-rays.

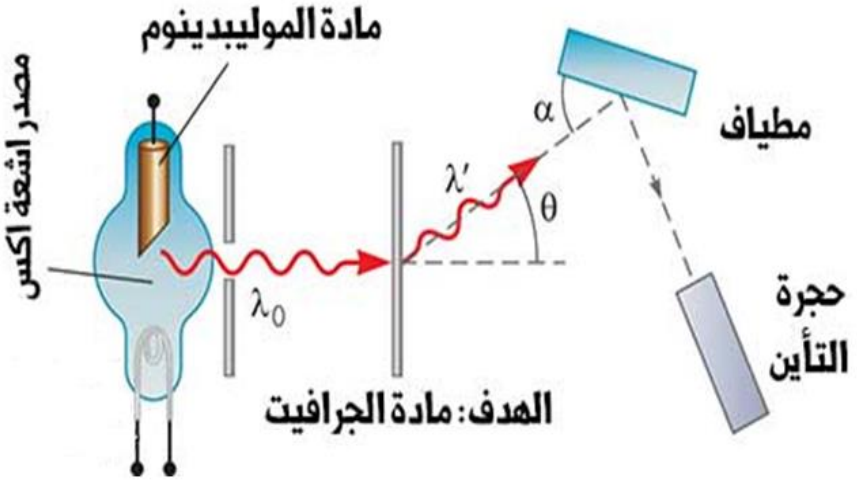


Figure (I-12): An experiment that Compton designed for his experiments on X-ray scattering.

Depending on the characteristics of classical physics, it is not possible in any way to explain the noticeable increase in the wavelength of radiation dispersed from the free electron, and by using Einstein's hypothesis that the radiation energy does not spread continuously, but spreads in the form of limited quantities of energy called the photon, and that the energy of each photon depends at his frequency. Since X-rays are only electromagnetic rays and they behave in the Compton phenomenon as if they were separate particles of energy, i.e. photons, it is easy to explain what is happening in the Compton experiment.

- The Compton phenomenon explains the relationship between the wavelength of an incident photon and the scattering photon after it collides with a free electron.

➢ IV-3- Mathematical equation for the Compton phenomenon:

By applying the **laws of conservation of energy** and **the momentum** of **the colliding bodies** before and after the collision, it is possible to find a relationship that calculates **the amount of change in the energy of the scattered radiation** (photon), or in other words, finding the change in its wavelength, as well as the change in the energy of the electron movement after the collision (Figure (I-13)). The mathematical equation describing the Compton phenomenon is given by the equation below:

$$\lambda_f - \lambda_i = \lambda_c(1 - cos\theta) \qquad (\mathbf{I-14})$$

Where **Θ** is the angle of scattering, i.e. the angle between the incident ray and the scattered ray and is given **λc** which is defined by the Compton wavelength which is equal to 2.43×10^{-12} meters.

$$\lambda_c = \frac{h}{m_e c} \qquad (\mathbf{I-15})$$

where **h** is Planck's constant, **m_e** is the mass of the electron, and **c** is the speed of light in a vacuum.

➢ The above equation confirms that the scattering angle does not depend on the wavelengths of radiation, but rather depends on the change in wavelength.

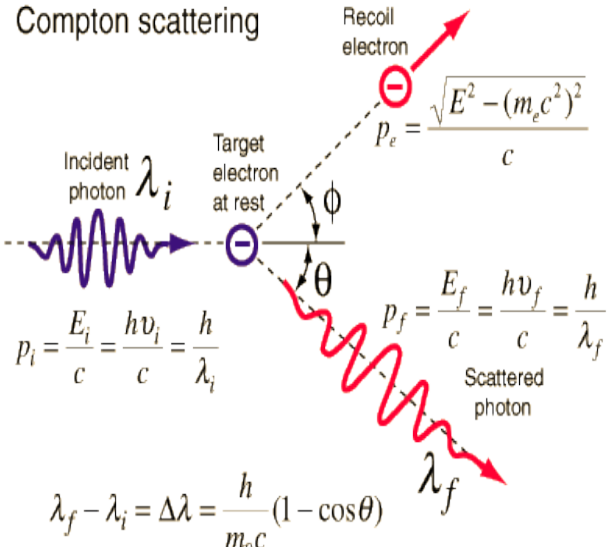


Figure (I-13): Plot describes the Compton phenomenon

V- De Broglie waves (أمواج دي برولي) :

In the 20th century, physicist Louis De Broglie suggested that it was not just light that could exhibit both wave and particle characteristics; he suggested that particles with mass, such as electrons and protons, could also behave like waves. He further proposed that certain relations describing the duality of light also apply to matter.

Recall that the momentum of a photon, p, is given by:

$$\boldsymbol{p = \frac{h}{\lambda}} \qquad \mathbf{(I-16)}$$

where h is Planck's constant and λ is the wavelength of the photon. De Broglie proposed that the same relationship is true for particles of matter. Rearranging the equation above to isolate the wavelength,

$$\boldsymbol{\lambda = \frac{h}{p}} \qquad \mathbf{(I-17)}$$

gives the de Broglie wavelength of a particle, as a function of its momentum.

Recall that, for a particle moving at a speed much slower than the speed of light, the momentum is equal to the product of the particle's mass, m, and its velocity, v. Thus, the de Broglie wavelength can also be calculated using:

$$\boldsymbol{\lambda = \frac{h}{mv}} \qquad \mathbf{(I-18)}$$

This concept also applies to sets of particles or objects - even very large objects, such as the objects we interact with in everyday life. Thus, any massive object with momentum has a de Broglie wavelength. It should be noted that "massive" refers to anything that has mass and not just very large objects.

The concept that a massive object behaves like a wave is often confusing because we do not observe effects such as diffraction with everyday objects we interact with. This is because the de Broglie wavelength of large objects is very small.

❖ **Example:** Calculate the wavelength of the following objects:

-A ball with a mass of 2g is moving at a speed of 300 m/s.

- An electron accelerated under a potential difference of 10^4 volts.

It is given: e = $1{,}6 \times 10^{-16}$C, h = $6{,}63 \times 10^{-34}$ j.s , me = $9{,}1 \times 10^{-31}$ Kg

❖ **Response:** the wavelength of the:

1-The ball: we have $\lambda_1 = \frac{h}{mv} = \frac{6.62\times10^{-34}}{(2\times10^{-3})300} = 1.1 \times 10^{-33} = 1.1 \times 10^{-23}$Å.

2-The accelerated electron: we have $E_c = \frac{1}{2}mv^2 = eV \Rightarrow mv = \sqrt{2meV}$

Substituting in the De-Brogli expression we find:

$$\lambda_2 = \frac{h}{mv} = \frac{h}{\sqrt{2meV}} = \frac{6.62 \times 10^{-34}}{\sqrt{2 \times (9.1 \times 10^{-31}) \times (1.6 \times 10^{-19}) \times 10^4}}$$

$$= \mathbf{0.12 \times 10^{-10} m}$$

VI-Davisson-Germer experiment (تجربة دافيسن وجيرمر):

The Davisson-Germer experiment demonstrated the wave nature of the electron, confirming the earlier hypothesis of de Broglie. Putting wave-particle duality on a firm experimental footing, it represented a major step forward in the development of quantum mechanics. The Bragg law for diffraction had been applied to x-ray diffraction, but this was the first application to particle waves. Davisson and Germer designed and built a vacuum apparatus (Figure (I-14)) for the purpose of measuring the energies of electrons scattered from a metal surface. Electrons from a heated filament were accelerated by a voltage and allowed to strike the surface of nickel metal.

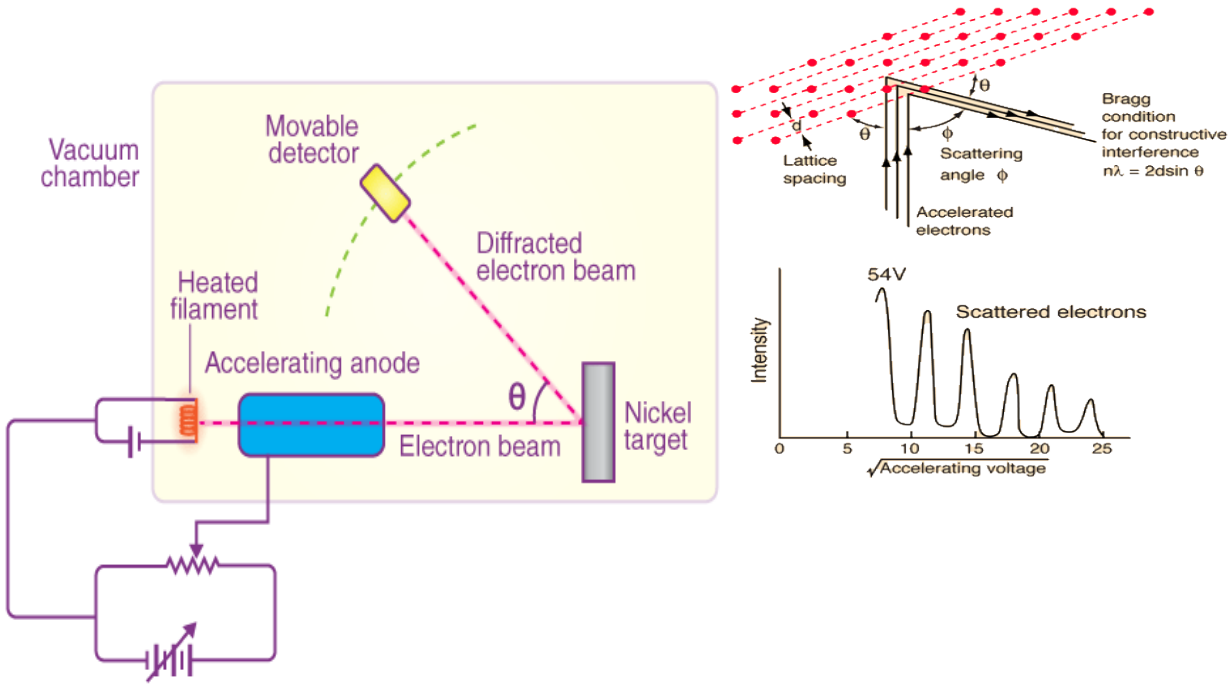


Figure (I-14): Davisson-Germer Experiment

Chapter II

Planetary model of the atom

I- Introduction :

In 1897, **Joseph John Thomson** identified the electron as a negatively charged elementary particle. Then he proposed "**Thomson's model**" where an atom consists of electrons immersed in a cloud of positive charge to balance the negative charge of the electrons. The latter are dispersed within the atom, but with many possible structures to locate them. This model was refuted in 1909 by **Ernest Rutherford's** gold leaf bombardment experiments, and in 1911 the latter showed the existence of a very small positively charged nucleus, which later prompted him to propose **Rutherford's atomic model**: an atom consists of negative electrons. It rotates in circular paths around a positive dense nucleus, like **the planets of the solar system** that revolve in a semi-circular direction around the sun, then the electromagnetic force replaces the gravitational force as the cohesion force of the system. However, Rutherford's planetary theory clashed with the theory of accelerated electron radiation. Indeed, according to experimental observations and Maxwell's laws, an electron undergoing acceleration emits energy in the form of an electromagnetic field. Back at the level of the Rutherford atom, the electron must describe a concentric spiral, not a circle, only to end up colliding with the nucleus after a few million revolutions, which is the equivalent of a nanosecond. So the orbitals are unstable.

▪ In 1913, **the Danish physicist Niels Bohr** (1885-1962) then introduced three postulates to make this model compatible with the observations of the spectrum of hydrogen: the first postulate supposes that there exist stable circular orbits for the electrons, that is that is, once in one of these orbits, the electron does not radiate any electromagnetic energy. It therefore does not decrease in a spiral and can remain in this orbit indefinitely. In addition, each of them corresponds to a well-defined energy of the electron (we then speak of the energy level of the electron). According to the second postulate, the electron can pass from one stable orbit to another, i.e. from one energy level to another, by absorption or emission of a quantum of energy h again called a photon. The absorption of a photon thus causes the electron to pass from a low orbit (close to the nucleus) of low energy to a high orbit (far from the nucleus) of higher energy. The emission of a photon corresponds to the reverse operation: the electron passes from a distant orbit of high energy to an orbit close to the nucleus of lower energy, the excess energy being expelled in the form of a photon.

Bohr then introduces a third postulate as simple as it is strange: for the hydrogen nucleus, the quantification of the energy levels follows from the quantification of the angular momentum.

- However, the Bohr model could not explain the differences in the relative intensity of the spectral lines, as well as the spectra of elements heavier than hydrogen, as it was hardly limited to explaining the hydrogen atom.
- The Bohr model remains the basis for the study of energy levels, despite the great deficit in many of the interpretations that objected to the model, which was the basis for many scientific discoveries that were later resolved.

II- The concept of atomic spectra (مفهوم الاطياف الذرية) :

Atomic spectra are defined as the band of electromagnetic wavelengths that are emitted by an excited atom when it returns to a steady state. What is meant by the excited atom is that the atom obtains energy that works to transfer its electrons from a lower energy level (stable) to a higher energy level (excited), and when these electrons return to the stable level, the energy it has gained is emitted in the form of light radiation, which is called the atomic spectrum and these radiations, which make up the spectrum, are either visible or invisible.

II-1- Emission spectrum (طيف الانبعاث) :

It is a set of frequencies of electromagnetic radiation that is emitted by an atom or molecule that moves from a higher energy level to a lower energy level, and the emitted energy is equal to the energy difference between the higher energy

level and the lower energy level, and each chemical element has its own emission spectrum in order to distinguish it from the rest of the elements.

An atomic emission device is used to measure the intensity of light emitted at a specific wavelength to determine the amount of element in the sample. There are two types of emission spectrum as follows:

a) **Continuous (continuous) spectrum (الطيف المتصل)** : It is a spectrum consisting of uninterrupted light beams, i.e. continuous frequencies, and appears in the form of a strip without spaces or breaks without color as shown in the Figure (II-1), and contains the seven colors of the spectrum (red, orange, yellow, green, blue, indigo, violet), A high temperature must be available for the chemical element for this spectrum to occur. Example: the solar spectrum.

Figure (II-1): continuous spectrum.

b) **Linear spectrum (non-continuous) (الطيف الخطي) :** It is a spectrum consisting of limited wavelengths (colors) (Figure (II-2)) such as (the spectrum of hydrogen H, the spectrum of neon Ne, the spectrum of mercury

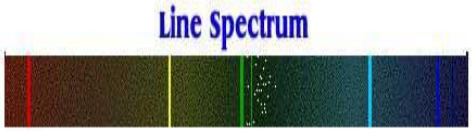


Figure (II-2): The non-continuous spectrum

Hg), and it is produced through the excitement of atoms of one of these elements, and these elements emit the energy they gained as a result of excitation on Limited color light form.

II-2- Absorption spectrum (طيف الامتصاص):

It is defined as a bundle of wavelengths produced when light passing through it is absorbed by an element or vapor of an element. This spectrum is produced when white light passes through the vapor of the element, which produces absorption spectrum lines, and these lines appear in the form of black lines.

III-Planetary model of the hydrogen atom(النموذج الكوكبي لذرة الهيدروجين):

III-1-Experimental study of the emission spectrum of the hydrogen atom:

By comparing the spectrum of thermal radiation emitted by the black body and the emission spectrum (emission) of the hydrogen atom, we note the following:

- The spectrum of thermal emission is continuous and contains all colors

-The emission spectrum of the hydrogen atom is not continuous, i.e. we distinguish only some colored lines that correspond to specific wavelengths that can be measured using a spectrophotometer.

Based on these experimental results, the scientist **Palmer**, in the year 1885, he published an experimental relationship that allows calculating the wavelengths of the spectrum of the hydrogen atom:

$$\lambda_m = h\frac{m^2}{m^2-4}, \qquad h = 364.56, \qquad m = 3,4,5,\ldots\ldots \qquad (\mathbf{II-1})$$

This relation was popularized by Rydberg in 1890 under the name of the **Palmer-Rydberg relation:**

$$\frac{1}{\lambda_m} = R_H\left(\frac{1}{2^2}-\frac{1}{n^2}\right), \qquad n = 3,4,5,\ldots\ldots\ldots \qquad (\mathbf{II-2})$$

Where R_H = 1,09677 × 10^8 (m^{-1}) is **Rydberg constant**.

III-2- Bohr model of the hydrogen atom (نموذج بور لذرة الهيدروجين):

In this model, Bohr assumes that the electron rotates in circular orbits around the proton.

III-2-1-Bohr's postulates:

In 1913 **Niels Bohr** proposed his atomic model, which is based on classical principles (Newton's second principle) as well as on the principle of energy transmission by indivisible beams (quanta). This model replaced **the Rutherford model**, the latter, which could not explain the discontinuous spectrum of hydrogen, nor could it explain the survival of the electron in its orbit around the nucleus (because in the classical theory, when a charge is in motion, it loses energy and therefore the electron will fall on the nucleus) and to explain what the Rutherford model could not explain Bohr proposed his model, which is based on the following axioms:

a) **The first axiom: the axiom of orbits:** The electron revolves around the nucleus in allowed orbits characterized by the following:

- The kinetic moment of the electron in these allowed orbits is quantized (**quantization condition**) according to the following relationship:

$$\vec{L} = \vec{r} \Lambda \vec{p} = m v_n r_n \vec{u}$$

$$L = m v_n r_n = n \frac{h}{2\pi} \qquad (\mathbf{II-3})$$

n is **the principal quantum number** (n=1,2,3,…)

m is the electron mass

r_n is the radius of the orbit around the nucleus.

v_n is the linear velocity in orbit. And **h** it is Planck's constant.

b) **The second axiom: the axiom of the emission and absorption of energy:** Each allowed orbit represents a specific energy level. Every transition of an electron from one permitted orbit to another permitted orbit is accompanied by the absorption or emission of an energy photon according to the relationship.

$$\left|E_f - E_i\right| = h\nu \qquad (\mathbf{II-4})$$

E_i is the energy of the starting orbit.

E_f is the energy of the access orbit.

ν is the frequency of the emitted or absorbed radiation.

- The emission spectrum has colored lines on a black background (Figure (II-3)).

Figure (II-3): The emission spectrum

- Absorption spectrum has black lines on a colored background Figure (II-4).

Figure (II-4): The Absorption spectrum.

III-2-2-Study of orbitals:

Consider the hydrogen atom consisting of an electron charge $q_e = (-e)$ and his mass m_e, it rotates at a linear speed around a proton of its charge $q_p = (+e)$ and his mass m_p (Figure (II-5)).

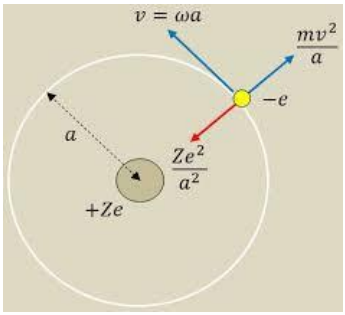


Figure (II-5): The hydrogen atom

The electron is under the influence of an electric attraction, the Coulomb force that the proton exerts on it.

As : $\boldsymbol{F_e = \frac{1}{4\pi\varepsilon_0}\frac{|q_e q_p|}{r^2}}$

According to Newton's second principle :

$$\sum \overrightarrow{F_{ext}} = m_e\vec{a}_n \Rightarrow \vec{F}_c = m_e\vec{a}_n \Rightarrow F_c\vec{n} = m_e a_n\vec{n}$$

$$\Rightarrow F_c = m_e a_n \Rightarrow \boldsymbol{\frac{1}{4\pi\varepsilon_0}\frac{|e^2|}{r^2} = m_e\frac{v^2}{r} \Rightarrow r = \frac{1}{4\pi\varepsilon_0}\frac{e^2}{m_e v^2}}$$

According to the first axiom, the electrons can only rotate in permitted orbits defined by the condition:

$$mv_n r_n = n\frac{h}{2\pi} \qquad (\mathbf{II-5})$$

Thus: $$\boldsymbol{v_n = n\frac{h}{2\pi m_e r_n}} \qquad (\mathbf{II-6})$$

It represents **the linear velocity of the electron** in its orbit.

$$r = \frac{1}{4\pi\varepsilon_0}\frac{e^2}{m_e(n\frac{h}{2\pi m_e r_n})^2} \Rightarrow r_n = \frac{1}{4\pi\varepsilon_0}\frac{4\pi^2 e^2 m^2 r_n^2}{m_e n^2 h^2}$$

$$\Rightarrow \boldsymbol{r_n = \frac{\varepsilon_0 h^2}{\pi e^2 m_e} n^2} \qquad (\mathbf{II-7})$$

It is the permissible radius of the orbit.

For n=1, $\boldsymbol{r_1 = 0.53}$Å, It is called the **Bohr radius** and is usually denoted by the symbol $\boldsymbol{a_0}$.

And we can write: $$\boldsymbol{r_n = a_0 n^2} \qquad (\mathbf{II-8})$$

This relationship ensures that the radius is quantized.

III-2-3-Energy study of the hydrogen atom (الدراسة الطاقوية لذرة الهيدروجين):

Consider the system that makes up the hydrogen atom (proton and electron).

The proton as a charge generates an electric potential around it $V_P(r)$:

$$\boldsymbol{V_p(r) = \frac{1}{4\pi\varepsilon_0}\frac{e}{r}} \qquad (\mathbf{II-9})$$

Thus, the electron under the influence of this potential has electrical **potential energy**:

$$\boldsymbol{E_p(r) = (-e)V_p(r) = -\frac{1}{4\pi\varepsilon_0}\frac{e^2}{r}} \qquad \textbf{(II – 10)}$$

However, since the proton has a large mass relative to the electron, it can be considered that the proton is stationary and the electron rotates around it with **kinetic energy** $\boldsymbol{E_c}$.

$$\boldsymbol{E_c = \frac{1}{2}mv^2}$$

And we have the above:

$$r = \frac{1}{4\pi\varepsilon_0}\frac{e^2}{m_e v^2} \Rightarrow m_e v^2 = \frac{1}{4\pi\varepsilon_0}\frac{e^2}{r}$$

$$E_c = \frac{1}{2}mv^2 = \frac{1}{2}\left(\frac{1}{4\pi\varepsilon_0}\frac{e^2}{r}\right) \Rightarrow E_c = -\frac{1}{2}\left(-\frac{1}{4\pi\varepsilon_0}\frac{e^2}{r}\right) = -\frac{1}{2}E_p$$

It is the total energy of the system:

$$E_T = E_c + E_p = -\frac{1}{2}E_p + E_p = \frac{1}{2}E_p \Rightarrow E_T = \frac{1}{2}(-\frac{1}{4\pi\varepsilon_0}\frac{e^2}{r})$$

$$\boldsymbol{E_T = -\frac{1}{8\pi\varepsilon_0}\frac{e^2}{r}} \qquad \textbf{(II – 11)}$$

Since the radius is quantized: $\boldsymbol{r = r_n = r_1 n^2} \Rightarrow$

$$\boldsymbol{E_n = -\frac{1}{8\pi\varepsilon_0}\frac{e^2}{r_n}} \qquad \textbf{(II – 12)}$$

This means that the energy is also quantized and each level relates to a specific energy.

An energy must be given to the hydrogen atom at least equal to $w = |E_n|$ to free an electron from orbital N number n.

If n=1 this work is called the work of exiting the hydrogen atom (photoelectric effect).

III-2-4- Energy (مستويات الطاقة لذرة الهيدروجين):

The term energy in terms of the radius of the orbit is given as follows:

$$E_n = -\frac{1}{8\pi\varepsilon_0}\frac{e^2}{r_n} \qquad (\mathbf{II-13})$$

and radius:

$$r_n = \frac{\varepsilon_0 h^2}{\pi m_e e^2} n^2 \qquad (\mathbf{II-14})$$

Substituting the radius into the expression for energy, we get:

$$E_n = -\frac{me^4}{8\varepsilon_0^2 h^2}\frac{1}{n^2} \qquad (\mathbf{II-15})$$

If n=1: $E_1 = -13.6\ (ev)$

It is the energy of the basic orbital of the hydrogen atom (energy of the ground state) and it is the energy of the layer K. Thus:

$$E_n = -13.6\ \frac{1}{n^2}\ (eV), \quad n = 1, 2, 3, \ldots\ldots \qquad (\mathbf{II-16})$$

It is **the bond energy** of the electron in the hydrogen atom as a function of the number n where the number **n** is called **the main quantum number** or **primary quantum number** (Figure (II-6)).

- We note that the higher the number n, the closer the levels are to each other until they become equal the form of a continuous spectrum after it was a discontinuous spectrum in the values of n.

N	Shell	r_n (nm)	E(eV)
1	K	0,0529	-13,6
2	L	0,2116	-3,4
3	M	0,4761	-1,51
4	N	0,8467	-0,85

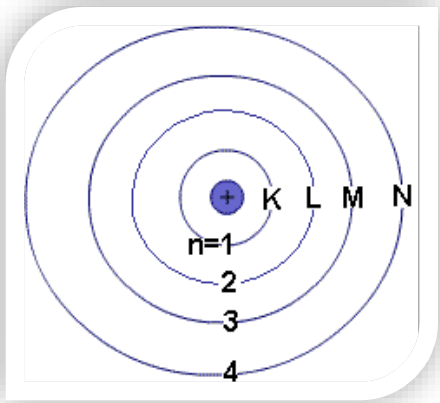


Figure (II-6): the basic orbital of the hydrogen

According to Bohr's second axiom: When an electron moves from one energy level n_i to another n_f, it emits or absorbs a photon. This photon carries an energy equal to the energy difference between the two levels.

- If n_i it is greater than n_f **the emission of a photon**, the atom loses energy and we obtain an emission spectrum consisting of colored lines on a black background (Figure (II-7)).

•If n_i it is less than n_f **the absorption of a photon**, the atom is excited, that is, it gains energy, and we get an absorption spectrum consisting of black lines on a background

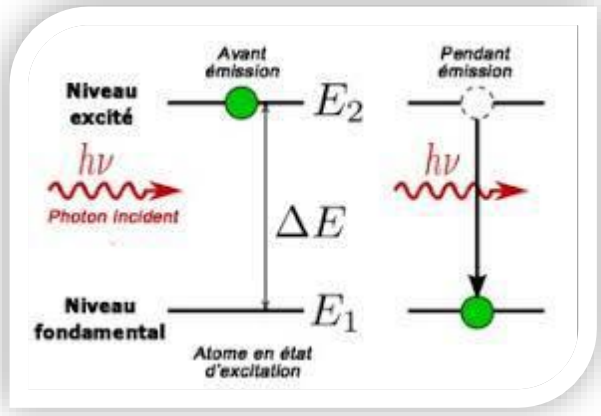


Figure (II-7): The emission of a photon

Thus, the energy of the emitted or absorbed photon is:

$$\Delta E_{i\to f} = \left|E_{n_f} - E_{n_i}\right| = |E_1|\left|\frac{1}{n_f^2} - \frac{1}{n_i^2}\right| = h\nu \qquad (\mathbf{II-17})$$

The wavelength related to this transition satisfies Rydberg's law:

$$\frac{1}{\lambda_{i\to f}} = R_H\left|\frac{1}{n_f^2} - \frac{1}{n_i^2}\right| \Rightarrow \frac{\nu_{i\to f}}{c} = R_H\left|\frac{1}{n_f^2} - \frac{1}{n_i^2}\right| \Rightarrow hc\frac{\nu_{i\to f}}{c} = hcR_H\left|\frac{1}{n_f^2} - \frac{1}{n_i^2}\right|$$

$$\Rightarrow h\nu_{i\to f} = hcR_H\left|\frac{1}{n_f^2} - \frac{1}{n_i^2}\right| \qquad (\mathbf{II-18})$$

Substituting in Bhor's transition law, we find:

$$|E_1| = R_H hc \Rightarrow -E_1 = R_H hc \Rightarrow R_H = -\frac{E_1}{hc}$$

Substituting in E_1, we get:

$$R_H = \frac{me^4}{8\varepsilon_0^2 h^2 c} \qquad (\mathbf{II-19})$$

Transitions between energy levels of electrons are classified into several groups. When an electron falls to a lower energy level (n), this transition has an assigned group name. The following list the names of these groups (Figure (II-8)):

n=1: **Lyman** Series

n=2: **Balmer** series

n=3: **Paschen** series

n=4: **Brackett** series

n=5: **Pfund** series

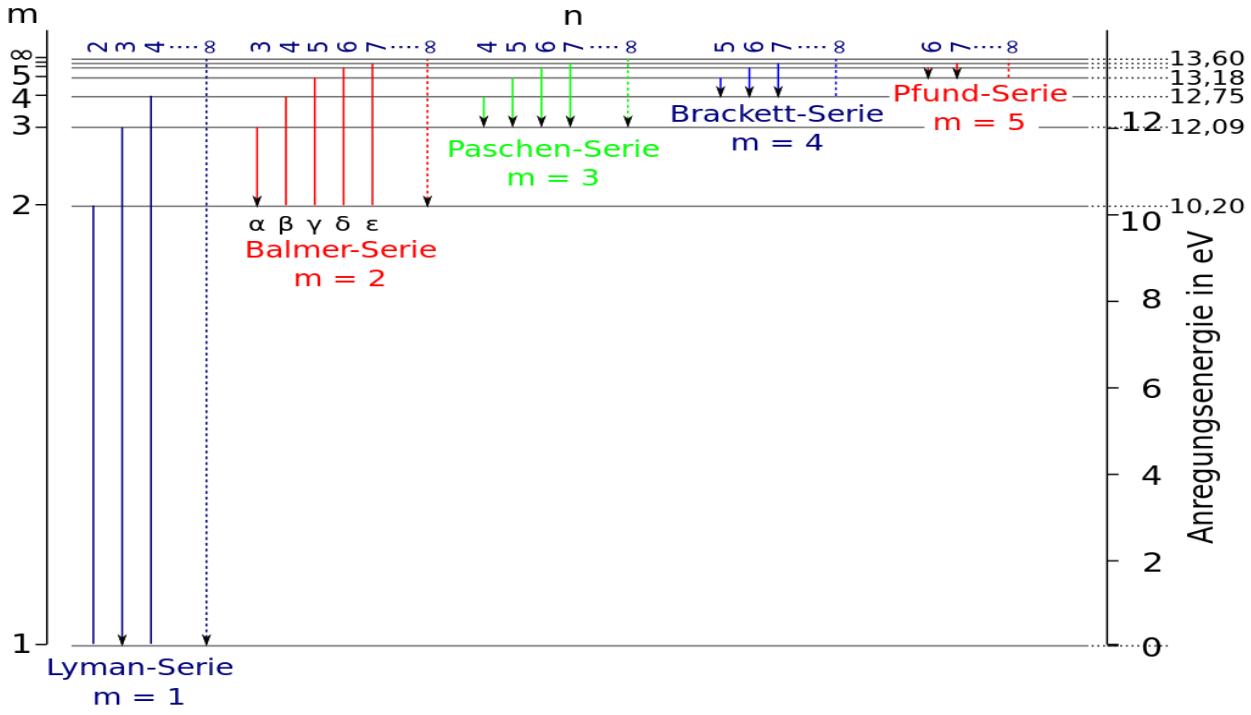


Figure (II-8): The Transitions groups.

- **Ionization energy** is the smallest energy that can be applied to an atom to remove an electron from the primary orbital.

- The ionization energy of the hydrogen atom is given in the form:

$$E_{ion} = \Delta E_{1\to\infty} = |E_\infty - E_1| = |0 - E_1| = |E_1| = 13.6\ eV$$

- The Bohr model can be reasonably applied to ionized atoms that contain one electron after ionization like He^{+}, Li^{++}, with compensation the charge (e) by the charge (Ze).

III-3-Inability of Bohr's theory (عجز نظرية بور):

The Bohr model is a simple model that could not explain some of the observations:

- It could not explain the line spectrum of multi electron atoms.
- This model failed to explain the effect of magnetic field on the spectra of atoms (Zeeman effect).
- The effect of electric field on the spectra could not be explained by Bohr's model (Stark effect).
- The shapes of molecules arising out of directional bonding could not be explained.
- The dual nature of electrons (both as wave and particle) and the path of motion of the electron in well-defined orbits were not correct.

III- 4- Bhor-Somerformed model (نموذج بور- سومرفيمد):

Summerfield hypothesized that in each n orbital there are n elliptical orbitals that have the same energy E_n.

This model explains the fine spectrum of Hydrogen atom. The important postulates of **Sommerfeld atomic model** are:

1- The orbits may be both circular and elliptical.

2- When path is elliptical, then there are two axis – major axis & minor axis (Figure (II-9)). When length of major & minor axis becomes equal then orbit is circular.

3- The angular momentum of electron moving in an elliptical orbit is (kh/2π). Where k is an integer except zero. Value of k = 1, 2,3,4….. . (n/k) = length of major axis / length of minor axis.

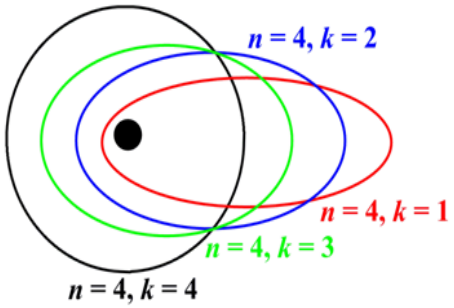


Figure (II-9): Sommerfeld atomic model

4- Sommerfeld suggested that orbits are made up of sub energy levels. These are s, p ,d, f. These sub shells possess slightly different energies.

- Bohr gave a quantum number '**n**', which determines the energy of electron.

- Sommerfeld introduced a new quantum number called Orbital or Azimuthal Quantum number (l) which determines the orbital angular momentum of electron.
- He proved that these elliptical orbits, in the presence of a magnetic field, do not direct in any direction, but rather in specific (possible) directions (2l+1).
- This led to the emergence of a new quantum number m, which is the magnetic quantum number, which takes values $-l \leq m \leq +l$.

Thus, Summerville's model was able to explain the waning of the spectral lines .

In 1924, Pauli discovered a new quantum number, spin, which takes two values for the electron $(-\frac{1}{2}, \frac{1}{2})$.

According to the Bohr-Sommerfield model, we arrange the orbitals $\psi_{n,l,m}(r)$ in the layer and below the layer as shown in the table:

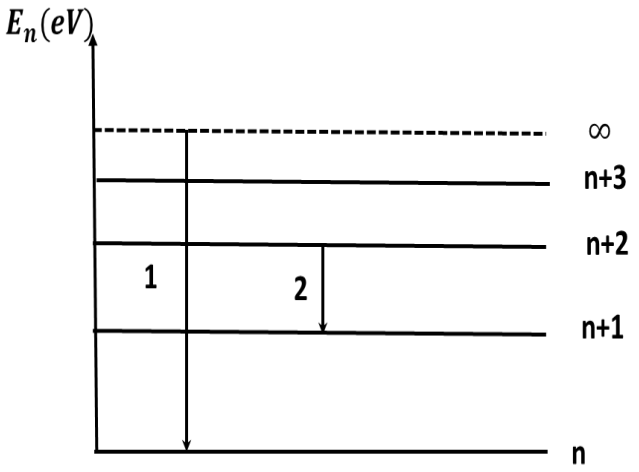
Layer n	sub-layer l	Magnetic quantum number m	wave function ψ	The quantity field
1	0	0	$\psi_{1,0,0}$	1s
2	0	0	$\psi_{2,0,0}$	2s
	1	-1	$\psi_{2,1,-1}$	$2p_x$
		0	$\psi_{2,1,0}$	$2p_y$
		1	$\psi_{2,1,1}$	$2p_z$
3	0	0	$\psi_{3,0,0}$	3s
	1	-1	$\psi_{3,1,-1}$	$3p_x$
		0	$\psi_{3,1,0}$	$3p_y$

		1	$\psi_{3,1,1}$	$3p_z$
	2	-2	$\psi_{3,2,-2}$	
		-1	$\psi_{3,2,-1}$	
		0	$\psi_{3,2,0}$	
		1	$\psi_{3,2,1}$	
		2	$\psi_{3,2,2}$	

Exercise:

If the wavelength of one of the spectral lines in the Brackett series of a hydrogen atom is 4040 nm, Select the corresponding transition and calculate for the second line in this series.

2-In the emission spectrum of the hydrogen atom, we consider transitions 1 and 2 represented on the following energy diagram:



3-If the wavelength of boundary transition 1 is 820.8 nm, determine the value of **n** and then deduce the name of series 1 and 2, indicating the transition occurring in each of them.

4-Calculate in $\lambda_2$nm to move 2.

5- Prove that $\frac{\Delta E_1}{\Delta E_2} = \frac{\lambda_2}{\lambda 1}$ and then calculate this ratio.

6-Calculate ΔE_1 and ΔE_2 for the transitions 1 and 2.

Response:

1- Determine the transition corresponding to a spectral line with wavelength λ = 4040 nm in the Brackett series for an H atom (Z=1):

In the Brackett series we have: $n_1 = 4$, so the resulting transition is:

($n_1 = 4 \mapsto n_2 = ?$).

We have:

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

$$= \frac{1}{4} - \frac{1}{(4040 \times 10^{-9})(1.097 \times 10^7)} \Rightarrow n_2 = 5$$

The resulting transition is: ($n = 4 \mapsto n = 5$)

2-Calculation ΔE of the second line transition ($n = 4 \mapsto n = 6$) (in this series) Brackett:

We have: $\Delta E = E_6 - E_4 \quad where\ E_n = \frac{Z^2}{n^2}(-13.6eV)$

$$\Rightarrow \Delta E = \left(\frac{1}{6^2} - \frac{1}{4^2}\right)(-13.6) = 0.472eV$$

3-In the emission spectrum of the hydrogen atom (Z=1), we have transitions 1 and 2 represented on the energy diagram:

1-Determine the value of n through the boundary transition 1 with a wavelength equal to λ_1 = 820.8 nm. The transition corresponding to this line is: (n = ∞ ↦ n = ?)

We have:

$$\frac{1}{\lambda} = Z^2 R_H \left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \Rightarrow \frac{1}{\lambda_1} = R_H \left(\frac{1}{n_1^2} - 0\right) \Rightarrow n_1 = \sqrt{R_H \lambda_1}$$

$$n_1 = \sqrt{(1.097 \times 10^7)(820.8 \times 10^{-9})} \Rightarrow n_1 = 3$$

Thus the value of n. Given in the chart is **3**.

4-So, the series 1 and 2 are the Paschen series and the Brackett series, respectively, and the transition occurring in each of them is n (n = ∞ ↦ n = 3) and (n = 5 ↦ n = 4), respectively.

2-Calculate λ_2 in nm for transition 2 (n = 5 ↦ n = 4):

$$\frac{1}{\lambda_2} = Z^2 R_H \left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \Rightarrow \frac{1}{\lambda_2} = 1.096 \times 10^7 \left(\frac{1}{4_1^2} - \frac{1}{5_2^2}\right)$$

$$\boldsymbol{\lambda_2} = 40.410^{-7} m = 4040 nm$$

5-Proving that $\frac{\boldsymbol{\Delta E_1}}{\boldsymbol{\Delta E_2}} = \frac{\boldsymbol{\lambda_2}}{\boldsymbol{\lambda 1}}$ and then calculate this ratio:

We have:

$$\Delta \boldsymbol{E_1} = \frac{\boldsymbol{hc}}{\boldsymbol{\lambda_1}} \ \boldsymbol{and}\ \Delta \boldsymbol{E_2} = \frac{\boldsymbol{hc}}{\boldsymbol{\lambda_2}}$$

$$\frac{\Delta E_1}{\Delta E_2} = \frac{\frac{hc}{\lambda_1}}{\frac{hc}{\lambda_2}} = \frac{\boldsymbol{\lambda_2}}{\boldsymbol{\lambda 1}} \Longrightarrow \frac{\boldsymbol{\Delta E_1}}{\boldsymbol{\Delta E_2}} = \frac{\boldsymbol{\lambda_2}}{\boldsymbol{\lambda 1}}$$

$$\frac{\boldsymbol{\Delta E_1}}{\boldsymbol{\Delta E_2}} = \frac{\boldsymbol{\lambda_2}}{\boldsymbol{\lambda 1}} = \frac{\mathbf{4040}}{\mathbf{820.8}} = \mathbf{4.9}$$

6-Calculate $\boldsymbol{\Delta E_1}$ and $\boldsymbol{\Delta E_2}$: for transitions 1 and 2:

$$\boldsymbol{\Delta E_1 = E_\infty - E_3 = \left(0 - \frac{1}{3^2}\right)(-13.6) = 1.51\ eV}$$

$$\boldsymbol{\Delta E_2 = E_5 - E_4 = \left(\frac{1}{5^2} - \frac{1}{4^2}\right)(-13.6) = 0.306\ eV}$$

Chapter III:

Atomic spectroscopy

I-Introduction:

Atoms cannot rotate or oscillate, so electronic transitions occur only when they absorb or emit energy and produce linear spectra. The atomic spectrum includes the emission or absorption of atoms, meaning that there are two techniques within the atomic spectra: the atomic **absorption** technique and the atomic **emission** technique

l-1-Excitation potential:

Atomic spectra are defined as a bundle of electromagnetic wavelengths that is emitted from an excited atom when it returns to a stable state (Figure (III-1)). What is meant by an excited atom is that the atom obtains energy that works to transfer its electrons from a lower energy level (stable) to a higher energy level (excited), and when these return Electrons to the stable level, it emits the energy it has acquired in the form of light radiation, which is called the atomic spectrum, and these radiations that make up the spectrum can be either visible or invisible.

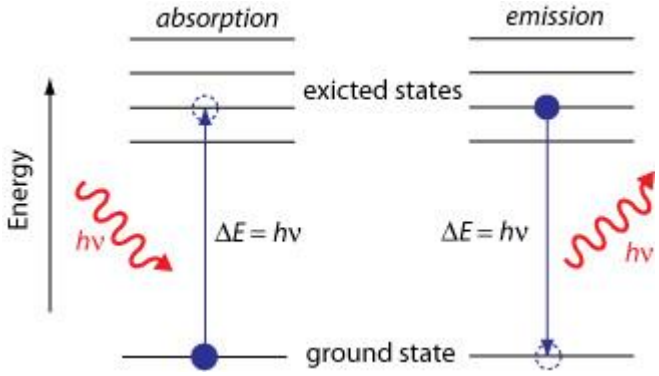


Figure (III-1): The excitation potential

• A distinction must be made between **excitation** and **ionization**, which means the **definitive removal** of an electron from the atom to become an ion. What matters to us in studying the spectrum is that we do not make the atom, while exposing it to external influences, reach the degree of ionization, otherwise we will fail to detect the energy levels.

I-2- The Frank-Hertz experiment (تجربة فرانك – هيرتز):

Bohr's theory showed that atomic electrons exist in specific or quantized levels of energy, and Planck had assumed at the beginning of this century that the vibrating electrons in the cavity behave in a way that indicates that they have specific levels of energy. Frank and Hertz were able in 1914- that is, after one year After the publication of Bohr's theory - experimental confirmation of the existence of quantum levels of the atom.

•So the point of the experiment:

Confirmation of Bohr's hypothesis that energy levels in an atom are quantized.

•The idea of the experiment:

The experiment aims to study the interaction of electrons with gas atoms.

The following figure (III-2) shows the experimental tools:

1) A vacuum tube containing **mercury gas** (Hg) and inside it **a filament** F and **three electrodes**:

a - Cathode C

b- Anode A that has many holes and voltage V is positive with respect to the cathode.

c- The Plate P whose voltage V_r is small and negative with respect to anode A and is constant throughout the experiment.

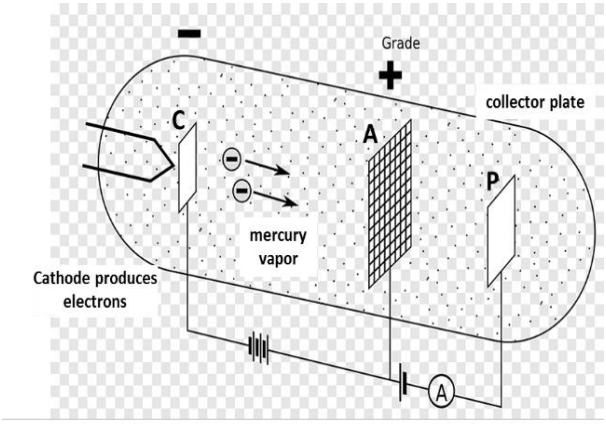


Figure 3: Schematic diagram of the Frank and Hertz experiment

Figure (III-2): Schematic diagram of the Frank and Hertz experiment.

•Explanation of the experiment:

When we start to turn on the voltage at a certain value, we notice that thermal electrons are emitted as a result of heating the cathode C by the filament F and

they accelerate towards the anode A. I will now put the curve that shows the relationship between the voltage difference and the current that the two scientists reached after the experiment.

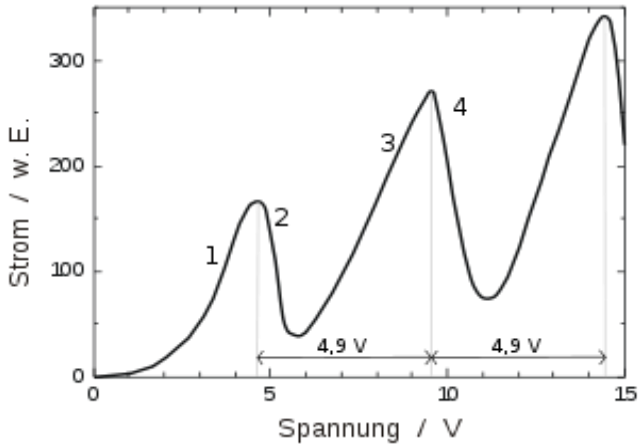


Figure (III-3): Current intensity as a function of voltage.

- And the question arises: Why in the graph do we notice that the current takes high and low values?
- If the electrons had elastic collisions with the mercury atoms, the electrons would reach the anode A with a movement energy equal to eV, then some electrons would pass through the holes A and head towards the plate P, after which any of the following would occur:

a- The electrons do not reach the plate P if their kinetic energy at A is not sufficient to overcome the impeding voltage, as the impeded voltage Vr is the voltage of the plate P.

b- The electrons reach the plate P if their kinetic energy at A is sufficient to overcome the obstructing voltage "the plate voltage".

- At a certain value of the voltage V, the number of electrons that reach P is calculated by measuring the electronic current I by the ammeter in the anode circuit A and the plate P.

- Figure (III-3) shows the results obtained by Frank and Herzl to change the current I against the voltage V. It is noted in this figure that when we start to increase the voltage from zero, the current also increases with it at the beginning, but when the voltage becomes equal to 4.9 volt, the current decreases sharply as the voltage increases, even if it is by slight amounts. After about 5 volts, the current begins to increase again.

Explanation:

Because when the electrons gained a movement energy of 4.9eV, an interaction occurred between the electrons and the mercury atoms, and this interaction did not occur when the energy was less than that.

It means that at this energy the probability of the electron interacting with the mercury atom becomes very large and that the interacting electron loses all its kinetic energy in excitation of the atom and cannot reach the P-plate.

- If the voltage V is slightly greater than 4.9V, then the electrons with energy of 4.9V have come very close to anode A, and a large number of these electrons have lost all their energy in the excitation processes near it. Then these electrons accelerate again towards the anode A and reach its holes with insufficient energy to overcome the impeding voltage Vr, the voltage of the plate P, and therefore they will not reach the plate P, i.e. the current will decrease sharply.
- If the voltage is relatively greater than 4.9V, the excitation processes will occur before the electrons approach the anode A and away from it, and there will be a greater chance for the electrons that lost 4.9eV and then reach the anode hole to have gained enough energy to overcome the impeding voltage Vr and thus reach the plate P and increase current I again. In other words, the

electron has excess energy after the elastic collision between electrons and atoms, so that this energy enables it to reach the elevator.

The previous explanations agree with the presence of intermittent levels of energy in the mercury atom, similar to the hydrogen atom. Assuming that the difference between the first excitation level and the ground level of the mercury atom is 4.9eV, the atom does not accept any energy less than 4.9V from the electrons, which is called the "critical voltage or excitation voltage." If this were true, then the atom excited by 4.9 eV of energy should spontaneously return from the first excitation level at the ground level by emitting a photon of wavelength.

$$\lambda = \frac{hc}{\Delta E} = \frac{1240eVnm}{4.9eV} \approx 253.1\text{nm} \qquad (\mathbf{III-1})$$

Frank and Hertz experimentally verified the existence of a wave line with a wavelength of 253.7 nm emitted from mercury gas at V = 4.9 V. The wavelength of this line corresponds to a difference in energy of 4.9 eV. It has also been verified after the emission of any line of the spectrum when the energy of the electrons is less than 4.9. eV.

- When V is increased to become greater than a sufficient value of 4.9V, the current will increase until we get a second peak at V=9.8. For the first level of excitement. By increasing the voltage, the excitation processes are repeated for multiples of 4.9eV.

In general, the second peak represents one of two possibilities:

1- Excitation of the atom from the ground level to a level higher than the excitation levels, and the electron loses energy equal to the energy difference ΔE between the stability orbit and the orbit in which the electron settled, and the V for this peak is greater than the V for the first peak…

2- Excitation of two or more atoms to the same level of excitation of the first, where the electron loses an energy of ΔE in each excitation, and the V of these peaks is equal to multiples of the V of the first peak, and the second possibility is predominant on the curve of Figure 4.

- The results of Frank Hertz's experiment were confirmed, which was considered the first practical evidence **of quantification of energy levels** in an atom. It also gives a direct measurement of the difference in energy levels in the atom, by increasing the difference in the voltage of accelerating the electrons to higher energies, where it was found that the current continues to increase and suddenly decreases sharply, which indicates that the energy of the electrons is absorbed by the mercury atom to be raised to the first excitation level as well as to the level of The second excitation, as in the figure below (Figure (III-4)) which shows a diagram of the energy levels of a mercury atom..

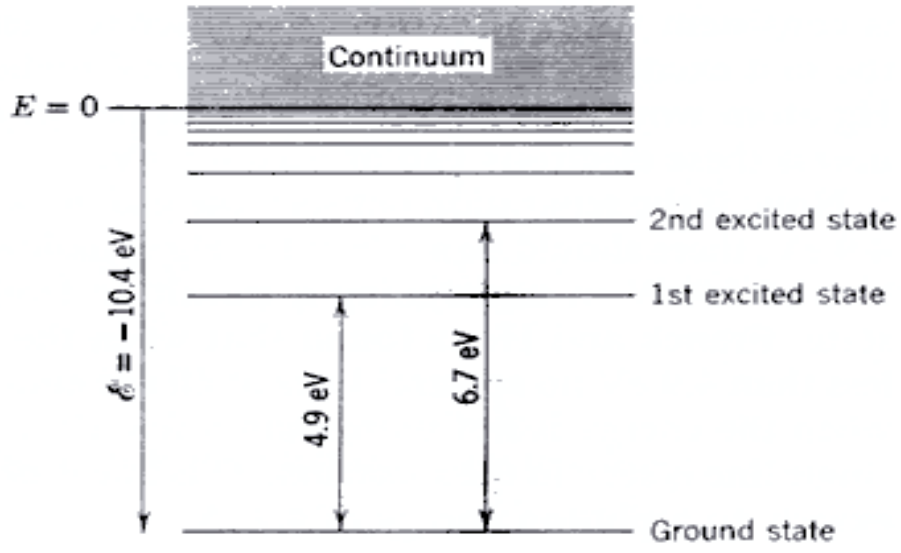


Figure (III-4): Energy level diagram of a mercury atom

This was verified by spectral analysis of the light emitted from the agitation of mercury buttons.

- Here is the summary of the experience:

The existence of intermittent energy levels has been achieved empirically with a series of experiments initiated by Frank and Hertz, which have directly demonstrated the existence of energy levels, and that these levels are actually those suggested by watching **the linear spectra**.

II- Atomic spectra (الأطياف الذرية):

In the second half of the 19th century, scientists studied the spectra of several gases when placed under low pressures and high temperatures. At these conditions, the gas molecules disintegrate into their atoms, and the recorded spectrum is the spectrum of the atoms that make up the gas. It was found that these spectra are very complex for atoms with a large atomic number, and relatively simple in the case of some elements such as hydrogen.

II-1- Hydrogen atomic spectrum (الطيف الذري للهيدروجين):

Inside a tube containing hydrogen gas and at low pressure, we apply a high voltage difference where the hydrogen gas is excited, it glows and produces red light as shown in Figure (III-5), and when the light beam passes through a prism, it decomposes into its primary compounds to draw on the photographic plate discontinuous discontinuous lines in the spectrum regions above Violet (UV), visible (V) and infrared (IR).

- Each of the lines represents electromagnetic radiation with a specific frequency and wavelength.
- In the year 1988, Balmer showed that the wavenumber $\bar{\upsilon}$ of the

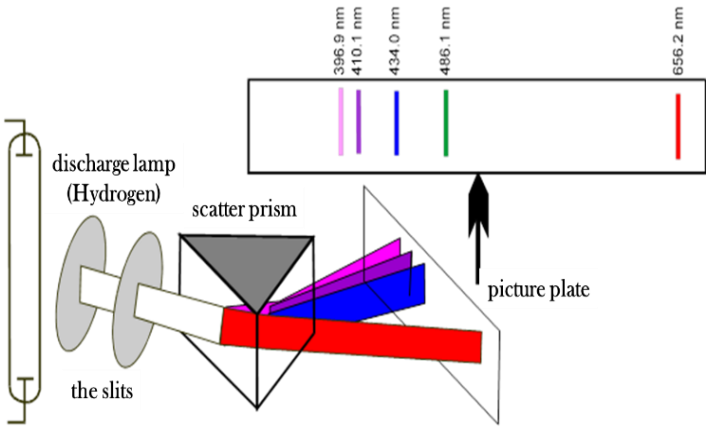


Figure (III-5): The production of hydrogen atomic spectrum

▪hydrogen spectral lines in the visible field can be expressed by the empirical relation:

$$\bar{\upsilon} = 1.097.10^5 \left(\frac{1}{2^2} - \frac{1}{n^2}\right) cm^{-1} \quad , n = 3, 4, 5, \ldots\ldots \qquad (III-2)$$

▪Rydberg also generalized this relationship after discovering other lines in the invisible field:

$$\bar{\upsilon} = \frac{1}{\lambda} = R_H \left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \qquad (III-3)$$

where: n_1 and n_2 are natural numbers and, R_H is Rydberg's constant, R_H = 1,0967758 .10^5 cm^{-1} (cgs), R_H = 1,0967758 .10^7 m^{-1} (MKSA).

While the energy of the emitted photon:

$$\Delta E = h\nu = h\frac{c}{\lambda} = hcR_H \left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \qquad (III-4)$$

▪There are five series of hydrogen emission spectrum as shown in the following table:

Table 1: Spectral groups of the hydrogen atom

Series	Region of spectrum	Equation for wavenumber($\bar{\upsilon}$)
Lyman series	Ultraviolet	$\bar{\upsilon} = R_H \frac{1}{1^2} - \frac{1}{n^2}$, n =2,3,4,5...
Balmer series	Visible/ultraviolet	$\bar{\upsilon} = R_H \frac{1}{2^2} - \frac{1}{n^2}$, n =3,4,5,6..
Paschen series	Infrared	$\bar{\upsilon} = R_H \frac{1}{3^2} - \frac{1}{n^2}$, n =4,5,6,7...
Breckett series	Infrared	$\bar{\upsilon} = R_H \frac{1}{4^2} - \frac{1}{n^2}$, n =5,6,7,8...
Pfund series	Infrared	$\bar{\upsilon} = R_H \frac{1}{5^2} - \frac{1}{n^2}$, n =6,7,8...

II-2- Explanation of the hydrogen atom emission spectrum:

When electrons from the cathode collide with hydrogen molecules, they disintegrate. And when these atoms are exposed to electric discharge and low pressure, they are in a state of excitement or activation, as their electrons gain a quantity of energy that transfers them to energy levels higher than their basic levels, those excited electrons do not settle in their new levels (every sentence prefers to be in a state stability), but soon loses part of its acquired energy to return to its basic levels either in one step or it passes other energy levels with the emission of light.

Note:

- An atom that is stable in energy means that its electrons occupy the lowest energy levels.
- An active (unstable) atom means that its electrons occupy the highest energy levels.

As shown in Figure (III-6), when an electron falls from any excited state to:

- Basic level: $n_2>1$ and $n_1=1$, where **n** is a natural number

It gives lines in the emission spectrum of the hydrogen atom specific to **the Lyman series.**

- Basic level: $n_2>2$ and $n_1=2$, where **n** is a natural number

It gives lines in the emission spectrum of the hydrogen atom specific to **the Balmer series.**

- Basic level: $n_2>3$ and $n_1=3$, where **n** is a natural number

It gives lines in the emission spectrum of the hydrogen atom specific to **the Paschen series.**

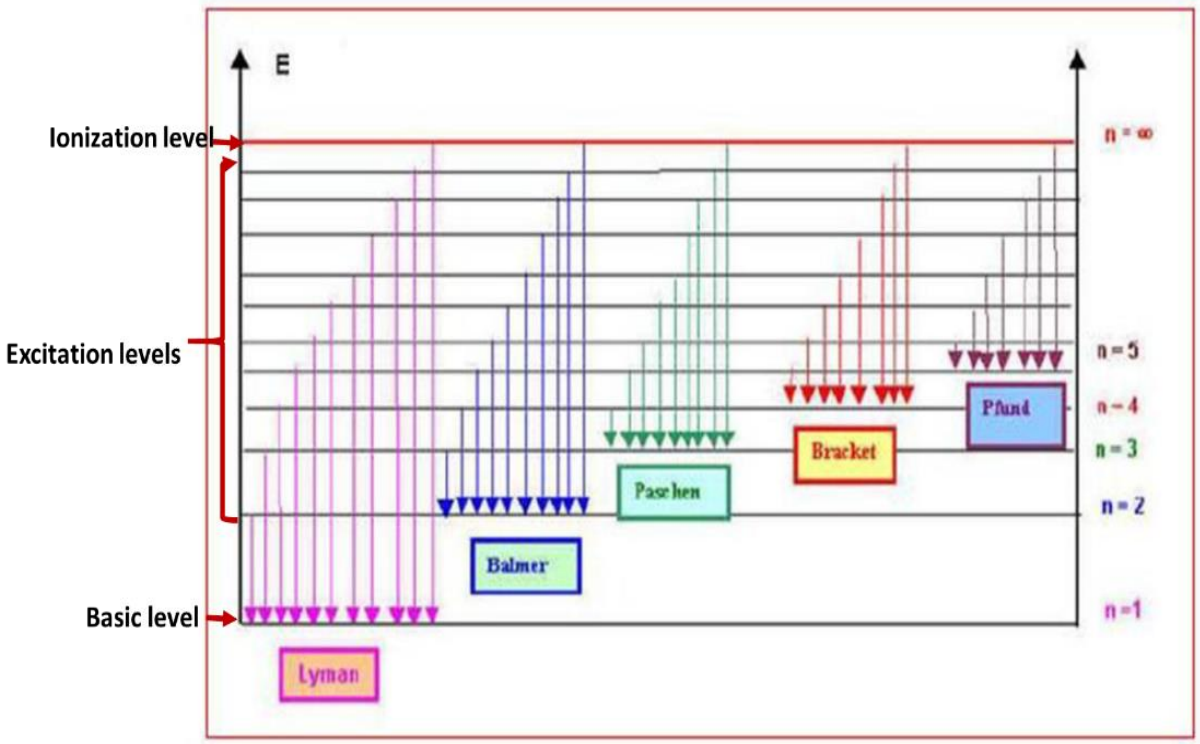


Figure (III-6): Electronic transitions of the spectrum of the hydrogen atom.

- Basic level: $n_2>4$ and $n_1=4$, where **n** is a natural number

It gives lines in the emission spectrum of the hydrogen atom specific to **the Brackett series.**

- Basic level: $n_2>5$ and $n_1=5$, where **n** is a natural number

It gives lines in the emission spectrum of the hydrogen atom specific to **the Pfund series.**

On this basis, the emission spectrum of the hydrogen atom can be represented as follows:

III-Rydberg–Ritz combination principle (مبدأ التوافق لريتز):

The Rydberg–Ritz combination principle is **an empirical rule** proposed by Walther Ritz in 1908 to describe the relationship of the spectral lines for all atoms, as a generalization of an earlier rule by Johannes Rydberg for

the hydrogen atom and the alkali metals. The principle states that the spectral lines of any element include frequencies that are either the sum or the difference of the frequencies of two other lines. Lines of the spectra of elements could be predicted from existing lines. Since the frequency of light is proportional to the wavenumber or reciprocal wavelength, the principle can also be expressed in terms of wavenumbers which are the sum or difference of wavenumbers of two other lines.

Another related version is that the wavenumber or reciprocal wavelength of each spectral line can be written as the difference of two terms. The simplest example is the hydrogen atom, described by the Rydberg formula:

$$\frac{1}{\lambda} = R_H\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \qquad (\mathbf{III-5})$$

Where λ is the wavelength, R_H is the Rydberg constant, n_1 and n_2 are positive integers such that $n_1<n_2$. This is the difference of two terms of form:

$$T_n = \frac{R_H}{n^2} \qquad (\mathbf{III-6})$$

I- Spectral lines broadening (تعريض الخطوط الطيفية):

In the **Atomic Spectroscopy**, the emission spectrum of a chemical element is made up of **discrete lines** corresponding to **the electromagnetic radiation** emitted by the electrons of its atoms when they "drop" from a higher energy state to one of less energy (Figure (III-7)). For each transition between states, the energy of the emitted photon is equal to the energy difference of the two states according to the **Planck equation**:

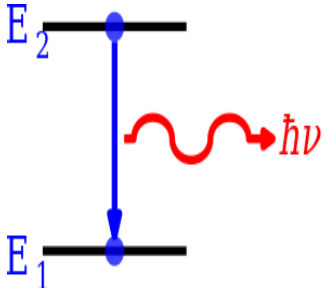


Figure (III-7): The emission of electromagnetic radiation

$$\Delta E = E_2 - E_1 = h\nu \qquad (\mathbf{III-7})$$

which relate **the energy of the transition** with **the frequency of the photon** of light emitted (h is the constant of Planck).

However, it can be verified experimentally, using high-resolution spectrometers, that the width of the **spectral lines** in terms of wavelength is **not infinitesimal** but it has a measurable value which depends on many factors. This phenomenon is known as "**spectral broadening**" and is widely used and studied to deeply understand the **light emission phenomena** (Figure (III-8)).

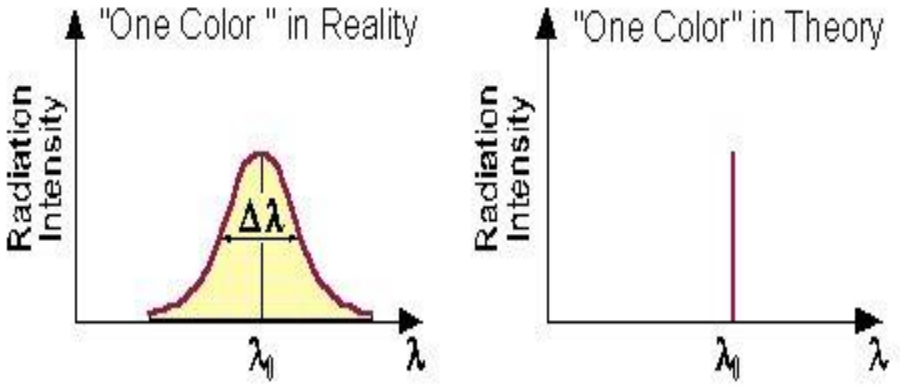


Figure (III-8): Width of spectral line (laser radiation) in theory and in reality.

Physical phenomena that broaden the spectral lines are essentially the following:

- Quantum mechanical uncertainty, ΔE, of the energy value E of atomic levels with not infinity lifetime: **natural broadening.**
- **Thermal (doppler) broadening**. It is due to the doppler shift caused by the motion, relative to the observer, of the atoms which emit light
- **Collisions** among the excited atoms that induce the electronic transition and consequent emission of light. This factor in practice results in a shortening of the lifetime of the excited state, resulting in an increase in energy uncertainty ΔE.

VI-1- Natural broadening (التعريض الطبيعي):

We have considered that the value of energy for each level is precisely defined, which means that the value of uncertainty in determining this value is nil. However, this contradicts the **principle of uncertainty**, because according to this principle, the excited atom of level E_2 must remain in this level for a final time until the uncertainty in determining the value of the energy of the level is equal to zero (Figure (III-9)).

$$\Delta E.\Delta t > h \Rightarrow h\Delta\nu.\Delta t > h \Rightarrow \boldsymbol{\Delta\nu > \frac{1}{\Delta t}} \qquad (\mathbf{III-8})$$

We know that the time for an atom to remain in the excited state is indefinite. If an atom is excited to an energy level, it will remain in it for a specific period of time, then return to the ground level of energy and emit photons. In order to overcome this contradiction between the principle of doubt and the limited lifetime of the atom remaining excited, we assume that the energy levels have amplitude and that the atoms are distributed with the greatest probability at the frequency ν_0 as in the figure shown.

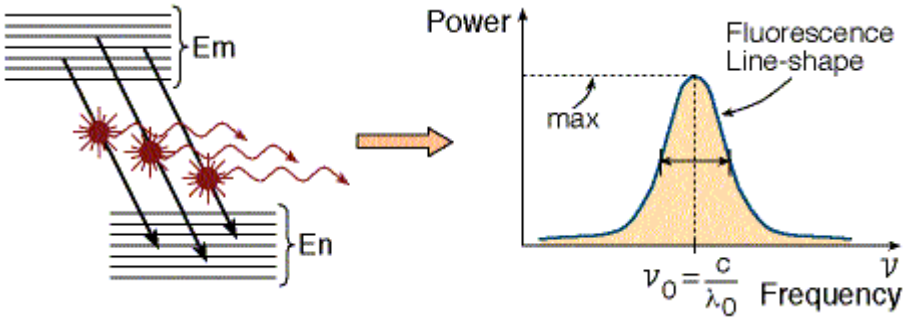


Figure (III-9): Emission line between wide (real) energy levels.

The spectral line amplitude due to the natural broadening of an energy level i can be estimated by the following equation:

$$\Delta\nu_i = \frac{1}{2\pi\tau_i} \qquad (\mathbf{III-9})$$

VI-2- Doppler broadening (تعريض دوبلر):

Thermal broadening is due to the Doppler effect that occurs when the radiating atoms have a movement relative to the observer. The random atomic movement of the atoms is directly related to the temperature, which is why this broadening mechanism is called thermal. As we know from the Maxwell-Boltzmann statistics the speed of gas atoms follows a **Gaussian** profile and the mean energy is on the order of **kT**, where k is the Boltzmann constant and T is the temperature. Mathematically it can be shown that the spectral line **broadening** profile is also **Gaussian**, with a value given by:

$$\Delta\upsilon_D = \frac{\upsilon_0}{c}\sqrt{\frac{2KT}{m}} \qquad (\mathbf{III-10})$$

The equation shows that broadening increases with temperature and is higher for light atoms. By doing the calculations you see that for hydrogen at the temperature of 6000°K, the width of the **Hα** line is **0.036 nm**.

We note also that the amplitude of broadening is directly proportional to the original frequency of the emitted spectrum. Therefore, the Doppler phenomenon affects large frequencies such as electromagnetic emission in the blue color range or more. As for the frequencies in the red color range or less, the Doppler phenomenon does not play a major role in the amplitude.

VI-3- Collision broadening (التعريض التصادمي):

It is a homogeneous broadening to the spectral line caused by the exposure of the radiating or absorbing atom to **collision with its neighboring molecules and atoms**, for example in the case of gas, the atom collides with atoms or other molecules similar or different to it as well as with neutral or charged particles

and even with the walls of the container that contains it. The collision process, whose time is very short, affects the radiation and causes a sudden change in phase, which causes exposure to the spectral line, and its amount depends on the average time between two collisions ($\boldsymbol{\tau_c}$). As for the shape of the spectral line resulting from the atoms of the substance that suffer from the collision process, it is also given by the Lorentz function, where the width of the line is at the middle of the intensity:

$$\boldsymbol{\Delta\nu = \frac{1}{\pi\tau_c}} \qquad \textbf{(III – 11)}$$

Where $\boldsymbol{\tau_c}$ is the time between collisions.

The prerequisite for this equation is that the time between collisions is much greater than the time of the collision itself.

The spectral lines broadening is also divided into two types known as **homogeneous and inhomogeneous.**

- **The homogeneous broadening (التعريض المتجانس) :**

All atoms in an ensemble are broadened in the same way by the same amount. Its origins are natural expansion, scattering by phonons in a crystal and collisional broadening in a gas. The shape of the spectral lines in this case is described by **the Lorentz function**, which is given by the formula:

$$\boldsymbol{g(\nu,\nu_0) = \frac{2/(\pi\Delta\upsilon)}{1+[2(\nu_0-\nu)/\Delta\upsilon]^2}} \qquad \textbf{(III – 12)}$$

- **The inhomogeneous broadening (التعريض الغير المتجانس) :**

All atoms in an ensemble are perturbed by a different amount. Its origins are Doppler broadening, Environmental variations: Composition or doping variation or impurities, Lattice imperfections... The shape of the spectral lines in this case is described by **the Gaussian function**, which is given by the formula:

$$g(\nu,\nu_0)=\frac{2}{\Delta\nu}\sqrt{\frac{ln2}{\pi}}exp((-2(\nu_0-\nu)/\Delta\nu)^2 ln2) \qquad (\mathbf{III-13})$$

V- Heisenberg's uncertainty principle (مبدا الارتياب لهايزنبارغ):

The Heisenberg uncertainty principle states that for an object with a small mass that cannot be determined and at the same time its position and velocity, this lack of accuracy is not due to an error in the measurement, but rather a disturbance due to the measurement itself. For the electron, its path cannot be determined, so we do not use the particle property of the electron, but we use the property This principle is given by the following relation:

$$\Delta x\Delta p \geq \frac{h}{2\pi} \qquad (\mathbf{III-14})$$

Whereas, $\boldsymbol{p}$ is the moment, which is the product of the mass **m** of the electron multiplied by its velocity **v**, $\boldsymbol{\Delta p}$ represents the error in determining the value of the moment, **h** is the Planck's constant, $\boldsymbol{\Delta x}$ is the error in determining the location of the electron.

Application:

1-Mention **Heisenberg's "principle** of indeterminacy" and write the mathematical relationship that expresses it?

2-A bullet has a mass of **10 g** and is moving at a speed of **1600 m/s**. If its location is known with an uncertainty of **0.1 cm**, determine the minimum absolute uncertainty and then the minimum relative uncertainty involved in calculating its speed.

3-Same as the previous question for an electron accelerated under a potential difference of 1200 volts and its location was determined with a uncertainty of 1Å? Compare the results of questions 2 and 3.

Response:

Heisenberg's indeterminacy principle or uncertainty principle: It states that it is not possible to determine the location (x) and momentum (P) of an electron with acceptable accuracy and at the same time, and it is expressed by the following mathematical relationship:

$$\boldsymbol{\Delta x \Delta p \geq \frac{h}{2\pi}} \qquad (\mathbf{III-15})$$

1- Determine the absolute minimum uncertainty and the minimum relative uncertainty involved in calculating the bullet speed:

-Minimum absolute uncertainty $\boldsymbol{\Delta\nu}$ for the bullet:

We have:

$\Delta x \Delta p \geq \frac{h}{2\pi}$ and we have too: $P = mV \Rightarrow \Delta P = m\Delta V$

Substituting in Heisenberg's expression we find:

$$m\Delta V \Delta x = \frac{h}{2\pi} \Rightarrow \Delta V = \frac{h}{2\pi m \Delta x} \qquad (\mathbf{III-16})$$

Where: $\Delta x = 0.1cm = 10^{-3}m$

$$\Delta V = \frac{6.62 \times 10^{-34}}{2 \times (10 \times 10^{-3})(10^{-3})} = 1.05 \times 10^{-29} m/s$$

2-Minimum relative uncertainty $\left(\frac{\Delta\nu}{\nu}\right)$ of the bullet:

$$\frac{\Delta\nu}{\nu} = \frac{1.05 \times 10^{-29}}{1600} = 6.5 \times 10^{-33}$$

3-Determine the absolute minimum uncertainty and the minimum relative uncertainty involved in calculating the electron speed:

The lowest absolute uncertainty $(\Delta\nu)$ for an electron; From the previous question we have:

$$\Delta V = \frac{h}{2\pi m \Delta x} = 0.1158 \times 10^{7} m/s$$

-The lowest relative uncertainty $(\boldsymbol{\frac{\Delta\nu}{\nu}})$ for an electron:

We first calculate the speed $\boldsymbol{V}$ of the electron:

We have: $\boldsymbol{E_c = \frac{1}{2}mV^2 = eV \Rightarrow V = \sqrt{\frac{2eV}{m}} = \sqrt{\frac{2\times(1.6\times10^{-19})\times1200}{9.1\times10^{-31}}} = 2.05 \times 10^7 m/s}$

The relative uncertainty is:

$$\frac{\Delta\nu}{\nu} = \frac{0.1158 \times 10^7}{2.05 \times 10^7} = 0.06$$

-Comparison between the results of questions 2 and 3:

We note that the absolute uncertainty and the relative uncertainty in the case of the bullet are very small compared to the case of the electron, and therefore it can be said that the uncertainty in the speed on the macroscopic scale has no physical meaning, while in the atomic (microscopic) scale it has great importance. The position of the electron is inaccurate, meaning it is not possible to determine the position and speed of the electron with extreme precision and at the same time, and this proves the validity of **Heisenberg's principle of indeterminacy**.

Chapter IV:

Atoms with many electrons

I-Introduction

We have previously shown how the Bohr model viewed the electron as a particle orbiting the nucleus in non-radiative quantum energy levels. This treatment led to an analysis that combines the classical and quantitative concepts. While the model achieved excellent successes in agreeing with some experimental results, it was not able to explain the splitting of spectral lines. And these difficulties have been removed when the complete quantitative model that relies on the Schrödinger equation was used to describe the atom.

The potential energy of the hydrogen atom is written in the following form:

$$U(r) = -k_e \frac{e^2}{r}$$

The steps used to solve the problem of the hydrogen atom are to substitute **U(r)** in the Schrödinger equation and find appropriate solutions to the equation, also U depending on the diagonal coordinate **r**. If the time-dependent Schrödinger equation is expanded to three-dimensional coordinates, the result is:

$$-\frac{\hbar}{2m}\left(\frac{\partial^2\psi}{2x^2}+\frac{\partial^2\psi}{2y^2}+\frac{\partial^2\psi}{2z^2}\right)+U\psi = E\psi \qquad (\mathbf{IV-1})$$

It is easy to solve this equation for the hydrogen atom if the rectangular coordinates are converted to spherical coordinates. In spherical coordinates, the point in space is represented by three variables, namely r, θ and φ, so **r** that is the radial distance from the point of origin ($r = \sqrt{x^2+y^2+z^2}$). As shown in the Figure (IV-1), the angular coordinate **θ** determines its angular position in relation

to the coordinate **z.** And when the position ray is projected onto the plane (**xy**), the angular coordinate **φ** will determine the projection of the angular position with respect to the coordinate **x**.

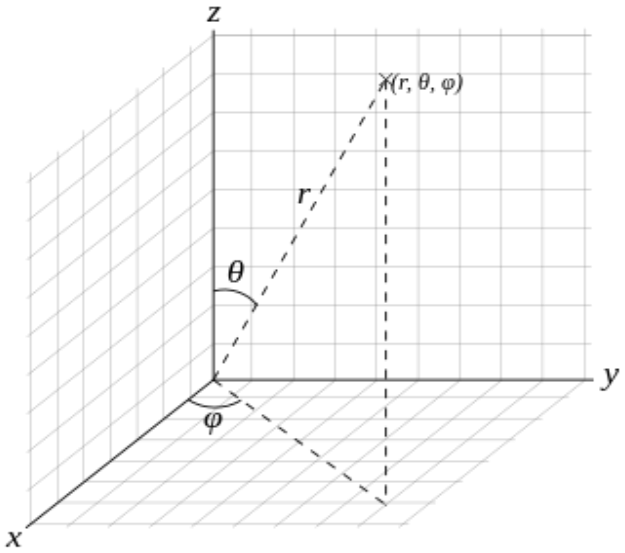


Figure (IV-1): The spherical coordinates

And when separating the dependence of time from the dependence of place in the solutions of the Schrödinger

equation for one dimension, in this case we can separate the three variables of place by writing $\boldsymbol{\psi}(r, \theta, \varphi)$ as a product of functions for each variable alone:

$$\boldsymbol{\psi(r,\theta,\phi) = R(r)f(\theta)g(\varphi) = R_{n,l}(r)Y_{l,m}(\theta,\varphi)} \qquad \textbf{(IV - 2)}$$

where $\boldsymbol{R_{n,l}(r)}$ is the diagonal function.

$\boldsymbol{Y_{l,m}(\theta,\varphi)}$ are the spherical harmonic wave functions.

When using **the boundary conditions** on all of these functions, we will get three different quantum numbers (**n, l, m**) for each allowed state of the hydrogen atom.

The first quantum number associated with the diagonal of the wave function R(r) is called **the principal quantum number** and is denoted by the symbol (**n**). The diagonal wave equation will lead to functions that give the probability of finding the electron at a certain diagonal distance from the nucleus. It was found that the energies of the allowed states of hydrogen are:

$$E_n = \left(\frac{k_e e^2}{2a}\right)\frac{1}{n^2} = -\frac{13.6}{n^2}\ eV, \quad n = 1, 2, 3, \ldots \ldots \qquad (\mathbf{IV-3})$$

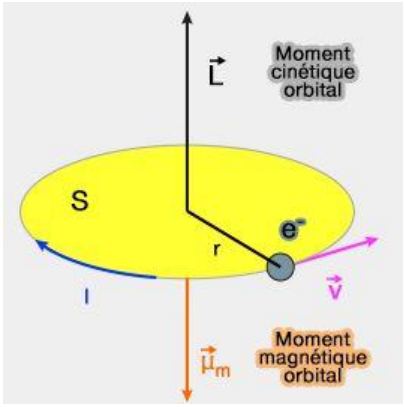
This result is in perfect agreement with that obtained **in Bohr's theory.**

II-Angular moments and shell filling:

II-1- Orbital angular momentum from the classical point of view:

Consider a particle of mass **m** moving in an elliptical orbit under the effect of a central force (Figure (IV-2)). The angular momentum vector or angular angular momentum or also orbital angular momentum L of the particle in question has an amplitude given by:

$$\vec{L} = \vec{r}\Lambda\vec{p} = \vec{r}\Lambda m\vec{v} \Rightarrow L = mvr \qquad (\mathbf{IV-4})$$



Figure(IV-2): The angular momentum of a particle moving under the effect of a central force

where **r** is the perpendicular distance between the direction of motion and the center of the force, **v** is the speed of the particle. The direction of the vector L is given by the usual right-hand rule.

The moment of the force (torque or moment) exerted on the particle is given by the variation of its orbital angular momentum:

$$\boldsymbol{\tau = \frac{d\vec{L}}{dt}} \qquad \textbf{(IV – 5)}$$

However, given that the force applied to the particle is central (Coulomb force for an electron orbiting a nucleus), the moment exerted **will be zero**. Thus, the orbital angular momentum vector L of a particle orbiting under the action of a central force will have a constant direction and amplitude at each point of the elliptical trajectory. We then say that **the orbital angular momentum** is **conserved**. Likewise, the component $L_z = L\cos\theta$ along the (Oz) axis will also be constant during the elliptical movement.

II-2-Magnetic dipole moment (classical):

An electron moving in a circular path will produce a current loop. The current loop will in turn produce a magnetic field similar to a magnet strip (Figure (IV-3)). In the same way as for the magnet, a magnetic dipole moment μ_L will be associated with the electron orbiting around the nucleus. It is given by:

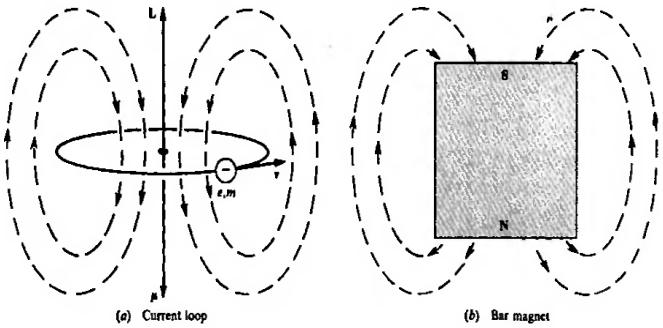


Figure (IV-3): The magnetic dipole moment

$$\boldsymbol{\overrightarrow{\mu_L} = -\frac{e}{2m}\vec{L}} \qquad \textbf{(IV – 6)}$$

➢ Because of **the negative charge** of the electron, **the direction of the magnetic moment vector will be opposite** that of the orbital moment vector $\vec{L}$.

II-3- Magnetic potential energy (classical):

Suppose that an electron orbiting around a nucleus forming a current loop (or equivalently the magnet bar) is placed in an external magnetic field B. The loop will undergo a twist:

$$\vec{\tau} = \overrightarrow{\mu_L} \Lambda \vec{B} \qquad (\mathbf{IV-7})$$

Who will try to align the magnetic moment vector $\vec{L}$ of the electron with the direction of the magnetic field $\vec{B}$. The electron + nucleus system placed in a magnetic field then has a magnetic potential energy E_B given by:

$$E_B = -\overrightarrow{\mu_L}.\vec{B} \qquad (\mathbf{IV-8})$$

By choosing the direction of the magnetic field B as the direction $\overrightarrow{e_z}$ and using eq. (IV-6) the magnetic potential energy for an orbiting electron is written:

$$E_B = \frac{e}{2m_e} L.B \Rightarrow \boldsymbol{E_B = \frac{e}{2m_e} L_z B} \qquad (\mathbf{IV-9})$$

II-4- Zeeman's experience:

An experiment measuring the interaction between an atom's internal magnetic moment and an external magnetic field was carried out by Dutch physicist Pieter Zeeman in 1896, before the emergence of quantum mechanics.

In Zeeman's experiment, an atom is subjected to an external magnetic field and its emission spectrum is measured (through the measurement of the wavelengths of the emitted light) and compared to the spectrum of the same atom measured by absence of the magnetic field.

Experiment shows that when the atom is immersed in an external magnetic field, each spectral line (line) of the atom is divided into a set of discrete lines. Furthermore, the change observed on the frequencies of the spectral lines is proportional to the amplitude of the applied magnetic field. This was called the Zeeman effect. The observation of these new spectral lines shows that an atom subjected to an external magnetic field has additional energy levels.

- Before the emergence of quantum mechanics, it was impossible to find an explanation for the results of Zeeman's experiment. Indeed, the explanation of the Zeeman effect requires a wave analysis which predicts a quantification of the orbital angular momentum.

II-5- Quantitative study:

II-5-1-Schrödinger equation for single atoms electron:

Consider a hydrogenoid atom composed of a nucleus with charge $\mathbf{Z_e}$ and an electron with charge (**-e**) interacting through the Coulomb potential:

$$U(r) = -\frac{1}{(4\pi\varepsilon_0)}\frac{Ze^2}{r} \qquad (\mathbf{IV-10})$$

Where r is the distance between the two particles. From eq. (6), we can see that U(r) depends only on r. It is therefore considered as a symmetrical central potential. We will note m_e the mass of the electron and M the mass of the nucleus. The relative momentum (relative electron-nucleus motion) will be designated by p while P will designate the total momentum associated with the movement of the center of mass of the atom. The energy of the atom can be separated into two parts: the kinetic energy of the center of mass given by

$P^2/(m_e + M)$and the energy of relative motion (internal energy) given by the Hamiltonian operator:

$$\widehat{\boldsymbol{H}} = \frac{\boldsymbol{p^2}}{\boldsymbol{2\mu}} - \frac{\boldsymbol{Ze^2}}{\boldsymbol{(4\pi\varepsilon_0)r}} \qquad (\mathbf{IV-11})$$

with a reminder:

$$\boldsymbol{\mu} = \frac{\boldsymbol{m_e M}}{\boldsymbol{m_e + M}} \qquad (\mathbf{IV-12})$$

The reduced mass of the two particles. In the center of mass reference frame (or P = 0) and in the position representation, the physical description of the nucleus-electron system amounts to solving the stationary Schrödinger equation (independent of time).

$$\widehat{\boldsymbol{H}}\boldsymbol{\psi(r)} = \boldsymbol{E\psi(r)} \qquad (\mathbf{IV-13})$$

which results in the equation:

$$\left[-\frac{\boldsymbol{\hbar^2}}{\boldsymbol{2\mu}}\boldsymbol{\nabla^2} - \frac{\boldsymbol{Ze^2}}{\boldsymbol{(4\pi\varepsilon_0)r}}\right]\boldsymbol{\psi(r)} = \boldsymbol{E\psi(r)} \qquad (\mathbf{IV-14})$$

or $\boldsymbol{\hbar}$=h/2π with h the Planck constant, $\boldsymbol{\nabla^2}$ is the Laplacian and **E** represents the set of possible energies for the atom in question.

Mathematically, the energies E correspond to the eigenvalues of the Hamiltonian operator $\widehat{\boldsymbol{H}}$.

The interaction potential given by eq. (IV − 10) being central, it will be convenient to write the wave equation in terms of spherical coordinates:

$$\boldsymbol{\psi(r)} = \boldsymbol{\psi(r,\theta,\phi)} \qquad (\mathbf{IV-15})$$

In this coordinate system, the radial and angular variables of the wave function can be separated and the solution to equation (IV-14) can take the form:

$$\psi_{n,l,m_l}(r,\theta,\phi) = R_{n,l}(r)Y_{l,m_l}(\theta,\varphi) \qquad (\mathbf{IV-16})$$

Where $\psi_{n,l,m_l}(r,\theta,\phi)$ represents the special quantum state by **the principal quantum number** n, **the orbital moment quantum number** l and **the magnetic quantum number** m_l. $R_{n,l}(r)$ represents the radial wave functions corresponding to the state designated by the principal quantum number **n** and the orbital moment quantum number l. The angular part is written as a function of the spherical harmonics $Y_{l,m_l}(\theta,\varphi)$ corresponding to the quantum number of the orbital moment l and the magnetic quantum number m_l.

Such wave functions describe the stationary state of the special system by the combination $(n; l; m_l)$ with a quantized energy E_n given by equation (IV-14) and **an orbital angular momentum** L whose amplitude is also quantized such as:

$$L = \sqrt{l(l+1)}\,\hbar \qquad (\mathbf{IV-17})$$

II-5-2-Quantifying the magnitude of angular momentum orbital:

Recall that Bohr's theory is based on the quantification of the radius of the orbit of the electron around the nucleus in the atom and consequently the quantification of the amplitude of its orbital angular momentum expressed by the equation:

$$L = n\hbar \qquad (\mathbf{IV-18})$$

A wave analysis shows that the orbital angular momentum does not have the single value $n\hbar$ as predicted by Bohr's theory (Figure (IV-4)). It turns out that for a given principal quantum number n (defining an energy level E_n) there are **n** possible values for the amplitude $L = |\mathbf{L}|$, given by:

$$L = \sqrt{l(l+1)}\,\hbar \qquad (\mathbf{IV-19})$$

where l is an integer called **the orbital Angular moment quantum number** taking the values l = 0, 1, 2, 3, …., n-1.

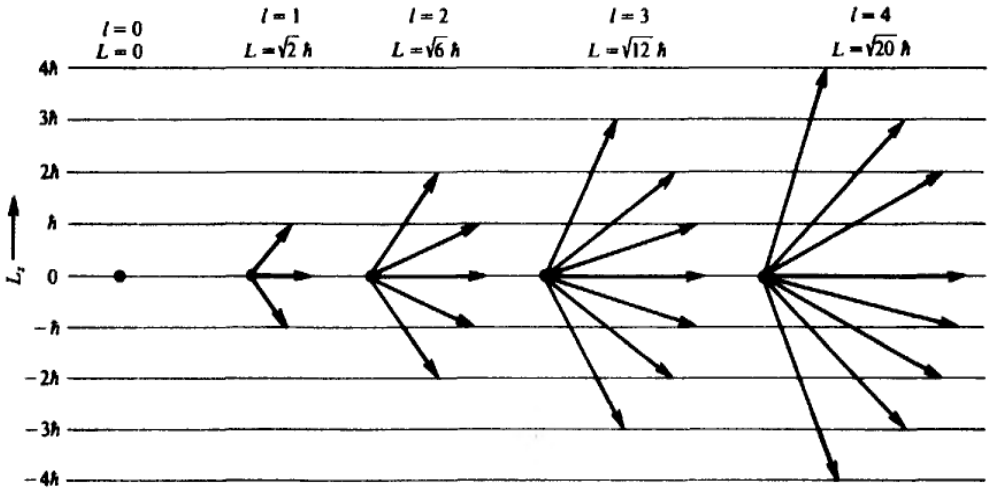


Figure (IV-4): The different possible orientations of the orbital angular momentum L for l = 0; 1; 2; 3 and 4.

Particularly, for the minimum energy state corresponding to n = 1, the only possible value of l is l = 0 and the orbital angular momentum is zero.

II-5-3-Quantification of the direction of angular momentum orbital

Suppose that an atom with a single electron is subjected to a magnetic field $\vec{B} = B\vec{e}_z$. A wave analysis shows that the direction of the orbital kinetic moment

cannot be arbitrary. $\boldsymbol{L}$ will be oriented such that the component $\boldsymbol{L_z}$ following the direction $\vec{e}_z$ corresponding to the direction of the magnetic field takes values discretized by the relation:

$$\boldsymbol{L_z = m_l \hbar} \qquad \boldsymbol{(IV-20)}$$

where $\boldsymbol{m_l}$ is an integer called **magnetic quantum number** defined in the interval:

$$\boldsymbol{m_l = l, l-1, l-2, \ldots\ldots - - l-1), -l.} \qquad \text{(IV-21)}$$

II-5-4-Interaction of an atom with a magnetic field external:

Explanation of the Zeeman effect:

The Zeeman effect can be described using a semi-classical model. This means that we consider the electron as a particle orbiting classically around the nucleus and the angular momentum as being a quantity following the results of quantum mechanics. We learned previously that when an atom with a single electron is subjected to a magnetic field, it acquires a magnetic potential energy $\boldsymbol{E_B}$ due to the magnetic field given by equation (IV-10). Total energy of a single-electron atom subjected to a magnetic field of magnitude $\boldsymbol{B = B_z}$ will be given by:

$$E_{B\neq 0} = E_n + E_B \Rightarrow \boldsymbol{E_{B\neq 0} = E_n + \frac{e}{2m_e} L_z B} \qquad \boldsymbol{(IV-22)}$$

where $\boldsymbol{E_n}$ is the energy quantified before switching on the magnetic field $\vec{\boldsymbol{B}}$. Taking into consideration the quantification of the component $\boldsymbol{L_z}$ given by eq. (IV − 16), the previous equation is written:

$$\boldsymbol{E_{B\neq 0} = E_n + m_l \frac{e\hbar}{2m_e} B} \qquad \boldsymbol{(IV-21)}$$

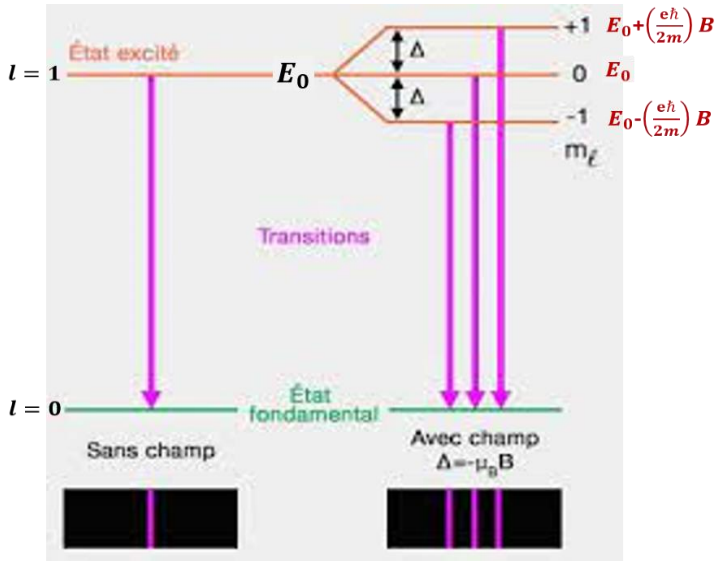


Figure (IV-5): Representation of the Zeeman effect: subdivision of an energy level $\boldsymbol{E_n}$ for a quantum state with $\boldsymbol{l = 1}$ in several energy sublevels under the effect of the external magnetic field.

Thus, in the presence of an external magnetic field each energy level $\boldsymbol{E_n}$ will be divided into $(\boldsymbol{2l + 1})$ sub-energy levels according to the $\boldsymbol{2l + 1}$ possible values of $\boldsymbol{m_l}$ (Figure (IV-5)). The separation between the sub-energy levels will be proportional to the intensity **B** of the magnetic field to which the atom is subjected. The factor:

$$\boldsymbol{\mu_B = \frac{e\hbar}{2m_e}} = 5.79 \times \frac{10^{-5} eV}{T} = 9.27 \times \frac{10^{-24} J}{T} \qquad \boldsymbol{(IV - 22)}$$

is called **the Bohr magneton** (the Bohr magneton) or also the **Bohr-Procopiu magneton**.

➢ Quantum mechanics then predicts that there are even more energy levels when the atom is subjected to a magnetic field. For this purpose, additional spectral lines will be detected on the emission spectrum of the atom as illustrated in Fig.$(IV - 2)$. These predictions are in perfect agreement with the experimental results leading to the Zeeman effect. The discrete subdivision of the energy levels then constitutes experimental evidence for the quantification of the

orbital kinetic moment following the predictions of quantum mechanics. If the orientation of the orbital kinetic moment was not quantized, the $\boldsymbol{L_z}$ component could have taken any value (as in Bohr's theory) and the atomic spectrum would have been continuous.

II-5-5- The spin of the electron:

In 1925, the physicists S.A. Goudsmit and G. E. Uhlenbeck suggested that the electron has an intrinsic angular momentum called the spin of the electron denoted **S**. This angular momentum of spin will give rise to a magnetic moment of spin $\boldsymbol{\mu_S}$.

In the previous section we were able to show that for the orbital kinetic moment characterized by the orbital quantum number $\boldsymbol{l}$, the component $\boldsymbol{L_z}$ in the direction of the magnetic field can have $\boldsymbol{2l + 1}$ possible discrete values following the $\boldsymbol{2l + 1}$ possible values of the magnetic quantum number ml leading to $\boldsymbol{2l + 1}$ possible directions of the orbital kinetic momentum vector $\vec{L}$. In the same way, if we specify the angular momentum of spin $\boldsymbol{S}$ by a quantum number of spin $\boldsymbol{s}$, knowing that there are only two possible orientations (following the results of the Stern-Guerlach experiment), we will have $\boldsymbol{2 = 2s + 1}$. This gives the unique value of $\boldsymbol{s = 1/2}$. The amplitude of the spin angular momentum will therefore be:

$$\boldsymbol{S = \sqrt{s(s+1)}\,\hbar = \frac{\sqrt{3}}{4}\hbar} \qquad \textbf{(IV-23)}$$

The $\boldsymbol{S_z}$ component of the spin angular momentum along the $\boldsymbol{\vec{e}_z}$ axis will be given by:

$$S_z = m_s\hbar, \quad with: \ m_s = -s, s = -\frac{1}{2}, \frac{1}{2} \qquad (IV-24)$$

The two spin orientations are generally called **spin up** for $m_s = 1/2$ and **spin down** for $m_s = -1/2$.

The magnetic moment of spin of the electron μ_S is proportional to its intrinsic angular momentum S through the relation:

$$\mu_S = -g_S \frac{e}{2m_e} S \qquad (IV-25)$$

where the dimensionless constant $g_S \approx 2$ is called **the Landé factor** (Landé factor or spin g-factor).

- It should be noted that particles other than the electron, such as the proton and the neutron, also have spin angular momentum.

II-5-6- Total angular momentum:

An electron in an atom has two angular moments: **the orbital angular moment** due to its movement around the nucleus and **the spin angular moment** (intrinsic, generally considered to be due to its movement around itself). The total angular momentum is obtained from the vector addition of the two angular momenta of the electron:

$$\vec{J} = \vec{L} + \vec{S} \qquad (IV-26)$$

Total angular momentum represents the change in total twist applied to the atomic system. Its amplitude is quantified:

$$J = \hbar\sqrt{j(j+1)} \qquad (IV-27)$$

where the quantum number j takes the values $\boldsymbol{l+s}$, $\boldsymbol{l+s-1}$, ... $\boldsymbol{l-s}$. The component of the total angular momentum along the ez axis is also quantified as follows:

$$\boldsymbol{J_Z = m_j\hbar, \quad m_j = j, j-1, \ldots\ldots, -j} \qquad \textbf{(IV-28)}$$

Thus, we summarize the quantitative numbers adopted to build the atom:

1- **The main quantum number** $\boldsymbol{n = 1, 2, 3, \ldots\ldots, n}$, which represents the basic energy levels without any fission and takes values.

2-**The Orbital quantum number**: $\boldsymbol{l = 0, 1, 2, 3, \ldots\ldots, n-1}$. It represents the sub-energy levels branching off from the basic levels. The quantum numbers of the orbital quantum number are described with lowercase English letters, i.e.:

$$\boldsymbol{l = 0, \leftrightarrow l = s}$$

$$\boldsymbol{l = 1, \leftrightarrow l = p}$$

$$\boldsymbol{l = 2, \leftrightarrow l = d}$$

$$\boldsymbol{l = 0, \leftrightarrow l = s}$$

$$\boldsymbol{l = 4, \leftrightarrow l = g}$$

3- **The Orbital magnetic quantum number**: $\boldsymbol{m_l = -l, -l+1, \ldots\ldots 0, \ldots\ldots, l-1, +l}$. It is another condition for the splitting of each state of the orbital quantum number, thus increasing the number of branches of the original plane.

4- **The spin magnetic quantum number**: $\boldsymbol{m_s = \mp\frac{1}{2}}$. It splits each state of the orbital magnetic quantum number into two energy levels.

III- Atoms with many electrons:

Unlike the hydrogen atom and hydrogen atoms composed of a nucleus and a single electron, it is not possible to obtain an exact analytical solution to the Schrodinger equation for atoms composed of a nucleus and two or more electrons (system with more than two particles). Disruptive methods can be used in the case of light atoms with two electrons (Helium) or three electrons (Lithium). However, these methods become insufficient for a larger number of electrons. Indeed, a detailed treatment of an atom with several electrons requires taking into consideration:

i. The kinetic energy of electrons as well as their potential energies in the attractive Coulomb electrostatic field of the nucleus.

ii. Coulomb electrostatic repulsion between electrons.

iii. The magnetic interaction of electron spins with their orbital moments (spin-orbit interaction).

iv. Other effects such as the spin-spin interaction between electrons, different attractive corrections, radiative and nuclear corrections due to the mass of the nucleus, to its size, to the magnetic dipole moment..... etc.

In the following study, we will initially neglect the spin-orbit interaction (iii) as well as all the small effects mentioned in (iv). Thus, we will only take into consideration the attractive Coulomb interaction between each electron and the nucleus (which we assume to have infinite mass) in addition to the force of

mutual repulsion between the electrons. The Hamiltonian of the atom with N electrons in the absence of an external field is written then in the form:

$$\widehat{H} = \sum_{i=1}^{N}\left[\frac{p_i^2}{2m_e} - \frac{1}{4\pi\varepsilon_0}\frac{Ze^2}{r_i}\right] + \frac{1}{2}\sum_{i\neq j=1}^{N}\frac{1}{4\pi\varepsilon_0}\frac{e^2}{r_{ij}} \qquad (\mathbf{IV-29})$$

where $\boldsymbol{r_i}$ represents the relative coordinate of electron i with respect to the nucleus and $\boldsymbol{r_{ij}} = |r_i - r_j|$ is the distance between electrons $\boldsymbol{i}$ and $\boldsymbol{j}$. Each term of the first sum represents the Hamiltonian of a single electron. It is the second sum, a term of mutual interaction between electrons also known as the electrostatic interaction, which differentiates the Hamiltonian of atoms with several electrons from that of the hydrogenoid atoms. The study of the bound states of the system consists of finding the stationary solutions of the Schrödinger equation (for the purely spatial wave function without the spin component):

$$\widehat{H}\psi(r_1, r_2, , \ldots . r_N) = E\psi(r_1, r_2, , \ldots . r_N) \qquad (\mathbf{IV-30})$$

Or,

$$\psi(r_1, r_2, , \ldots . r_N) \approx \psi_1(r_1)\psi_2(r_2) \ldots . \psi_N(r_N) \qquad (\mathbf{IV-31})$$

is the wave function of the many-particle system and $\boldsymbol{E}$ is the total energy of the system.

As we have already alluded to, the analytical solution of the many-body Schrödinger equation is very difficult and approximations must be used for the study of many-electron atoms. The simplest approximation is **the central mean field approximation**.

The central mean field approximation consists of assuming that in an atom with N electrons, each electron moves independently of the other (N-1) electrons of the atom. Thus, the Schrödinger equation for the wave function mono-electronic ($\boldsymbol{r_i}$) given by:

$$\left[-\frac{\hbar^2}{2m_e}\nabla_i^2 - U(r_i)\right]\psi(r_i) = E_i\psi(r_i) \qquad (\mathbf{IV-32})$$

In the mean **central field approximation**, since the potential acting on each electron is central, the spatial part of the single-electron atomic orbitals (r) can be decomposed:

$$\psi(r) = R'_{n,l}(r)Y_{l,m_l}(\theta,\varphi) \qquad (\mathbf{IV-33})$$

where the angular component $Y_{l,m_l}(\theta,\varphi)$ remains identical to the angular part of the atomic orbitals of the Hydrogen atom. The radial part $R'_{n,l}(r)$ will be the solution of the equation:

$$-\left(\frac{1}{2}\frac{d^2}{dr^2}+\frac{1}{r}\frac{d}{dr}-\frac{\hbar^2}{2m_e}\frac{l(l+1)}{r^2}\right)R'_{n,l}(r)+U(r)R'_{n,l}(r) = E_nR'_{n,l}(r) \qquad (\mathbf{IV-34})$$

Therefore, the radial solutions $R'_{n,l}(r)$ from which we can arrive at the atomic orbitals $\psi(r)$ to describe the structure and dynamics of many-electron atoms depends on the exact expression of $U(r)$.

IV-Electronic structure of the atom:

Until now, we have studied quantum systems at several energy levels, but with only one electron (hydrogenoids). We found that the behavior of the electron is

described through the values of its four quantum numbers n, l, m_l, m_s. When these four quantum numbers are known, we say that the state of the single-electron system is specified.

IV-1-Pauli exclusion principle:

By analyzing spectroscopic data of atoms with several electrons, **Wolfgang Pauli** concluded **in 1924** that **two electrons cannot occupy the same quantum state**. In other words, **two electrons cannot have the same combination of quantum numbers** (n, l, m_l, m_s). This is called **the Pauli exclusion principle**. This principle allows the explanation of the electronic configuration of atoms and thus of the periodic table of elements.

IV-2-Hund's rule:

Hund's rule states that: Every orbital in a subshell is singly occupied with one electron before any one orbital is doubly occupied, and all electrons in singly occupied orbitals have the same spin.

IV-3-Building an atom with electrons:

For simplicity, we build each basic level separately, as follows:

- **The first energy level**: It is usually called the **K** level and contains:

$$n = 1, \quad l = 0, \quad m_l = 0, \quad m_s = \mp\frac{1}{2}$$

1. There are two energy levels here according to the magnetic quantum number, and therefore the maximum capacity for electrons according to Pauli's principle in this level is two electrons.

2. This level takes the following notation $1s^2$ for the electronic distribution and means that we are in the first principal level and the orbital state s where the orbital quantum number is equal to zero, and the exponent 2 means the maximum electron accommodation and is a complete and accurate description of the position of the energy electron in the atom.

- **The second energy level**: It is usually called the **L** level and contains:

$$n = 2, \qquad l = 0, 1, \qquad m_l = \begin{cases} m_0 = 0 \\ m_1 = -1, 0, +1 \end{cases}$$

1. Each of the previous states of m_l values split into two states according to the spin magnetic quantum number $m_s = \pm\frac{1}{2}$.
2. According to the previous two conditions, the number of fission states from the basic state is **eight**, and the number of energy levels ready to receive electrons according to the Pauli principle is **eight**.
3. The electronic distribution of this level takes the following form:

$$2s^2\ 2p^6$$

- **The thrid energy level**: It is usually called the **M** level and contains:

$$n = 3, \qquad l = 0, 1, 2, \qquad m_l = \begin{cases} m_0 = 0 \\ m_1 = -1, 0, +1 \\ m_2 = -2, -1, 0, +1, +2 \end{cases}$$

1. Each of the previous states of m_l values split into two states according to the spin magnetic quantum number $m_s = \pm\frac{1}{2}$.

2. According to the previous two conditions, the number of fission states from the basic state is **eighteen**, and the number of energy levels ready to receive electrons according to the Pauli principle is **eighteen**.
3. The electronic distribution of this level takes the following form:

$$3s^2\ 3p^6 3d^{10}$$

- **The fourth energy level**: It is usually called the **N** level and contains:

$$n = 4, \qquad l = 0, 1, 2, 3, \qquad m_l = \begin{cases} m_0 = 0 \\ m_1 = -1, 0, +1 \\ m_2 = -2, -1, 0, +1, +2 \\ m_3 = -3, -2, -1, 0, +1, +2, +3 \end{cases}$$

1. Each of the previous states of m_l values split into two states according to the spin magnetic quantum number $m_s = \pm\frac{1}{2}$.
2. According to the previous two conditions, the number of fission states from the basic state is **thirty-two**, and the number of energy levels ready to receive electrons according to the Pauli principle is **thirty-two**.
3. The electronic distribution of this level takes the following form:

$$4s^2\ 4p^6 4d^{10} 4f^{14}$$

And so on for the rest of the cases. The following table shows all cases:

Table 1: Detailed table of all fullness states for sub-energy levels

n	s $l=0$	p $l=1$	d $l=2$	f $l=3$	g $l=4$	h $l=5$	k $l=6$	The total number of electrons in the shell $N_n = 2n^2$	Shell name
1	$1s^2$							2	K
2	$2s^2$	$2p^6$						8	L
3	$3s^2$	$3p^6$	$3d^{10}$					18	M
4	$4s^2$	$4p^6$	$4d^{10}$	$4f^{14}$				32	N
5	$5s^2$	$5p^6$	$5d^{10}$	$5f^{14}$	$5g^{18}$			50	O
6	$6s^2$	$6p^6$	$6d^{10}$	$6f^{14}$	$6g^{18}$	$6h^{22}$		72	P
7	$7s^2$	$7p^6$	$7d^{10}$	$7f^{14}$	$7g^{18}$	$7h^{22}$	$7k^{26}$	98	Q

IV-4-Quantitative structure of the atom with electrons:

Due to the difficulty of preserving the electronic distribution, which is subject to anomalies, physicists and chemists have developed several diagrams that guide the distribution process at energy levels. The diagram shown below in Figure (IV-6) represents one of the easiest of these diagrams, which enables one to write the electronic configuration of an atom, regardless of the sufficient number of electrons.

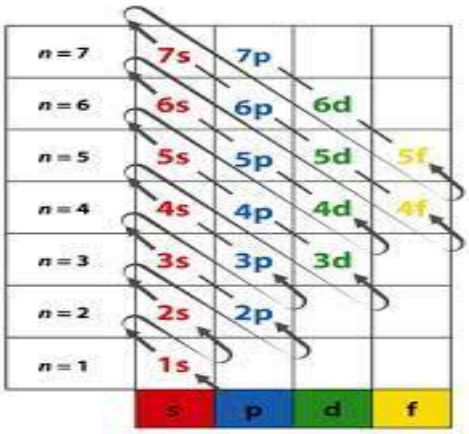


Figure (IV-6): The filling of the atomic orbitals is done following the order given by the arrows.

IV-5-Atomic angular moments:

The orbital angular momentum of an atom is obtained through the vector sum of the orbital angular momenta of the electrons.

$$\vec{L} = \sum_i \vec{L_i} \qquad (\mathbf{IV-35})$$

Similarly, the spin angular momentum of the atom is the vector given by the sum of the individual spin angular moments of the electrons:

$$\vec{S} = \sum_i \vec{S_i} \qquad (\mathbf{IV-36})$$

The total angular momentum of the atom is given by:

$$\vec{J} = \sum_i \vec{J_i} \qquad (\mathbf{IV-37})$$

In the same way as for single-electron atoms, the amplitudes of the angular momenta are quantified in magnitude and direction by:

$$|\boldsymbol{L}| = \hbar\sqrt{\boldsymbol{L(L+1)}}, \quad |\boldsymbol{S}| = \hbar\sqrt{\boldsymbol{S(S+1)}}, \quad |\boldsymbol{J}| = \hbar\sqrt{\boldsymbol{J(J+1)}}, \qquad \textbf{(IV-38)}$$

$$\boldsymbol{L_z = M_L\hbar}, \quad \boldsymbol{S_z = M_S\hbar}, \quad \boldsymbol{J_z = M_J\hbar} \qquad \textbf{(IV-39)}$$

The magnetic quantum numbers of the atom are related to those of the electrons by the following addition relations:

$$\boldsymbol{M_L = \sum_i (m_l)_i}, \qquad \boldsymbol{M_S = \sum_i (m_s)_i}, \qquad \boldsymbol{M_J = M_L + M_S} \qquad \textbf{(IV-40)}$$

By knowing the values of $\boldsymbol{M_L}$, $\boldsymbol{M_S}$ and $\boldsymbol{M_J}$, it is possible to deduce the values of $\boldsymbol{L, S}$ and $\boldsymbol{J}$ from conditions:

$$M_L = L, L-1, L-2, \ldots\ldots, -L,$$

$$M_S = S, S-1, S-2, \ldots\ldots, -S,$$

$$M_J = J, J-1, J-2, \ldots\ldots, -J,$$

In spectroscopy, the value of L corresponding to the atomic state is designated by a capital letter according to the following table:

Values of L	0	1	2	3
Symbol	S	P	D	F

IV-6-The ground state of an atom that has a single valence electron:

IV-6-1- State of the Helium atom:

The helium atom consists of a charged nucleus $(-Ze)$ and two charged electrons $q = -e$. The Schrödinger equation for the helium atom in the atomic mass unit is given by the expression:

$$\left\{-\frac{\nabla_1^2}{2}-\frac{Z}{r_1}-\frac{\nabla_2^2}{2}+\frac{Z}{r_2}+\frac{1}{r_{12}}\right\}\psi = E\psi \qquad (\mathbf{IV-41})$$

Where r_1 and r_2 are the positions of the first and second electrons, respectively, and $|r_1 - r_2|$ is the distance between the first and second electrons, and the electrostatic repulsion of the electrons is proportional to $\frac{1}{r_{12}}$, by neglecting this repulsion and separating the wave function in the form:

$$\psi(r_1, r_2) = \psi_1(r_1)\psi_2(r_2) \qquad (\mathbf{IV-42})$$

Equation (35) is written in the form:

$$\left\{-\frac{\nabla_1^2}{2}-\frac{Z}{r_1}\right\}\psi_1(r_1) = E_1\psi_1(r_1)$$

$$\left\{-\frac{\nabla_2^2}{2}-\frac{Z}{r_2}\right\}\psi_2(r_2) = E_2\psi_2(r_2)$$

Where: $E = E_1 + E_2$

Both of these equations are similar to the Schrödinger equation for the hydrogen atom, and using this approximation, where $Z = 2$, the ground state energy of helium $n = 1$ is obtained, considering the independence of the movements of the two electrons from each other. The calculated energy value is not close to the experimental value of the ground state of the helium atom, so this approximation is very far from the results obtained experimentally, as it is expected that the

energy of the fundamental level is close to the value of 108.8 eV, while the experimental value is close to -79 eV, so more effective approximate methods must be used.

IV-6-2- The state of alkali atoms:

The valence electron is at ns^1 where:

$$L = l = 0, \qquad S = s = \frac{1}{2}$$

$$|L - S| \leq J \leq |L + S| \Rightarrow \frac{1}{2} \leq J \leq \frac{1}{2} \;\Rightarrow\; J = \frac{1}{2}$$

Therefore, the spectral symbol for the ground state of an alkali atom is: $^2S_{\frac{1}{2}}$.

- **Excited states of alkali atoms**

1-The transition of a valence electron from layer s to layer p:

$$\begin{cases} L = l = 1 \\ S = s = \frac{1}{2} \end{cases} \Rightarrow J = \frac{1}{2}, \frac{3}{2} \Rightarrow {}^2P_{\frac{1}{2}}, {}^2P_{\frac{3}{2}}$$

2-The transition of a valence electron from layer s to layer d:

$$\begin{cases} L = l = 2 \\ S = s = \frac{1}{2} \end{cases} \Rightarrow J = \frac{3}{2}, \frac{5}{2} \Rightarrow {}^2D_{\frac{3}{2}}, {}^2D_{\frac{5}{2}}$$

Chapter V

Absorption and stimulated emission (Laser effect)

I-Introduction:

In 1917, Einstein laid the theoretical foundation for the operation of lasers by studying the interaction of **electromagnetic radiation** with **matter** through the following three transitional processes: **Absorption process**, **Spontaneous Emission** and **Stimulated Emission**.

Einstein assumed that the atoms that make up matter are distributed into two energy levels: E_0 and E_1, where the energy level E_1 is known as the Ground State, while the energy level E_2 is known as the Excited State. The previous three transitions occur in matter between the two energy levels at any temperature, and this is known as **thermal equilibrium**.

- The relationship between the number of atoms in energy levels at **thermal equilibrium** is described by the **Maxwell-Boltzman** equation for statistical distribution (Figure (V-1)).

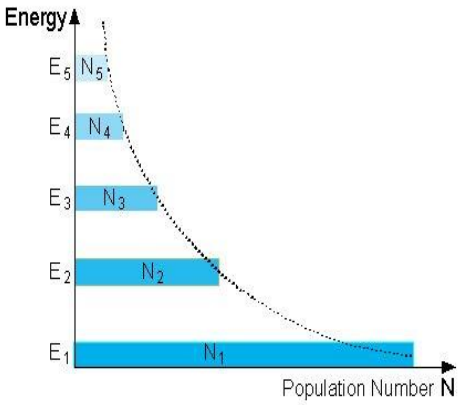


Figure (V-1): The Maxwell-Boltzman distribution

$$N_1 = \frac{g_1}{g_0} N_0 \exp\left(\frac{-h\nu}{KT}\right) \qquad (V-1)$$

Where **T** is the temperature in Kelvin and there is a thermal equilibrium at T, g is the statistical weight which represent the different ways of distribution of atoms all have the same energy (degeneracy).

I-1- Absorption:

When a stable atom is bombarded with a photon of appropriate energy, this leads to an increase in the speed of the electron's rotational movement in its own orbit, or it forces the electron to move from the stability level E_1 (fundamental level)

to a higher energy level E_2. Thus, the atom becomes in **an excited state**, and this phenomenon is known as **absorption**.

As shown in Figure (V-2) and since the absorption process occurs if a photon is available with an energy equal to **the energy difference** between the levels E_1 and E_2, that is:

$$\boldsymbol{E_2 - E_1 = \Delta E = h\nu} \qquad \textbf{(V - 2)}$$

In this case, we say that the atom is excited and the electron is excited.

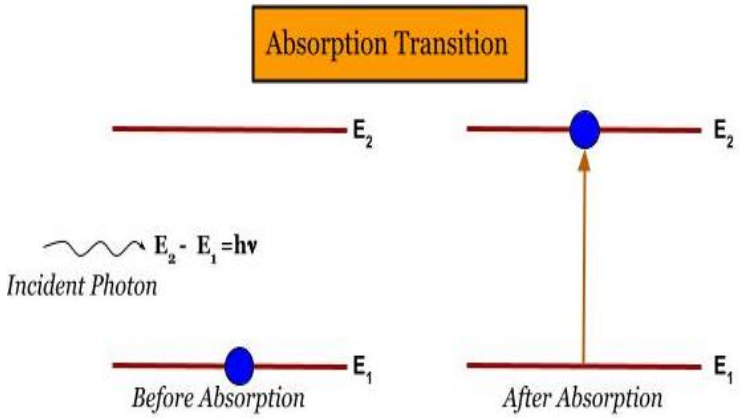


Figure (V-2): Mechanism of the absorption process.

The absorption process depends on the number of atoms in volume unit ($\boldsymbol{N_1}$) of the level $\boldsymbol{E_1}$, that is, the greater the $\boldsymbol{N_1}$, the greater the absorption process. This transition also depends on the parameter $\boldsymbol{B_{01}}$, which expresses **the probability of the absorption process occurring**. The rate of change in the $\boldsymbol{E_1}$ level population with respect to time is positive because the greater the rate of change, the greater $\boldsymbol{N_1}$.

Since the absorption process occurs if a photon is available with an energy equal to the energy difference between the levels $\boldsymbol{E_1}$ and $\boldsymbol{E_2}$, that is:

$$\boldsymbol{E_2 - E_1 = \Delta E = h\nu} \qquad \textbf{(V-3)}$$

If N_1 and N_2 is the population of energy E_1 and E_2, the number of atoms per unit volume that makes upward transitions from **the lower levels** to **the upper level per second** is called **the rate of absorption transitions (R_{abb})**. It is represented by:

$$R_{abb} = -\frac{dN_1}{dt} \qquad (V-4)$$

Where $-\frac{dN_1}{dt}$ is rate of decrease of population at the lower energy level E_1.

The rate of absorption transition can also be represented by the rate of the increase of population at the upper energy level E_2 . i.e

$$R_{abb} = \frac{dN_2}{dt} \qquad (V-5)$$

From equation (V-4) and equation (V-5):

$$R_{abb} = \frac{dN_2}{dt} = -\frac{dN_1}{dt} \qquad (V-6)$$

The number of **absorption transitions** occurring within the material at any instant will be **proportional to** the population in the lower energy level and the number of photons per unit volume in the incident beam. The rate of absorption can be expressed conveniently:

$$R_{abb} = B_{12}N_1\rho(\nu) \qquad (V-7)$$

Where $\rho(\nu)$ Energy density of incident light, B_{12} is **Einstein coefficient** for induced absorption and it indicates **the probability of an induced transition from level** 1→2.

At thermal equilibrium, the population in the lower energy state is much larger than that in the higher energy state. Therefore, as light propagates through the medium. These lower energy state atoms get absorbed.

I-2- Spontaneous emission:

Spontaneous emission is the process in which a quantum mechanical system (such as a molecule, an atom or a subatomic particle) transits from an excited energy state E_2 to a lower energy state E_1 (e.g., its ground state) and emits a quantized amount of energy in the form of a photon (Figure (V-3)).

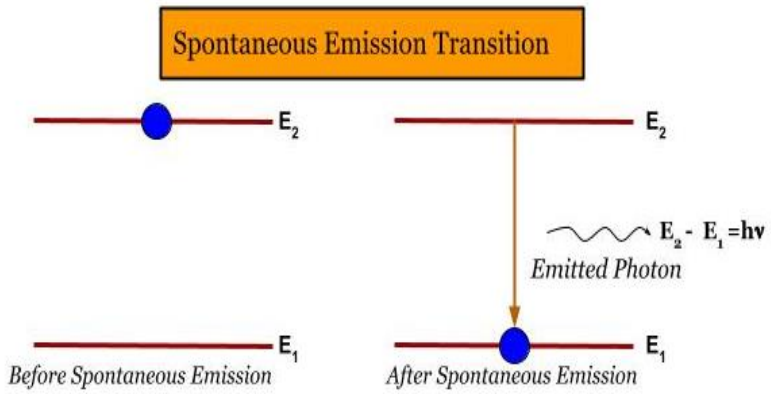


Figure (V-3): Mechanism of the Spontaneous emission process.

- The process in which an excited atom emits a photon all by itself and without any **external impetus** is known **as spontaneous emission**.

The rate of spontaneous transition $\boldsymbol{R_{sp}}$ is given by:

$$\boldsymbol{R_{sp} = -\frac{dN_2}{dt} = \frac{N_2}{\tau_{sp}}} \qquad \textbf{(V - 8)}$$

Where $\boldsymbol{\tau_{sp}}$ is the spontaneous radiative lifetime of the upper state.

The number of emitted photons will be proportional to the population of the excited energy state only and can be expressed as follows:

$$\boldsymbol{R_{sp} = -\frac{dN_2}{dt} = A_{21}N_2} \qquad \textbf{(V-9)}$$

Where A_{21} is known as **the Einstein coefficient** for **spontaneous emission** and is a function of frequency and properties of the material. It indicates the probability of spontaneous emission is independent of light energy.

We can deduce that from equation (V-8) and equation (V-9), the A_{21} coefficient is related to the spontaneous lifetime as:

$$A_{21} = \frac{1}{\tau_{sp}} \qquad (\mathbf{V-10})$$

I-2-1-Important features of spontaneous emission:

1. The process of spontaneous emission isn't amenable for control from outside.
2. It is essentially probabilistic in nature.
3. The light isn't monochromatic due to various line broadening processes.
4. Due to a lack of directionality, the light spreads in all directions around the source. The intensity of light decreases as the distance from the source increases.
5. The light is incoherent.
6. An atom can radiate into any of the 4π steradians with any sense of polarization.

I-3-Stimulated emission

If a photon with appropriate energy interacts with the excited atom, it can trigger the atom to undergo a transition to the lower level and emit another photon. This process is known as stimulated emission.

Thus the process of emission of a photon by an excited state atom through a forced transition occurring under the influence of an external agent is called

induced or stimulated emission (Figure (V-4)). The process may be represented as:

$$A^* + h\upsilon \rightarrow A + 2h\upsilon \qquad (\mathbf{V-11})$$

Where A is the lower energy state atom, A^* is the excited or higher energy state atom.

As a result of the stimulated emission process, we have two identical photons created from one photon and one excited state. Thus we have **amplification** in the sense that the number of photons has increased.

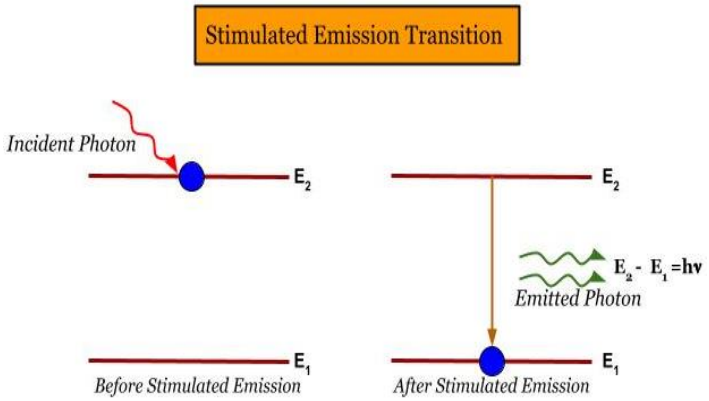


Figure (V-4): Mechanism of the Spontaneous emission process.

The rate of stimulated emission of photons is given as by:

$$R_{st} = B_{21}\rho(\upsilon)N_2 \qquad (\mathbf{V-12})$$

Where B_{21} is Einstein coefficient for stimulated emission.

I-3-1-Important features of spontaneous emission:

1-The process of stimulated emission is controlled from the outside.

2-The photon emitted in this process propagates in the same direction as that of the stimulated photon.

3-The emitted photon has exactly the same frequency, phase, and plane of polarization as the incident photon.

4-The light produced in the process is directional, coherence and monochromatics.

The third equations mentioned above represent the different cases through which electromagnetic radiation can **interact** with atoms of matter. In the case of thermal equilibrium at temperature $\boldsymbol{T}$, the number of atoms $\boldsymbol{N_1}$ in the energy level $\boldsymbol{E_1}$ is constant, i.e:

$$\boldsymbol{N_1 = constant} \qquad and \qquad \boldsymbol{\frac{dN_1}{dt} = 0}$$

Therefore:

$$\boldsymbol{\frac{dN_1}{dt} = -A_{21}N_2 + B_{12}N_1\rho(\nu) - B_{12}N_2\rho(\nu) = 0} \qquad \textbf{(V-13)}$$

Hence:

$$N_2\left(-A_{21} - B_{21}\rho(\upsilon)\right) + B_{12}N_1\boldsymbol{\rho(\nu)} = \mathbf{0}$$

$$N_2\left(A_{21} + B_{21}\rho(\upsilon)\right) = B_{12}N_1\boldsymbol{\rho(\nu)}$$

We get:

$$\boldsymbol{\frac{N_2}{N_1} = \frac{B_{12}\rho(\nu)}{A_{21} + B_{21}\rho(\nu)}} \qquad \textbf{(V - 14)}$$

Whereas the last three equations were derived from the condition of thermal equilibrium, and therefore the Maxwell-Boltzmann equation is satisfied.

$$\boldsymbol{\frac{N_2}{N_1} = \frac{g_2}{g_1}e^{\frac{-h\nu}{KT}}} \qquad \textbf{(V - 15)}$$

By comparing equation (V-14) with equation (V-15), we get the following equation:

$$\frac{B_{12}\rho(\nu)}{A_{21}+B_{21}\rho(\nu)}=\frac{g_2}{g_1}e^{\frac{-h\nu}{KT}} \qquad (V-16)$$

At high temperatures, the radiation intensity is large, and here the effect of the spontaneous emission process can be neglected, as it is not affected by temperature change.

When $KT >> h\nu$ we get $g_2/g_1 = N_2/N_1$ hence:

$$\frac{B_{12}}{B_{21}}=\frac{g_2}{g_1} \qquad (V-17)$$

From equation (V-14) we get:

$$\frac{g_2}{g_1}e^{\frac{-h\nu}{KT}}A_{21}+\frac{g_2}{g_1}e^{\frac{-h\nu}{KT}}B_{21}\rho(\nu)=B_{12}\rho(\nu) \qquad (V-18)$$

But:

$$\frac{g_2}{g_1}=\frac{B_{12}}{B_{21}}$$

$$\frac{g_2}{g_1}e^{\frac{-h\nu}{KT}}A_{21}+\frac{g_2}{g_1}e^{\frac{-h\nu}{KT}}B_{21}\rho(\nu)=\frac{g_2}{g_1}B_{12}\rho(\nu)$$

We get:

$$\frac{A_{21}}{B_{21}}=\rho(\nu)\left[e^{\frac{-h\nu}{KT}}-1\right]$$

$$\rho(\nu)=\frac{A_{21}}{B_{21}}\frac{1}{(e^{\frac{-h\nu}{KT}}-1)} \qquad (V-19)$$

Equation (V-19) called **Einstein equation for black body radiation**.

From the Bank equation of black body radiation:

$$\rho(\nu)=\frac{8\pi h\nu^3}{c^3}\frac{1}{\left(e^{\frac{-h\nu}{KT}}-1\right)}$$

we get:

$$\frac{A_{21}}{B_{21}} = \frac{8\pi h\nu^3}{c^3} \qquad (\mathbf{V-20})$$

The equation (V-17) and (V-20) are called **Einstein relations**. The second relation enables us to evaluate the ratio of the rate of **spontaneous emission** to the rate of **stimulated emission** for a given pair of energy levels.

- To evaluate the ratio between the spontaneous emission and the stimulated emission:

$$\rho(\nu) = \frac{A_{21}}{B_{21}}\frac{1}{R}$$

Where: $$R = \left(e^{\frac{-h\nu}{KT}} - 1\right)$$

- Thus the ratio for the spontaneous emission to the stimulated emission can be written as:

$$R = \frac{A_{21}}{B_{21}}\frac{1}{\rho(\nu)} \qquad (\mathbf{V-21})$$

From the above, we conclude that the process of stimulated emission competes with the processes of spontaneous emission and absorption, and in order to enlarge a light beam with stimulated emission, we must increase the rate of this process in relation to the other two processes. In order for this to be achieved, the radiation intensity and the number of the E_1 level must be increased, and this is known as Population Inversion.

I-4-Population inversion:

Population inversion is the process by which a laser medium is excited to create more atoms in higher energy state than in the ground state. This allows stimulated emission to happen and produces a coherent and monochromatic

beam of light. It is a fundamental principle in the operation of lasers. To achieve population inversion, atoms must be continuously excited from a lower energy level to a higher energy level and the process by which the atoms are excited to a higher energy level is called **pumping**. The laser must be pumped at a suitable wavelength to achieve this condition.

- Electrons within an atom occupy discrete energy levels. When an atom is in the ground energy state, its electrons jump to higher energy levels. When they return to their original energy levels, they release energy in the form of light. This process is called **spontaneous emission**. If the atoms are excited by an external photon, the process is known as **stimulated emission**. The light output then obtained will be coherent and monochromatic. In population inversion, more electrons in the ground state are excited to higher energy levels. This state is necessary for lasing action, as it allows stimulated emission to take place. In other words, **a population inversion** occurs when the number of atoms in an excited state is greater than the number of atoms in the ground state.

I-4-1-Condition for population inversion:

Let N_1 be the number of atoms in the ground state E_1 and N_2 be the number of atoms in the higher energy state E_2. Generally, the atoms in the ground state will be higher than that of the higher energy state and this is the thermal equilibrium condition given by $N_1 > N_2$. But, for population inversion to occur, the number of atoms in E_2 must be greater than E_1. i.e., $N_2 > N_1$ (Figure (V-5)).

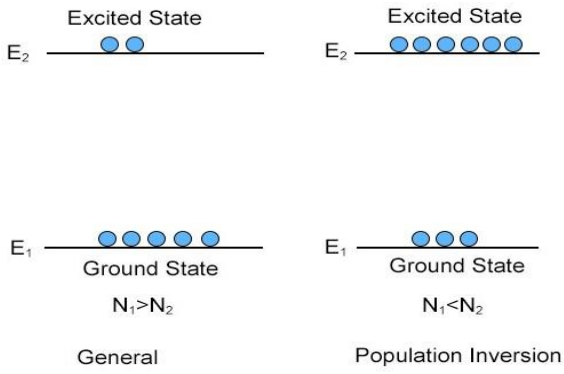


Figure (V-5): Energy level diagram

However, we need three or more energy states to achieve population inversion. The greater is the number of energy states the greater is the optical gain.

I-4-2-Three-level laser:

Consider a system consisting of three energy levels E_1, E_2, E_3 with N number of electrons as shown in Figure (V-6).

We assume that the energy level of E_1 is less than E_2 and E_3, the energy level of E_2 is greater than E_1 and less than E_3, and the energy level of E_3 is greater than E_1 and E_2.

Let us assume that initially the majority of electrons will be in the lower energy state or ground state (E_1) and only a small number of electrons will be in excited states (E_2 and E_3).

When we supply light energy which is equal to the energy difference of E_3 and E_1, the electrons in the lower energy state (E_1) gains sufficient energy and jumps into the higher energy state (E_3). This process of supplying energy is called pumping.

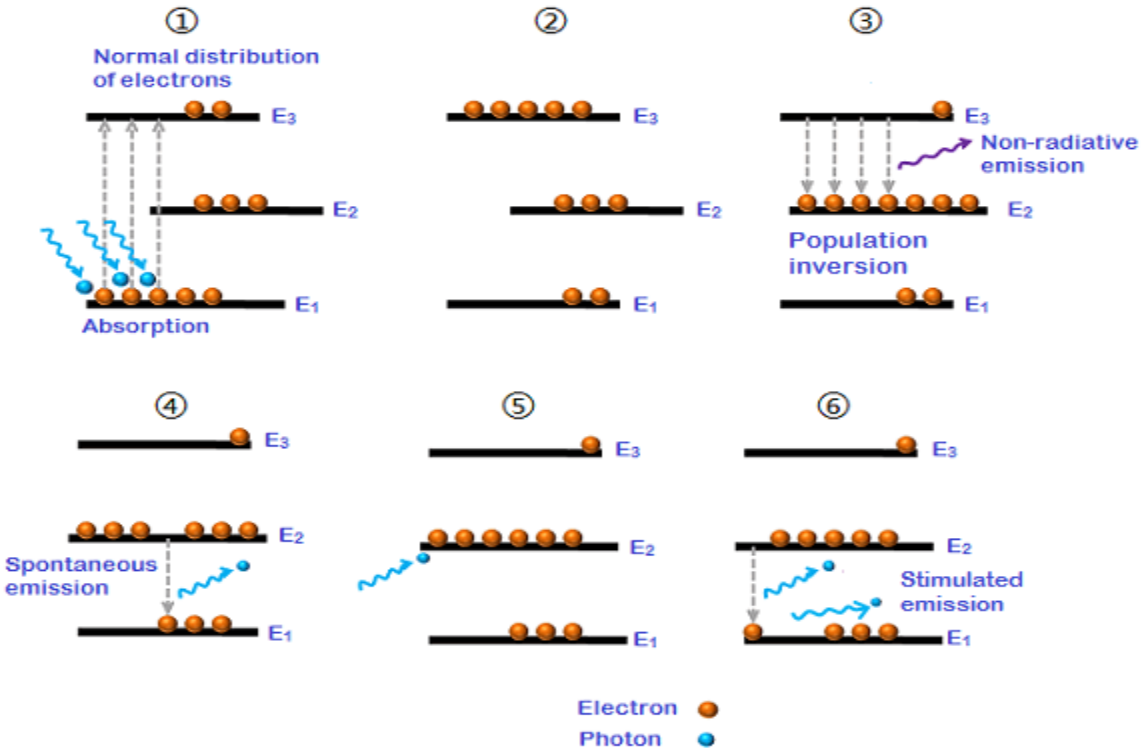


Figure (V-6): Population inversion in 3-level laser

We also use other methods to excite ground state electrons such as electric discharge and chemical reactions. The flow of electrons from E_1 to E_3 is called pump transition.

The lifetime of electrons in the energy state E3 is very small as compared to the lifetime of electrons in the energy state E_2. Therefore, electrons in the energy level E_3 does not stay for long period. After a short period, they quickly fall to the Meta stable state or energy state E_2 and releases radiation less energy instead of photons.

Because of the shorter lifetime, only a small number of electrons accumulate in the energy state E3.

The electrons in the Meta stable state E_2 will remain there for longer period because of its longer lifetime. As result, a large number of electrons accumulate

in Meta stable state. Thus, the population of metal stable state will become greater than the population of energy states E_3 and E_1. It can be simply written as $N_2 > N_1 > N_3$.

In a three level energy system, we achieve population inversion between energy levels E_1 and E_2.

After completion of lifetime of electrons in the Meta stable state, they fall back to the lower energy state or ground state E_1 by releasing energy in the form of photons. This process of emission of photons is called spontaneous emission. When this emitted photon interacts with the electron in the Meta stable state E2, it forces that electron to fall back to the ground state. As a result, two photons are emitted. This process of emission of photons is called stimulated emission.

When these photons again interacted with the electrons in the Meta stable state, they force two Meta stable state electrons to fall back to the ground state. As a result, four photons are emitted. Likewise, a large number of photons are emitted.

As a result, millions of photons are emitted by using small number of photons.

- In a 3-level laser, at least half the population of electrons must be excited to the higher energy state to achieve population inversion. Therefore, the laser medium must be very strongly pumped. This makes 3-level lasers inefficient to produce photons or light. The three level lasers are the first type of lasers discovered.

I-4-3-Four-level laser:

Consider a group of electrons with four energy levels E_1, E_2, E_3, E_4 as shown in the Figure (V-7).

We assume that $E_1 < E_2 < E_3 < E_4$. The lifetime of electrons in the energy state E_4 and energy state E2 is very less. Therefore, electrons in these states will only stay for very short period.

When we supply light energy which is equal to the energy difference of E_4 and E_1, the electrons in the lower energy state E1 gains sufficient energy and jumps into the higher energy state E_4.

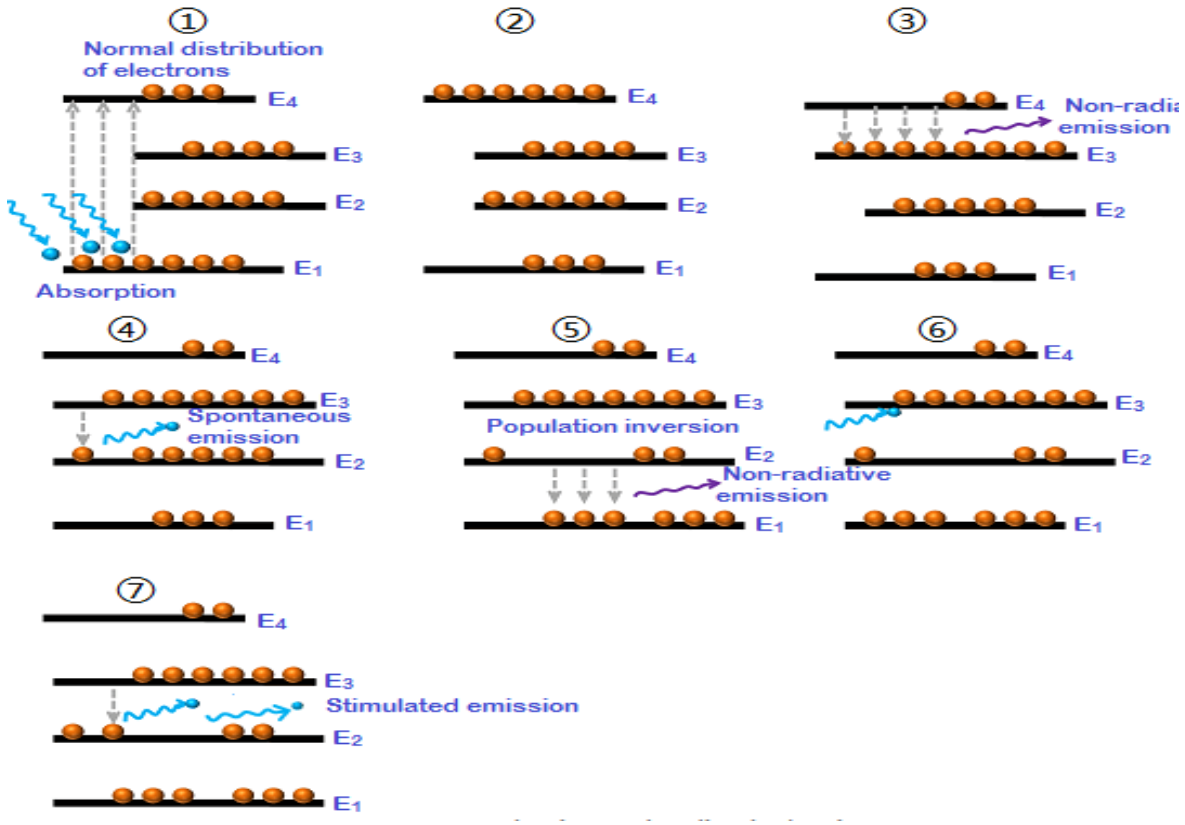


Figure (V-7): Population inversion in 4-level laser

The lifetime of electrons in the energy state E_4 is very small. Therefore, after a short period they fall back into the next lower energy state E_3 by releasing non-radiation energy.

The lifetime of electrons in the energy state E_3 is very large as compared to E_4 and E_2. As a result, a large number of electrons accumulate in the energy level E_3. After completion of their lifetime, the electrons in the energy state E_3 will fall back into the next lower energy state E_2 by releasing energy in the form of photons.

Like the energy state E_4, the lifetime of electrons in the energy state E_2 is also very small. Therefore, the electrons in the energy state E_2 will quickly fall into the next lower energy state or ground state E_1 by releasing non-radiation energy. Thus, population inversion is achieved between energy states E_3 and E_2.

In a 4-level laser, only a few electrons are excited to achieve population inversion. Therefore, a 4-level laser produces light efficiently than a 3-level laser.

In practical, more than four energy levels may be involved in the laser process.

In 3-level and 4-level lasers, the frequency or energy of the pumping photons must be greater than the emitted photons.

I-4-4-Methods of achieving population inversion:

Under normal conditions, more electrons are in a lower energy state than in a higher energy state. Population inversion is a process of achieving more electrons in the higher energy state than the lower energy state.

In order to achieve population inversion, we need to supply energy to the laser medium. The process of supplying energy to the laser medium is called pumping. The source that supplies energy to the laser medium is called pump source. The type of pump source used is depends on the laser medium. Different pump

sources are used for different laser mediums to achieve population inversion. Some of the most commonly used pump sources are as follows:

- Optical pumping
- Electric discharge or excitation by electrons
- Inelastic atom-atom collisions
- Thermal pumping
- Chemical reactions

Population inversion is easily achieved when the system of molecules or atoms have the energy levels with favorable properties. For example, the upper energy level has a long lifetime and the lower energy level has a short lifetime.

A-Optical pumping: As the name suggests, in this method, light is used to supply energy to the laser medium. An external light source like xenon flash lamp is used to produce more electrons (a high population) in the higher energy level of the laser medium.

When light source provides enough energy to the lower energy state electrons in the laser medium as shown in the Figure (V-8), they jump into the higher energy state E_3. The electrons in the higher energy state do not stay for long period. After a very short period, they fall back to the next lower energy state or meta stable state E_2 by releasing radiation less energy.

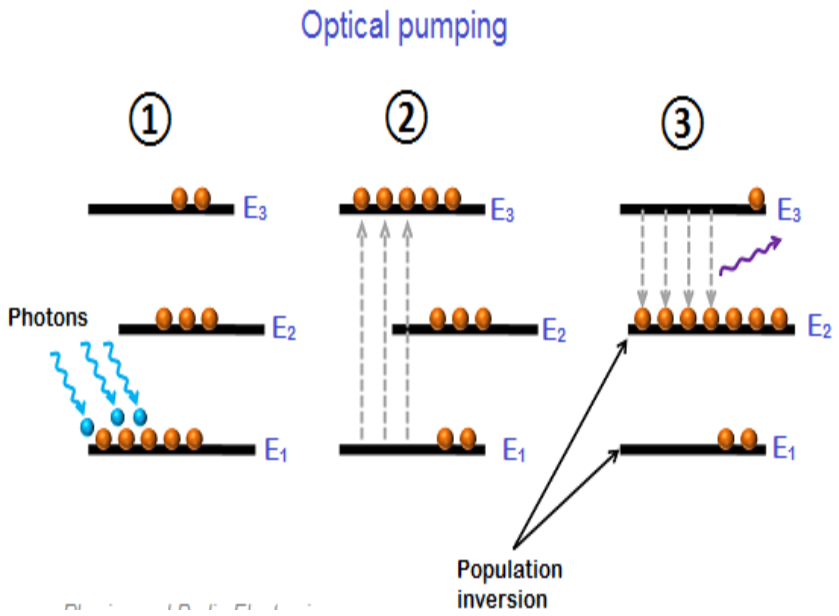


Figure (V-8): Optical Pumping

The meta stable state E_2 has greater lifetime than the lower energy state or ground state E_1. Hence, more electrons are accumulated in the energy state E_2 than the lower energy state E_1. Thus, population inversion is achieved. Optical pumping is used in solid-state lasers such as ruby lasers.

B-Electric discharge or excitation by electrons: Electric discharge refers to flow of electrons or electric current through a gas, liquid or solid. In this method of pumping, electric discharge acts as the pump source or energy source. A high voltage electric discharge (flow of electrons, electric charge, or electric current) is passed through the laser medium or gas (Figure (V-9)). The intense electric field accelerates the electrons to high speeds and they collide with neutral atoms in the gas.

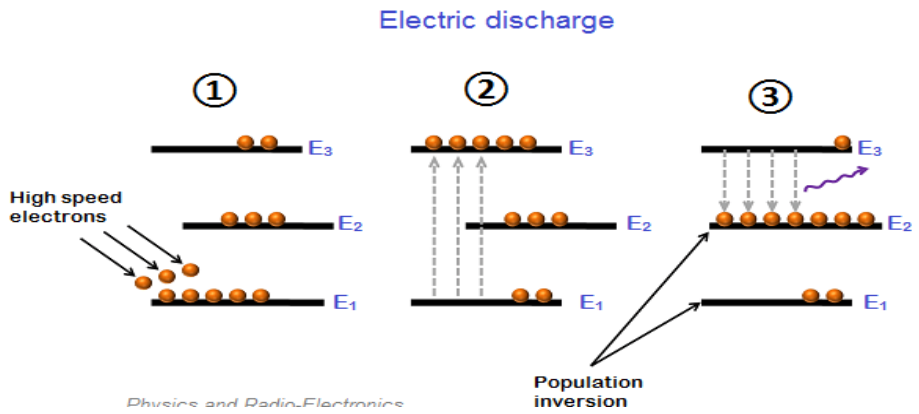


Figure (V-9): Electric Discharge

As a result, the electrons in the lower energy state gains sufficient energy from external electrons and jumps into the higher energy state. This method of pumping is used in gas lasers such as argon lasers.

The process of achieving population inversion in the gas laser is almost similar to the solid laser. The only difference is the pump source used for supplying energy and the type of material or medium (solid or gas) used as a laser medium. In solid lasers, an external light source like xenon flash lamp is used as pump source whereas, in gas lasers, a high voltage electric discharge is used as a pump source.

C-Inelastic atom-atom collisions: Like the electric discharge method, here also a high voltage electric discharge acts as a pump source. However, in this method, a combination of two types of gases, say X and Y are used. The excited state of gas X is represented as X^+ whereas gas Y is represented as Y+. Both X and Y gases have the same excited states (X^+ and Y^+).

When high voltage electric discharge passes through a laser medium having two types of gases X and Y, the lower energy state electrons in gas X will move to the excited state X^+ similarly the lower energy state electrons in gas Y moves to the excited state Y^+.

Initially, during electric discharge, the lower energy state electrons in gas X or atom X gets excited to X^+ due to continuous collision with electrons. The excited state electrons in gas X^+ now collide with the lower energy state electrons in gas Y. As a result, the lower energy state electrons in gas Y gains sufficient energy and jump into the excited state Y+. This method is used in the Helium–Neon (He-Ne) laser.

D-Thermal pumping: Sometimes we can achieve population inversion by heating the laser medium. In thermal pumping, heat acts as the pump source or energy source. In this method, population inversion is achieved by supplying heat into the laser medium (Figure (V-10)).

When heat energy is supplied to the laser medium, the lower energy state electrons gains sufficient energy and jumps into the higher energy level.

The process of achieving population inversion in thermal pumping is almost similar to the optical pumping or electric discharge method, except that in this method heat is used as pump source instead of light or electric discharge.

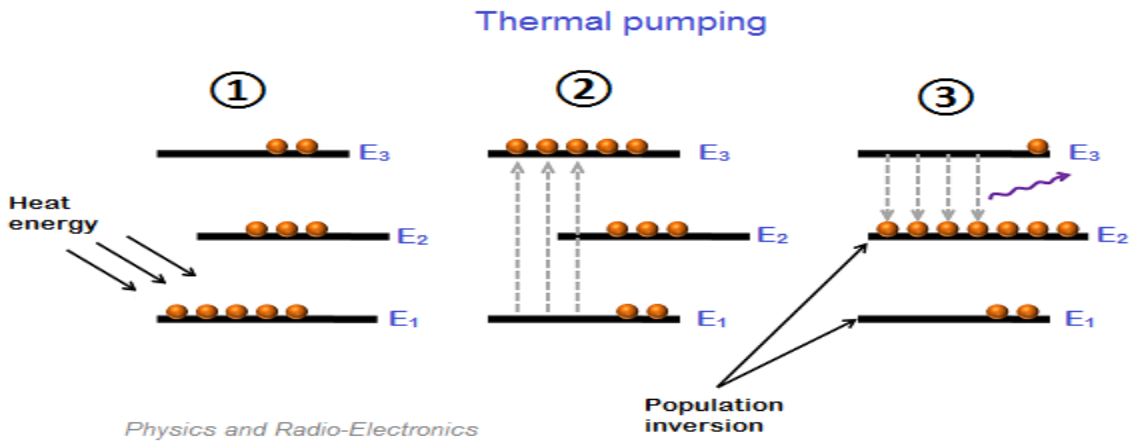


Figure (V-10): Thermal Pumping

E-Chemical reactions: If an atom or a molecule is produced through some chemical reaction and remains in an excited state at the time of production, then it can be used for pumping. The hydrogen fluoride molecule is produced in an excited state when hydrogen and fluorine gas chemically combine. The number of produced excited atoms or molecules is greater than the number of normal state atoms or molecules. Thus, population inversion is achieved.

For example, $H_2 + F_2 \rightarrow 2HF$, in this chemical reaction, hydrogen (H_2) and fluorine (F_2) molecules are chemically combined to produce hydrogen fluoride molecule (2HF) in an excited state.

Chapter VI

Introduction to molecular physics

I-Introduction:

A molecule is a group of two or more atoms that stick together. A molecule is an electrically neutral group of two or more atoms held together by covalent chemical bonds. Molecules are distinguished from ions by their lack of electrical charge. However, in quantum physics, organic chemistry, and biochemistry, the term molecule is often used less strictly, also being applied to polyatomic ions.

II-Linear molecular:

As shown in Figure (VI-1), a linear molecule is one in which the atoms are arranged in a straight line (less than a 180° angle). The sp hybridization occurs at the central atom of molecules with linear electron-pair geometries. Carbon dioxide (O=C=O) and beryllium hydride BeH_2 are examples of linear electron pairs and molecular geometry.

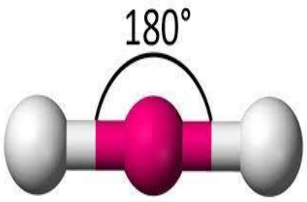


Figure (VI-1): A linear molecule

III- Diatomic molecules:

Diatomic molecule, any chemical compound that is made up of only two atoms (Figure (VI-2)). The two atoms can be the same type of atom, such as oxygen (O2), where both atoms in the molecule are oxygen atoms; such molecules are known as homonuclear diatomic molecules. Diatomic molecules can also consist of two different atoms, such as sodium chloride (NaCl; also called table salt); such molecules are called heteronuclear diatomic molecules. Both homonuclear and heteronuclear diatomic molecules are bonded to each other in a straight line; these bonds can be single,

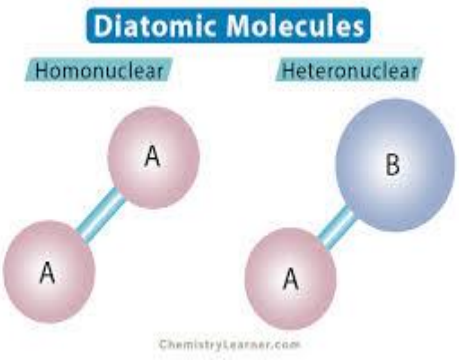


Figure (VI-2): Diatomic molecules

double, or triple bonds, referring to the number of interacting electron pairs between the two atoms. The bonds also can be ionic, covalent, or polar covalent. An example of bonding in diatomic molecules is carbon monoxide (CO), which contains a triple bond. A standard double bond first forms between a carbon atom and an oxygen atom, which completes the valence shell for the oxygen. To stabilize the double bond, a lone pair of electrons from the oxygen atom is shared by the carbon atom, forming a coordinate covalent bond (or dative bond).

III-1-Diatomic molecule – Harmonic oscillator:

III-1-1-Vibration energy and frequency:

Consider a molecule AB (Figure (VI-3)); made up of atoms AB, such that $\boldsymbol{m_1}$ and $\boldsymbol{m_2}$ are the respective masses of the atoms A and *B* and G the center of mass of the system. As a 1st approximation (neglecting the rectilinear translation movement), we can choose G as the origin of the coordinates.

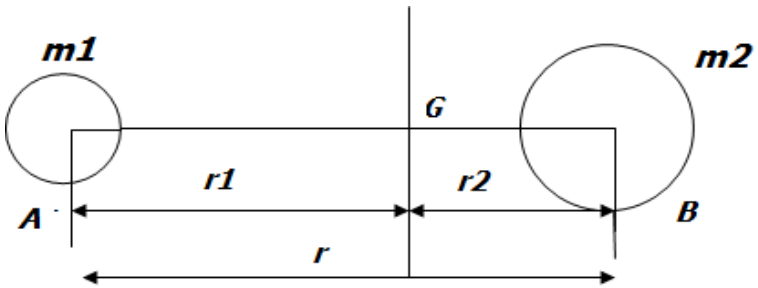


Figure (VI-3): A molecule AB; made up of atoms AB

Let $\boldsymbol{r}$ be the variable distance and which is equivalent to $\boldsymbol{r_1 + r_2}$, as in the case of the rotator, we have:

$$\boldsymbol{r_1 = \frac{m_2}{m_1 + m_2} r} \qquad \text{and} \qquad \boldsymbol{r_2 = \frac{m_1}{m_1 + m_2} r}$$

The accelerations to which atoms $\boldsymbol{A}$ and $\boldsymbol{B}$ are subjected are respectively:

$$\boldsymbol{\overrightarrow{a_1} = \frac{d^2\overrightarrow{r_1}}{dt^2} = \frac{m_2}{m_1 + m_2}\frac{d^2\vec{r}}{dt^2}} \qquad \text{and} \qquad \boldsymbol{\overrightarrow{a_2} = \frac{m_1}{m_1 + m_2}\frac{d^2\vec{r}}{dt^2}}$$

Which gives the forces of attraction of A on B and vice versa:

$$\overrightarrow{f_1} = m_1\overrightarrow{a_1} = \frac{m_1 m_2}{m_1 + m_2}\frac{d^2\vec{r}}{dt^2} \quad \text{and} \quad \overrightarrow{f_2} = -m_2\overrightarrow{a_2} = -\frac{m_2 m_1}{m_1 + m_2}\frac{d^2\vec{r}}{dt^2}$$

We have $\boldsymbol{\mu}$ is the reduced mass of the system:

$$f_1 = f_2 = \mu\frac{d^2r}{dt^2} \qquad (\mathbf{VI-1})$$

If r_e is the equilibrium distance between the 2 atoms (that is to say the distance corresponding to the minimum energy of the molecule), we can observe vibration movements (elongation, contraction) of the molecule around its equilibrium geometry (Figure (VI-4)).

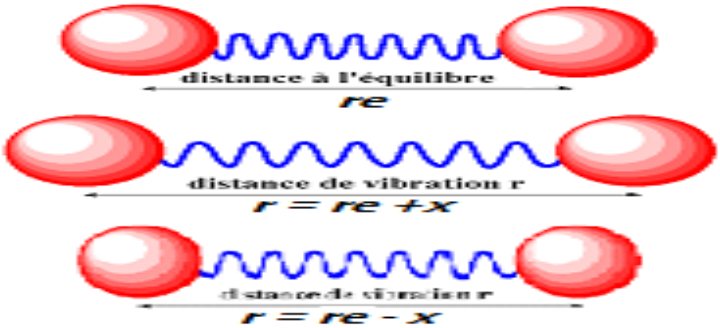


Figure (VI-4): The vibration movements of the molecule around its equilibrium geometry

The restoring force to which the masses A and B are subjected when they are at the distance r, are proportional to $(x = r - r_e)$ and we obtain:

$$\mu\frac{d^2(r - r_e)}{dt^2} = -K(r - r_e) \qquad (\mathbf{VI-2})$$

By setting $(x = r - r_e)$, we obtain the equation of motion:

$$\frac{d^2x}{dt^2} + \frac{k}{\mu}x = 0 \qquad (\mathbf{VI-3})$$

Which is the classical equation of a particle of mass μ performing a simple harmonic oscillatory motion along r. It appears, as a first approximation, that we

can use the harmonic oscillator model to describe the vibration movement in a diatomic molecule as shown in the Figure (VI-5).

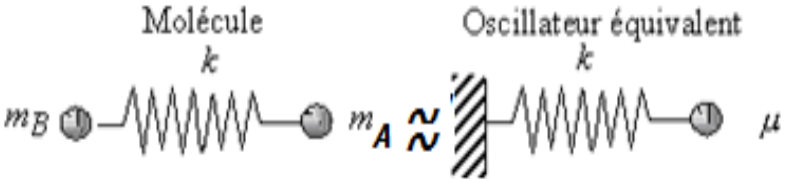


Figure (VI-5): The harmonic oscillatory motion.

A solution to the equation is: $\boldsymbol{x = A\cos\omega t}$ with $\omega = 2\pi\nu_0$

$\boldsymbol{x = A\cos\omega t}$ with $\omega^2 = \dfrac{k}{\mu} = (2\pi\nu_0)^2 \Rightarrow$

$$\boldsymbol{\nu_{Osc} = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}} \qquad (\mathbf{VI-4})$$

$\boldsymbol{\nu_{Osc}}$ represents the oscillation frequency in the case of the harmonic approximation (classic oscillator).

$\boldsymbol{\nu_{Osc}}$ frequency vibration of the molecule.

$\boldsymbol{\mu}$**:** reduced mass

$\boldsymbol{k}$: bond force constant (N/m)

NB: In the case of the classic oscillator, we observe only one oscillation frequency $\boldsymbol{\nu_{Osc}}$.)

The potential energy of the system is:

$$F = -\frac{dE_p}{dx} \Rightarrow E_p = \int -F dx = \int kx dx = \frac{1}{2}kx^2 \qquad (\mathbf{VI-5})$$

We have the equation of a parabola, the potential energy, in the case of the harmonic approximation, can be represented by a parabola as described in the Figure (VI-6).

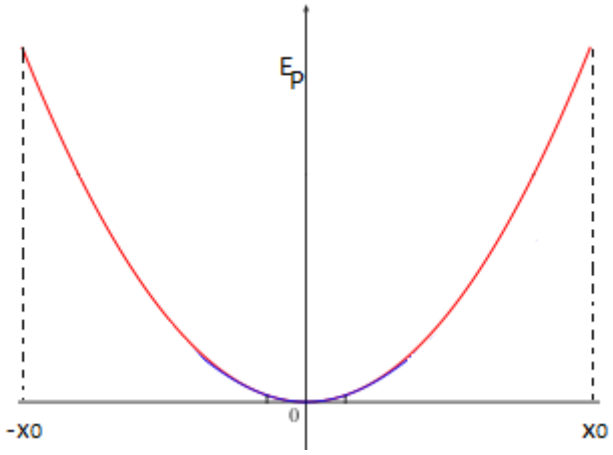


Figure (VI-6): The potential energy of the system

From the microscopic point of view, to determine the vibration wave function $\boldsymbol{\psi_{vib}}$ and the associated eigenvalues, i.e. $\boldsymbol{E_{vib}}$ (vibration energy of the system), it is necessary to solve the Schrödinger equation knowing the molecule does not can only move along the internuclear axis):

$$\frac{d^2\Psi_{vib}}{dx^2} + \frac{8\pi^2\mu}{h^2}\left(E - \frac{1}{2}kx^2\right)\Psi_{vib} = 0 \qquad (\mathbf{VI-6})$$

The solution to this equation provides the proper values of the total energy:

$$\mathbf{E}_{vib} = \frac{h}{2\pi}\sqrt{\frac{k}{\mu}} \times \left(v + \frac{1}{2}\right) = h\nu_{vib}\left(v + \frac{1}{2}\right) \qquad (\mathbf{VI-7})$$

With:

$$\nu_{vib} = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}} \qquad (\mathbf{VI-8})$$

$\boldsymbol{\nu_{vib}}$ is the vibration frequency and $\boldsymbol{v}$ is the vibration quantum number which can take the values $\boldsymbol{v}$ = 0, 1, 2. . .

We note that in the lowest energy state ($\boldsymbol{v = 0}$), the molecule still has a vibrational energy equal to $\frac{1}{2}\,h\nu_{vib}$; it is called **zero-point energy**. It represents the lowest vibrational energy that the molecule can take.

III-1-2- Energy level diagram:

Vibrational energy is the sum of kinetic energy and potential energy. At maximum elongation, it is reduced to the potential energy: When the system approaches its equilibrium position, the kinetic energy tends towards a maximum and the potential energy decreases.

The energy variation between 2 consecutive vibration levels is:

$$\Delta E_{vib} = h\upsilon = \left[\frac{h}{2\pi}\sqrt{\frac{k}{\mu}} \times \left(\upsilon + 1 + \frac{1}{2}\right)\right] - \left[\frac{h}{2\pi}\sqrt{\frac{k}{\mu}} \times \left(\upsilon + \frac{1}{2}\right)\right] \qquad (VI-9)$$

$$\Delta E_{vib} = \frac{h}{2\pi}\sqrt{\frac{k}{\mu}} \Rightarrow \upsilon = \upsilon_{vib} = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}} \qquad (VI-10)$$

In the case of the harmonic oscillator approximation, the levels are equidistant, the vibrational transitions generate a single line and the frequency of the emitted or absorbed light is equal to the frequency of the classical harmonic oscillator (Figure (VI-6)).

The molecule vibrates at a frequency equal to that of the radiation absorbed or emitted.

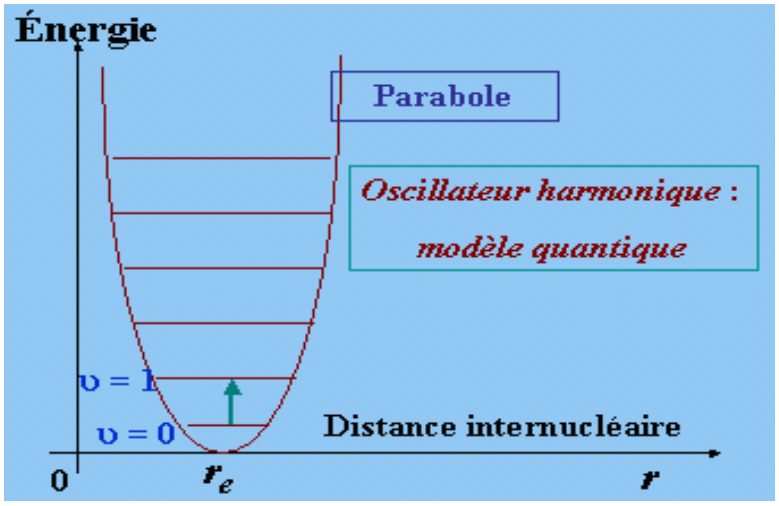


Figure (VI-6): The quantum model of harmonic oscillator

The vibration energy is thus represented by a parabola, in the case of the approximation of the harmonic oscillator.

III-1-3- Selection rule:

- The dipole moment of a diatomic molecule must vary during a vibration for it to be spectroscopically active.
- Homonuclear diatomic molecules do not have a vibration spectrum because the dipole moment remains zero when the bond stretches. Heteronuclear molecules present a vibration spectrum in absorption and emission because the dipole moment varies with the length of the bond.

A selection rule identical to that we saw for the rotational levels applies and limits the transitional levels to $\Delta\boldsymbol{v} = \pm \mathbf{1}$. This rule is based on the conservation of the angular momentum of the system.

At room temperature, the vast majority of molecules are in their fundamental vibrational level ($\boldsymbol{v} = \mathbf{0}$). Thus the dominant transition in IR spectroscopy corresponds to the passage $\boldsymbol{v} = \mathbf{0} \rightarrow \boldsymbol{v} = \mathbf{1}$.

NB: Spectral terms are generally associated with vibrational energy. We thus define the vibrational term $\boldsymbol{G(v)}$ and the vibrational wave number:

$$\boldsymbol{G(v)} = \frac{\boldsymbol{E_{vib}}}{\boldsymbol{hc}} = \frac{\mathbf{1}}{\mathbf{2\pi c}}\sqrt{\frac{\boldsymbol{k}}{\boldsymbol{\mu}}}\left(\boldsymbol{v} + \frac{\mathbf{1}}{\mathbf{2}}\right) = \boldsymbol{\sigma}\left(\boldsymbol{v} + \frac{\mathbf{1}}{\mathbf{2}}\right) \qquad \text{(by cm}^{-1}\text{ or m}^{-1}\text{)} \qquad \mathbf{(VI-11)}$$

$\boldsymbol{\sigma}$: nombre d'onde de la vibration classique ou nombre d'onde vibrationnel

$$\boldsymbol{G(v+1) - G(v) = \sigma} \qquad \mathbf{(VI-12)}$$

Connaissant le nombre d'onde on peut en déduire la constante de force k :

$$\boldsymbol{\sigma} = \frac{\mathbf{1}}{\mathbf{2\pi c}}\sqrt{\frac{\boldsymbol{k}}{\boldsymbol{\mu}}} \Rightarrow \boldsymbol{k = 4\pi^2\sigma^2 c^2 \mu} \qquad \mathbf{(VI-13)}$$

III-2-Diatomic molecule – Anharmonic oscillator:

In fact, the harmonic oscillator is not a very good model for studying molecular vibrations except for low energy levels, near the minimum of the vibration energy curve. When the distance between the atoms of the molecule increases, the force of attraction decreases and for sufficient energy, the molecule can dissociate and the transitions no longer obey the selection rule $\Delta v = \pm 1$.

It is no longer possible to represent potential energy by:

$$E_P = \frac{1}{2}kx^2 = \frac{1}{2}k(r - r_e)^2 \qquad (\mathbf{VI-14})$$

Real interactions must be taken into account and a series expansion of this expression makes it possible to find a value close to the energy of reality:

$$E_P = k\left[\frac{1}{2}(r - r_e)^2 - x_e(r - r_e)^3 + y_e(r - r_e)^4 \dots\dots\right] \qquad (\mathbf{VI-15})$$

Solving the Schrödinger equation taking into account anharmonicity gives the real vibration energy:

$$\mathrm{E_{vib}} = \frac{h}{2\pi}\sqrt{\frac{k}{\mu}} \times \left[\left(v + \frac{1}{2}\right) - x_e\left(v + \frac{1}{2}\right)^2 + y_e\left(v + \frac{1}{2}\right)^3 \dots\dots\dots\dots\dots\right]$$

$$= h\nu_{vib}\left[\left(v + \frac{1}{2}\right) - x_e\left(v + \frac{1}{2}\right)^2 + y_e\left(v + \frac{1}{2}\right)^3 \dots\dots\dots\dots\dots\right]$$

Depending on the spectral terms:

$$G(v) = \frac{E_{vib}}{hc} = \sigma\left(v + \frac{1}{2}\right) + \sigma x_e\left(v + \frac{1}{2}\right)^2 + \sigma y_e\left(v + \frac{1}{2}\right)^3 \dots\dots\dots \qquad (\mathbf{VI-16})$$

x_e and y_e are the anharmonicity coefficients, they have very low numerical values which allows us to limit ourselves to the first terms of the limited development; we then have:

$$E_{vib} = h\nu_{vib}\left[\left(v + \frac{1}{2}\right) - x_e\left(v + \frac{1}{2}\right)^2\right] \qquad (\mathbf{VI-17})$$

The energy levels are no longer equidistant, are closer and closer together (this is explained by the fact that the 2nd term is subtracted from the 1st) when ν increases and tend towards a limiting value: the dissociation energy of the molecule (Figure (VI-7)).

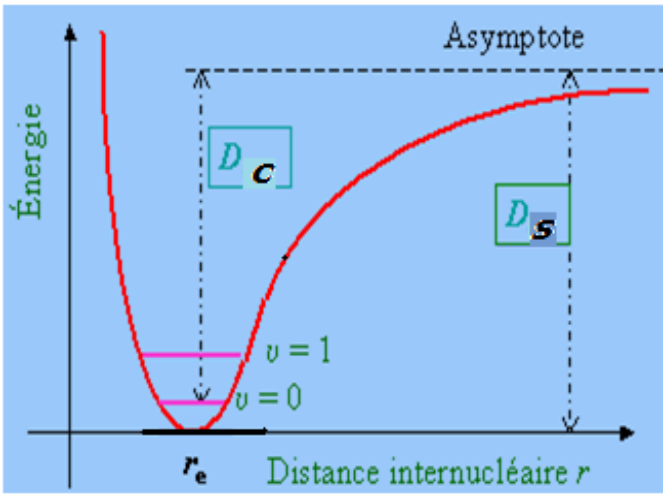


Figure (VI-7): The energy levels for Anharmonic oscillator

This vibrational energy curve is very often described by the Morse potential curve given by the expression:

$$E_{vib} = D_S\left(1 - e^{-\beta\rho}\right)^2 \qquad (\mathbf{VI-18})$$

With: $\rho = r - r_e$ and

$$\beta = \nu_{vib}\left(\frac{2\pi^2\mu}{D_S}\right)^{\frac{1}{2}} \qquad (\mathbf{VI-19})$$

D_s: spectroscopic dissociation energy (or binding energy) is the interval between the asymptote and the minimum.

D_s is linked to the chemical dissociation energy (determined by thermochemistry) D_c (interval between the zero-point energy and the dissociation asymptote) by the relation:

$$D_c = D_S - \frac{1}{2}h\nu_{vib} \qquad (\mathbf{VI-20})$$

In the case of the harmonic approximation, all transitions give photons of the same frequency (equidistance of energy levels):

$$\nu_{vib} = \nu \qquad (\mathbf{VI-21})$$

In the case of anharmonicity, we have:

$$\Delta E = h\nu = h\nu_{vib}[1 - 2(v+1)x_e]$$

$$\nu = \nu_{vib} - 2(v+1)x_e\nu_{vib} \qquad (\mathbf{VI-22})$$

Transitions from different levels generate photons of frequencies slightly different and several lines appear on the spectrum as shown in the Figure (VI-8).

- The selection rules are slightly modified compared to the previous simple model. We find that if the transition $\Delta v = \pm 1$ always occurs with high probability, the transitions $\Delta v = \pm 2, \pm 3$, etc. can also occur, but with a probability much weaker.

$\Delta v = \pm 1$ correspond to primary or fundamental harmonics.

$\Delta v = \pm 2$ are the secondary harmonics.

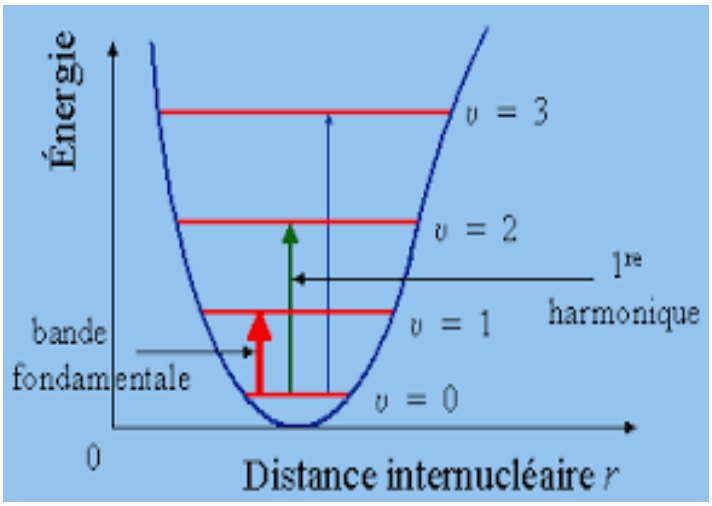


Figure (VI-8): Anharmonic curve and vibrational transitions.

III-3- Rotation spectra of diatomic molecules:

III-3-1-Case of rigid rotators:

As a first approximation, the rotational states of molecules are based on a model called a rigid rotator, which is a body that is not deformed by rotation; the simplest type of rotator is called a linear rotator and corresponds to a molecule linear, like HCL.

III-3-1-1-In Classical mechanics:

A-The moment of inertia:

Consider a system composed of two particles $\boldsymbol{m_1}$ and $\boldsymbol{m_2}$ linked together by a rod of negligible mass as described the Figure (VI-9). The assembly is rotating at an angular speed $\boldsymbol{\omega}$(in rad/s) around an axis located at a distance $\boldsymbol{r_1}$ from $\boldsymbol{m_1}$ and $\boldsymbol{r_2}$ from $\boldsymbol{m_2}$.

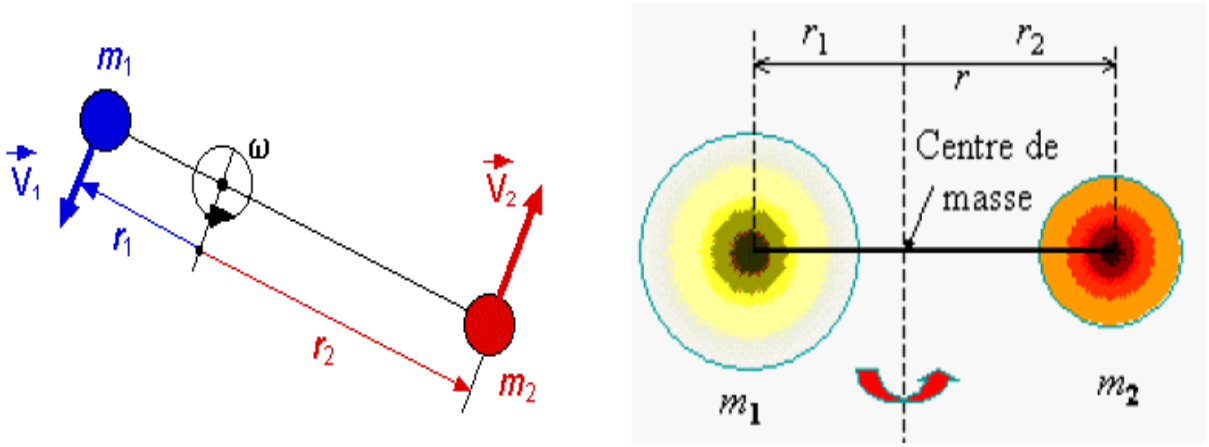


Figure (VI-9): A system composed of two particles m_1 and m_2.

In rotation, it is the moment of inertia $\boldsymbol{I}$ which represents the measure of the opposition offered by this system to having to change its state of rotational movement around an axis.

The expression of the moment of inertia of the system is given by the relation:

$$\boldsymbol{I = m_1\, r_1^2 + m_2\, r_2^2} \text{ (Its unit is kg.m}^2\text{).} \qquad (\mathbf{VI-23})$$

This expression highlights the importance of the distribution of mass around the axis of rotation. So, the closer the mass is to the axis of rotation, the smaller the rotational inertia (the moment of inertia) will be (and vice versa of course). More generally, for a system composed of $\boldsymbol{n}$ particles (point masses), the moment of inertia is given by:

$$\boldsymbol{I = \sum_i m_i {r_i}^2} \qquad (\mathbf{VI-24})$$

The axis of rotation passes through the center of gravity $\boldsymbol{G}$ of the system; therefore $m_1 r_1 = m_2 r_2$

Let's call $\boldsymbol{r}$: interatomic distance = bond length of the diatomic molecule: $\boldsymbol{r_1 + r_2 = r}$

From the two previous relationships we obtain:

$$\boldsymbol{r_1 = \frac{m_1}{m_1 + m_2} r} \qquad \boldsymbol{r_2 = \frac{m_2}{m_1 + m_2} r}$$

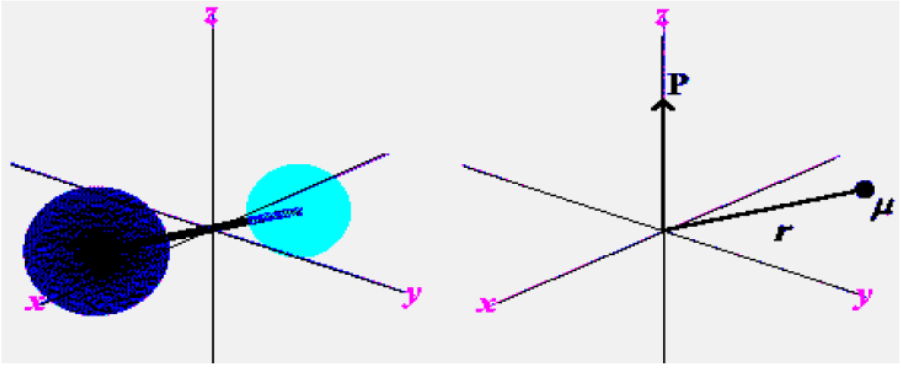
The moment of inertia $\boldsymbol{I}$ is then written:

$$\boldsymbol{I = m_1 \left[\frac{m_2}{m_1 + m_2} r\right]^2 + m_2 \left[\frac{m_1}{m_1 + m_2} r\right]^2}$$

$$\boldsymbol{I = \left[\frac{m_1 m_2}{m_1 + m_2}\right] r^2 \Rightarrow I = \mu r^2} \qquad \boldsymbol{(VI - 25)}$$

μ is the reduced mass.

This relationship means that from a mechanical point of view, the diatomic molecule can be studied as an atom of single mass $\boldsymbol{\mu}$ rotating around a point located at a fixed distance r equal to the internuclear distance (Figure (VI-10)).



Equivalent mécanique du rotateur diatomique rigide

Figure (VI-10): Rigid diatomic rotator

B-Kinetic energy (rotational energy):

The rotational kinetic energy corresponding to these two atoms is:

$$E_c = \frac{1}{2} m_1 v_1^2 + \frac{1}{2} m_2 v_2^2 \qquad \boldsymbol{(VI - 26)}$$

When the molecule rotates around its center of gravity, the atoms of mass $\boldsymbol{m_1}$ and $\boldsymbol{m_2}$ have the same angular speed $\boldsymbol{\omega}$:

$$\begin{cases} v_1 = r_1\omega \\ v_2 = r_2\omega \end{cases}$$

$$\boldsymbol{E_c = \frac{1}{2}m_1(\omega r_1)^2 + \frac{1}{2}m_2(\omega r_2)^2} \qquad (\mathbf{VI-27})$$

Therefore:

$$\boldsymbol{E_c = \frac{1}{2}I\omega^2} \qquad (\mathbf{VI-28})$$

In the case of a discrete system formed of n rotating particles, the total angular momentum is given by:

$$\boldsymbol{\vec{L} = \sum_{i=1,n} \vec{L_i} = \sum_{i=1,n} \vec{r_i} \Lambda \vec{p_i}} \qquad (\mathbf{VI-29})$$

Let us now calculate the angular momentum of this diatomic molecule:

$$\boldsymbol{\vec{L} = \vec{r_1}\Lambda\vec{p_1} + \vec{r_2}\Lambda\vec{p_2} = \vec{r_1}\Lambda(m_1\vec{v_1}) + \vec{r_2}\Lambda(m_2\vec{v_2}) \Rightarrow L = r_1 v_1 m_1 + r_2 v_2 m_2}$$

$$\Rightarrow L = (\boldsymbol{r_1}^2\boldsymbol{m_1} + \boldsymbol{r_2}^2\boldsymbol{m_2})\omega$$

Thus:

$$\boldsymbol{E_c = \frac{1}{2}I\omega^2} \qquad (\mathbf{VI-30})$$

C-In quantum mechanics:

In quantum mechanics, the angular momentum of a microscopic system (electron, atom, molecule, etc.) is quantified:

$$L = \frac{h}{2\pi}\sqrt{j(j+1)} \qquad \text{j} = 0,1,2,3 \ldots \ldots$$

j: rotation quantum number (positive integer or zero).

So the rotation energies allowed are given by the relation:

$$\boldsymbol{E_{rot} = \frac{L^2}{2I} = \frac{\hbar^2}{2I}J(J+1)} \qquad \text{With J} = 0,1,2,3 \ldots \ldots \qquad (\mathbf{VI-31})$$

With $\hbar = \text{h}/2\pi$

$$\boldsymbol{E_{rot} = \frac{h^2}{8\pi^2 I}j(j+1)} \qquad (\mathbf{VI-32})$$

We pose $B = \frac{h^2}{8\pi^2 I}$ / B: rotation constant

$$E_{rot} = E_j = Bj(j+1) \qquad (\mathbf{VI-34})$$

Noticed

- The gap between energy levels increases with j.
- For $j = 0, E_j = 0$ (the lowest possible energy) there is no rotational energy at the zero point for the molecules.
- The energy level diagram of the rotating molecule appears as a series of horizontal lines representing the possible levels (Figure (VI-11)). These possible energy levels correspond to the values $J = 0, 1, 2, \ldots$

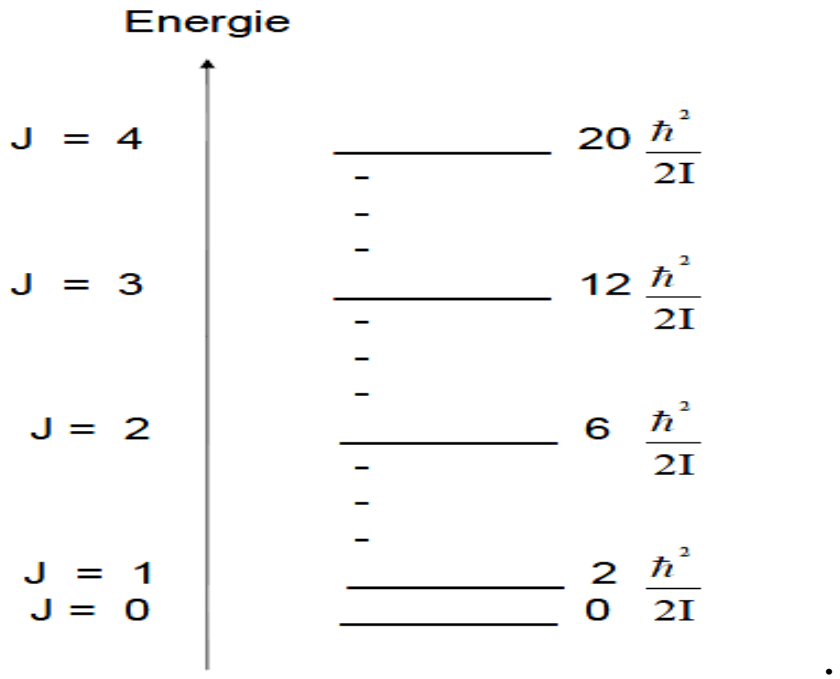


Figure (VI-11): The energy level diagram of the rotating molecule

D-Case of non-rigid rotators:

Molecules are not completely rigid and undergo centrifugal distortion (increase in r) which increases the moment of inertia I.

Solving the Schrödinger equation leads to:

$$E_{rot} = Bj(j+1) - Dj^2(j+1)^2 \qquad (\mathbf{VI-35})$$

D: centrifugal distortion constant.

E-Pure rotation spectrum of diatomic molecules:

1- Rotation selection rules:

The general selection rule for observing a pure rotation spectrum is that a molecule must possess a permanent electric dipole moment. It expresses that only transitions are possible for which the variation of the rotation quantum number is equal to unity, i.e.: $\Delta j = \pm 1$

- ✓ The transition $\boldsymbol{\Delta j = +1}$ corresponds to an absorption.
- ✓ The transition $\boldsymbol{\Delta j = -1}$ corresponds to an emission.

Molecules with zero electric dipole moment (homonuclear diatomic molecules like (H_2, N_2, O_2) exhibit neither rotational absorption nor emission.

1-1-Selection rule for rotation:

$\boldsymbol{\Delta j = +1}$; $\boldsymbol{J}$ being the rotation quantum number.

Only transitions between a level $\boldsymbol{J}$ and a level $\boldsymbol{J+1}$ absorption or between a level $\boldsymbol{J}$ and a level $\boldsymbol{J-1}$ in emission are therefore permitted.

2-Aspect of rotation spectra (case of rigid rotators):

Since the distances between energy levels are not equal; each transition corresponds to a different line, the result is that the rotation spectrum is composed of a bung formed of several lines (Figure (VI-12)).

When we apply the selection rules to the expressions of the energy levels of a rigid rotator, we find the following absorption wavenumbers $\boldsymbol{j \rightarrow j+1}$ allowed:

The energy difference between two successive levels $\boldsymbol{J}$ and $\boldsymbol{J+1}$ is:

$$\boldsymbol{E_{J \rightarrow J+1} = E_{J+1} - E_J} \qquad (\mathbf{VI-36})$$

$$E_j = B_j(j+1)$$

$$E_{j+1} = B(j+1)(j+2)$$

$$\Delta E = 2B(j+1)$$

$$\boldsymbol{\Delta E = hc\bar{\nu}} \qquad (\mathbf{VI-37})$$

$$\boldsymbol{\bar{\nu} = \frac{2B}{hc}(j+1)} \qquad / \qquad \bar{\mathrm{B}} = \frac{B}{hc}$$

$$\bar{\nu}_{j\to j+1} = 2\bar{B}(j+1) \qquad (\mathbf{VI-38})$$

3-Distance between two neighboring lines (between two consecutive lines, Rigid rotators):

The next line of the transition ($j \to J+1$) corresponds to the transition ($J+1 \to J+2$). Its frequency is:

$$\bar{\nu}_{j\to j+2} = 2\bar{B}(j+2) \qquad (\mathbf{VI-39})$$

So the distance between neighboring lines is expressed by the difference between the two wavenumbers of the lines:

$$\Delta\bar{\nu} = \bar{\nu}_{j=1\to j+2} - \bar{\nu}_{j\to j+1}$$

$$\Delta\bar{\nu} = 2\bar{B}(j+2) - 2\bar{B}(j+1)$$

$$\Delta\bar{\nu} = 2\bar{B} \qquad (\mathbf{VI-40})$$

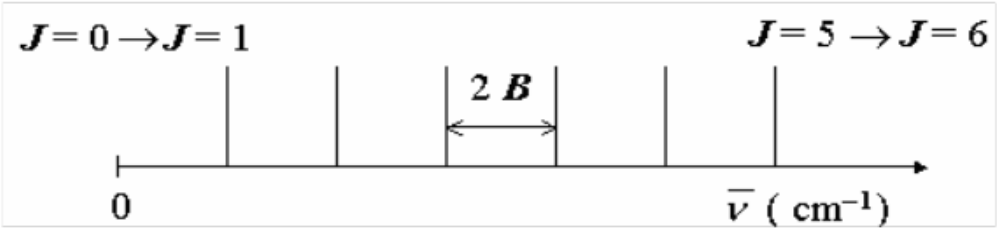


Figure schématique du spectre de rotation

Figure (VI-12): Schematic figure of the rotation spectrum

3-1-Example and application and Intensity of lines:

The rotation spectrum of diatomic molecules actually shows rotation lines that do not have the same intensity.

The figure below (Figure (VI-13)) shows the absorption spectrum of HCl. We observe deferential intensities and approximately equidistant bands. In fact, the molecule is not absolutely rigid and for high values of J, the molecule undergoes an elongation which increases its moment of inertia and decreases B: the gap between the bands therefore tends to decrease. HCl absorption occurs at relatively high wavenumbers in the area of rotational spectroscopy. Indeed, it is a molecule having

a fairly small size ($r_{HCl} = 1.27$ Å) and a reduced mass close to 1 amu, like all AH type molecules. The moment of inertia is low, so B is high.

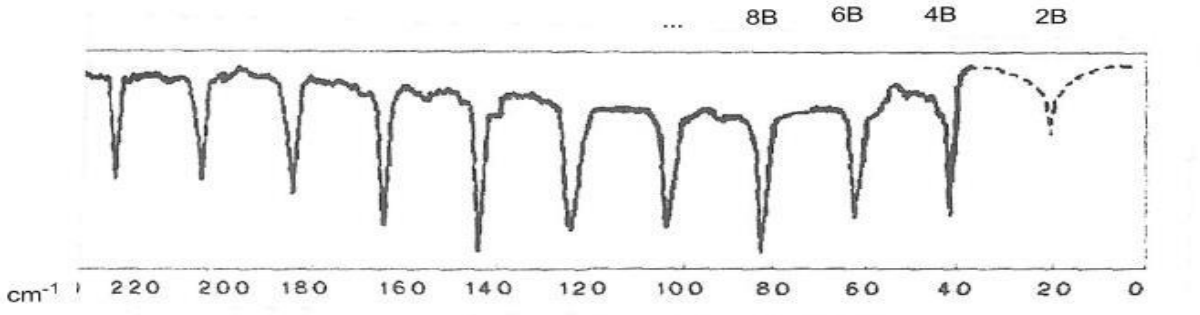


Figure (VI-13): The absorption spectrum of HCl.

4-Aspect of rotation spectra (case of non-rigid rotators):

When centrifugal deformation is taken into account (non-rigid rotator) the expression for the wave number is:

$$\overline{E_J} = \bar{B}j(j+1) - \bar{D}j^2(j+1)^2$$

$$\overline{E_{J+1}} = \bar{B}j(j+1)(j+2) - \bar{D}(j+1)^2\,(j+2)^2$$

$$\overline{E_{J+1}} - \overline{E_J} = \left[\bar{B}j(j+1)(j+2) - \bar{D}(j+1)^2\,(j+2)^2\right] - \left[\bar{B}j(j+1) - \bar{D}j^2(j+1)^2\right]$$

$$\overline{E_{J+1}} - \overline{E_J} = 2\bar{B}j(j+1) - 4\bar{D}(j+1)^3$$

$$\bar{v} = 2\bar{B}(j+1) - 4\bar{D}(j+1)^3 \qquad (VI-41)$$

III-4- Rotation-vibration spectra of diatomic molecules:

III-4- 1-Total system energy:

- $E_{v,j} = E_v + E_j + \text{Couplage rotation} - \text{vibration}$

$$E_{v,j} = Bj(j+1) + \left(v+\frac{1}{2}\right)\omega_e - D_e j^2(j+1)^2 - x_e\omega_e\left(v+\frac{1}{2}\right)^2 - \alpha_e\left(v+\frac{1}{2}\right)j(j(+1) \qquad (VI-42)$$

α_e Represents the rotation – vibration molecular coupling constant (positive value)

$$\omega_e = \frac{1}{2\pi}\sqrt{\frac{k}{m}}, \qquad \alpha_e = 6[x_e B_e^3/\omega_e]^{\frac{1}{2}}6B_e^2/\omega_e, \qquad I_e = \mu r_e^2,$$

$$D_e = \frac{3B_e^3}{w_e^2}, \qquad B_e = \frac{h^2}{8\pi^2 I_e} \qquad (\mathbf{VI-43})$$

I_e this is the moment of inertia corresponds to the interatomic distance at equilibrium

1st Case: We assume that the molecule is a rigid rotator - Harmonic Oscillator without coupling.

So the total energy is:

$$E_{v,j} = B_e j(j+1) + \left(v + \frac{1}{2}\right)\omega_e \qquad (\mathbf{VI-44})$$

B_e Depends on the state of vibration because, when v increases, the molecule expands slightly and the moment of inertia changes.

III-4- 2-Selection rules:

A detailed analysis by quantum mechanics of the simultaneous variations of vibrations and rotations shows that:

When the vibrational transition $v \rightarrow v+1$ takes place j varies from $\pm 1 (\Delta j = \pm 1)$ and in certain cases from zero (when $(\Delta j = 0)$ is allowed.

III-4- 3-Bonds characteristics

It follows from the previous selection rules that there are, for the same vibration of the vibration number v, several rotational transitions. The following figure (Figure (VI-14)) schematically presents these transitions:

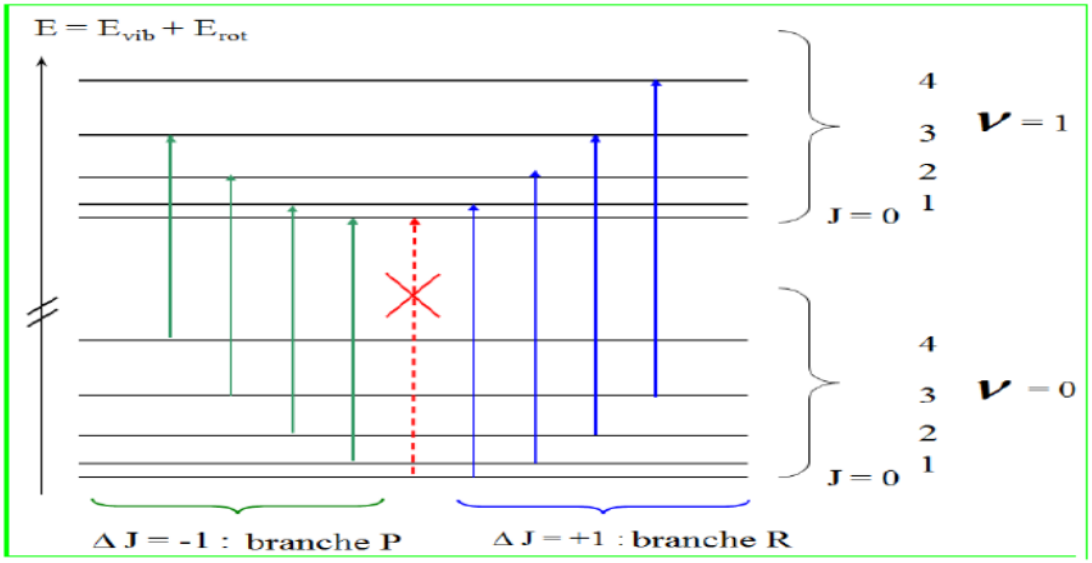


Figure (VI-14): The rotational transitions of the vibration number v.

III-4- 4- Spectral Branches:

The absorptions fall into three spectral branches:

Branche P: consistes of transitions for winch $\Delta j = -1$, $v \to v+1$,

$j+1 \to j$

$$(E_{(v+1,j)} - E_{(v,j+1)})/hc$$

$$= \bar{B}_e\, j(j+i) + (v+\frac{3}{2})\bar{\omega}_e - \bar{B}_e\,(j+1)(j+2) - (v+\frac{1}{2})\bar{\omega}_e$$

$$\bar{\nu}_{v,j+1\to v+1,j} = \bar{\omega}_e - 2\overline{B_e}(j+1) \qquad \textbf{(VI-45)}$$

The distance between two consecutive lines:

$$\Delta\bar{\nu} = \bar{\nu}_{j+1\to j} - \bar{\nu}_{j+2\to j+1} = \bar{\omega}_e - 2\overline{B_e}(j+1) - \bar{\omega}_e + 2\overline{B_e}(j+2) = 2\overline{B_e}$$

$$(\mathbf{VI-46})$$

Branch Q: consists of transitions for which $\Delta j = 0$; $v \to v+1$; $j \to j$

The same steps as branch **P**

$$(E_{(v+1,j)} - E_{(v,j)})/hc = \bar{B}_e\, j(j+i) + (v+\frac{3}{2})\bar{\omega}_e - \bar{B}_e\,(j)(j+1) - (v+\frac{1}{2})\bar{\omega}_e$$

$$\bar{\nu}_{v,j\to v+1,j} = \bar{\omega}_e \qquad (\mathbf{VI-47})$$

- This branch, when permitted, forms a single line.
- In the spectrum of HCl we observe a hole because this branch is prohibited

Branch R: consists of transitions for which $\Delta j = +1$, $v \to v+1$, $j \to j+1$

$$(E_{(v+1,j+1)} - E_{(v,j)})/hc$$

$$= \bar{B}_e\, j(j+i)(j+2) + (v+\frac{3}{2})\bar{\omega}_e - \bar{B}_e\,(j)(j+1) - (v+\frac{1}{2})\bar{\omega}_e$$

$$\bar{\nu}_{v,j\to v+1,j+1} = \bar{\omega}_e + 2\bar{B}_e\,(j+1) \qquad (\mathbf{VI-48})$$

The distance between two consecutive lines:

$$\Delta\bar{\nu} = \bar{\nu}_{j+1\to j+2} - \bar{\nu}_{j\to j+1} = \bar{\omega}_e + 2\overline{B_e}(j+2) - \bar{\omega}_e - 2\overline{B_e}(j+2) = 2\overline{B_e}$$

$$(\mathbf{VI-49})$$

The gap between two branches R and P

- For branch R ($j = 0 \to j = 1$)

$$\bar{\nu} = \bar{\omega}_e + \bar{B}_e$$

- For branch P ($j = 1 \rightarrow j = 0$)

$$\bar{\nu} = \bar{\omega}_e - \bar{B}_e$$

$$\Delta\bar{\nu} = 4\bar{B}_e \qquad (VI-50)$$

- So the gap is twice as large as the intervals between two lines.

2nd Case: We assume that the molecule is a rigid rotator - Harmonic Oscillator with coupling:

$$\bar{E}_{v,j} = \bar{B}_e j(j+1) + \left(v + \frac{1}{2}\right)\omega_e - \alpha_e\left(v + \frac{1}{2}\right) j(j+1) \qquad (VI-51)$$

We pose:

$$\bar{B}_v = \bar{B}_e - \bar{\alpha}_e\left(v + \frac{1}{2}\right)$$

$$\bar{E}_{v,j} = \bar{B}_e j(j+1) + \left(v + \frac{1}{2}\right)\bar{\omega}_e$$

$$I_v = \mu r_v^2 \qquad \bar{B}_v = \frac{h}{8\pi^2 c I_v}$$

Branch R: $\Delta j = +1$

$$v = 0 \rightarrow v = 1; \quad j \rightarrow j+1$$

$$\bar{\nu}_{0,j\rightarrow 1,j+1} = \bar{E}_{(v,j+1)} - \bar{E}_{(0,j)}$$

$$\bar{\nu}_{0,j\rightarrow 1,j+1} = \overline{w_e} + (j+1)[2\overline{B_1} + j(\overline{B_1} - \overline{B_0})]$$

The distance between two consecutive lines:

$$\Delta\bar{\nu} = 2(j+1)(\overline{B_1} - \overline{B_0}) + 2\overline{B_1} \qquad (VI-52)$$

Note: the gap $\Delta\bar{\nu}$ between two consecutive lines of the branch **R** decreases when j increases, which explains the tightening of the lines at large wave numbers.

Branch P: $\Delta j = -1$

$$v = 0 \rightarrow v = 1$$

$$j + 1 \rightarrow j$$

$$\bar{\nu}_{(0,j+1)\rightarrow(1,j)} = \bar{E}_{(1,j)} - \bar{E}_{(0,j+1)}$$

$$\bar{\nu}_{(0,j+1)\rightarrow(1,j)} = \bar{w}_e + (j+1)[(\overline{B_1} - \overline{B_0}) - 2\overline{B_0}]$$

The distance between two consecutive lines:

$$\Delta\bar{\nu} = 2\overline{B_1} - 2(j+1)(\overline{B_1} - \overline{B_0}) \qquad (\mathbf{VI-53})$$

Note: the gap $\Delta\bar{\nu}$ between two consecutive lines of the branch **P** increases when (j) increases, which is explained by the spreading of the lines.

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Abstract

These lessons, entitled Lectures on Spectroscopy, are a set of lessons directed to second-year students of the L-M-D system physics specialty. The content of these lessons was prepared in accordance with the official program and was presented in a simple manner. It is divided into six chapters. The first chapter is entitled Wave-Particle Duality, to familiarize the student with the concept of blackbody radiation, the photoelectric effect, the Compton effect, and de Broglie waves. The second chapter gives information related to the planetary model of the atom, followed by the third chapter, which deals with atomic spectroscopy, which covers ionization potential, the excited state of the atom, atomic spectra, the Ritz principle, and the Heisenberg uncertainty principle. The fourth chapter is entitled: Atoms with multiple electrons. The fifth chapter explains the absorption and stimulated emission (laser effect). Finally, the sixth chapter is an introduction to molecular physics, which deals with diamolecules. These chapters are supported by illustrative diagrams and practical examples.

ملخص

هذه الدروس بعنوان محاضرات في التحليل الطيفي هي مجموعة دروس موجهة لطلاب السنة الثانية تخصص فيزياء نظام L-M-D. تم إعداد محتوى هذه الدروس وفق البرنامج الرسمي و تم عرضها بشكل مبسط. وهي مقسمة إلى ستة فصول. الفصل الأول بعنوان ازدواجية الموجة والجسيم، وذلك لتعريف الطالب بمفهوم إشعاع الجسم الأسود، والتأثير الكهروضوئي، وتأثير كومبتون، وموجات دي برولي. ويتناول الفصل الثاني معلومات تتعلق بالنموذج الكوكبي للذرة، ويتبعه الفصل الثالث الذي يتناول التحليل الطيفي الذري، والذي يغطي احتمال التأين، والحالة المثارة للذرة، والأطياف الذرية، ومبدأ ريتز، ومبدأ عدم اليقين هايزنبرغ. الفصل الرابع بعنوان الذرات ذات الإلكترونات المتعددة. الفصل الخامس يشرح الامتصاص والانبعاث المحفز (تأثير الليزر). وأخيرًا، الفصل السادس عبارة عن مقدمة للفيزياء الجزيئية، والتي تتناول الجزيئات الثنائية. وجميع هذه الفصول مدعمة برسوم بيانية توضيحية وأمثلة عملية.