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Tissemsilt University

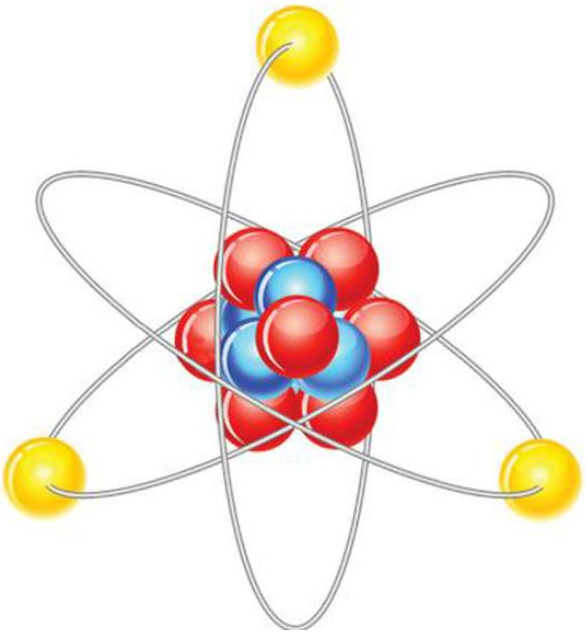
Sciences and Technology Faculty

Matter Sciences Department

2nd year LMD: Fundamental Physics

LECTURE NOTES

ATOMIC PHYSICS



Dr. Fatiha BESAHRAOUI

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Preface

Atomic physics is a field of physics that studies atoms as isolated systems that include electrons and the atomic nucleus. It consists of studying the arrangement of electrons around the nucleus as well as the way in which it is modified. Most areas of study in physics are either theoretical or experimental. The same is true of atomic physics. Progress in a research field is most often made by relying on two pillars: modeling and validation. If the validation cannot confirm the model, the latter must be revised. Likewise, if the model predicts behavior that cannot be validated with the available tools, other tools are possibly developed to confirm or refute the model. Obviously, the essential first step in developing an atomic theory is the recognition that matter is composed of atoms, in the modern sense of the basic unit of chemical elements. This theory was mainly developed by the chemist and physicist John Dalton in the 18th century. At that time, the concept of an atom was vague, although the properties could be described and classified in a periodic table. The modern birth of the theory dates back to the discovery of spectral lines and attempts to describe the phenomenon, with Fraunhofer particularly standing out. The study of these lines led to the construction of Bohr's model and the birth of quantum theory. By attempting to describe the atomic spectrum mathematically, a completely new mathematical model has emerged. Regarding atoms and their electron cloud, this model not only provided a better description via the orbital atomic model, but also gave new theoretical foundations to chemistry, quantum chemistry, and spectroscopy.

This course handout constitutes a personal effort made to understand the appearance of the atom and its components by introducing models and theories to describe the atom from a quantum point of view.

In the first chapter, we give a little history of the famous equivalence or wave-particle duality, going from Christian Huygens and Issac Neuton to Louis De Broglie.

The second chapter is devoted to the study of atomic spectra obtained by atomic absorption and emission spectroscopies. The different models of the atom are thus

described in this part. A detailed study of atomic absorption and emission spectra is introduced in this chapter.

The study of the emission spectra of the hydrogen atom and hydrogenoid atoms is carried out in the third chapter by giving their quantum description according to the Schrödinger model.

In the fourth chapter, we studied atoms with several electrons according to the Schrödinger model, giving the quantum factors which differentiate this study from that for the case of hydrogenoid atoms. In this chapter, we introduced the Pauli exclusion principle as well as the different rules used for the electronic configuration of atoms with several electrons.

The last chapter is devoted to describing the characteristics of X-rays, their source and their spectrum as well as the physical mechanisms responsible for the emission of X-rays.

In the end, I hope that this lecture notes will serve as a valuable working tool for students.

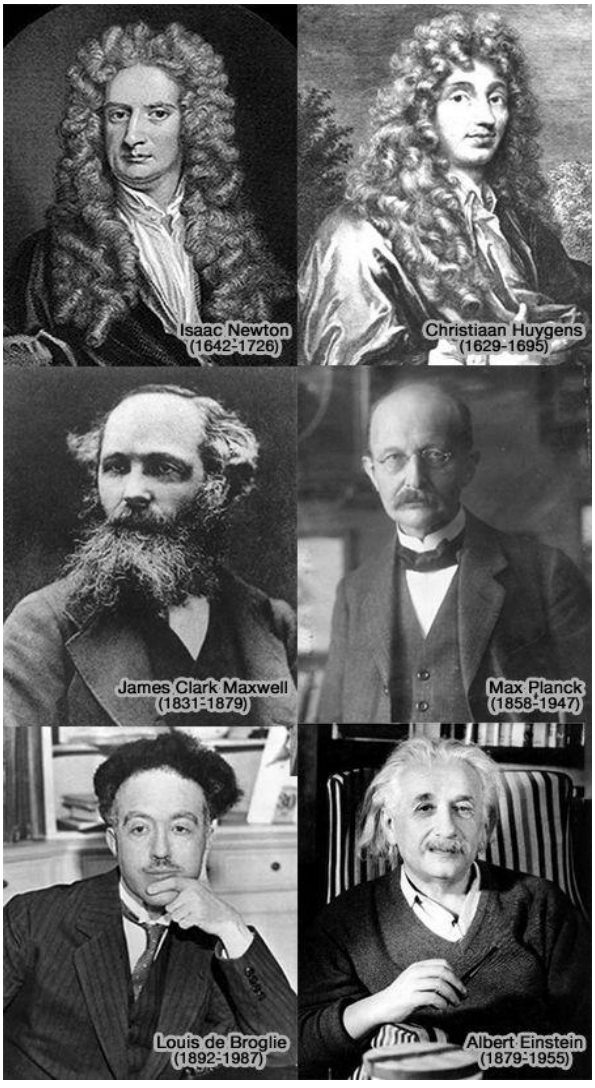
Dr. Fatiha BESAHRAOUI

CHAPTER. I. WAVE - CORPUSCLE DUALITY

Introduction

In physics, wave - corpuscle duality is the concept in quantum mechanics that quantum entities exhibit particle or wave properties according to the experimental circumstances. It expresses the inability of the classical concepts such as particle or wave to fully describe the behavior of quantum objects.

1. Little history (Thought Experiment)



- In the 17th century, two physicists clashed: Christian Huygens (1629-1695) who thought that light is a wave based on diffraction and interference experiments and Issac Neuton (1642-1726) who thought that light is like a stream of corpuscles moving at infinite speed.
- At the end of the 19th century, two discoveries were made in opposition. The movements of a solid thanks to Isaac Newton's theory of gravitation and wave movements thanks to the theory of electromagnetism of James Clerk Maxwell (1831-1879) who unified electric and magnetic phenomena by creating an electromagnetic wave . Maxwell also believed that the speed of light is independent of the speed of an observer relative to the source that emits the light. Which is incompatible with the laws of classical Newtonian mechanics.
- In 1900, it was Max Planck (1858-1947) who first thought that an electromagnetic wave of frequency ν can only emit electromagnetic energy (E) in packets of integer

- multiple values of the quantum $h\nu$ which means how many in Latin (plural of "quantum is quanta) where h is a new fundamental constant ($h = 6{,}62618.10^{-34}\ J.s$) introduced to describe the size of the quanta, a constant which plays a central role in the quantum mechanics.

$$E = h\nu \text{…….} \text{…….(Eq.1)}$$

- In 1905 Albert Einstein (1879-1955) introduced the notion of light quanta which were later named "photons" in 1926. A photon is a particle that carries a quantum of energy hν to explain the threshold effect of the photoelectric effect. Certain experiences, in fact, can only be explained thanks to a corpuscular description of light. Thus, the Compton effect results from an elastic collision between a photon and an electron, a collision during which the photon transfers energy to the electron. The light is both
  - a wave phenomenon, hence the concept of electromagnetic wavelength,
  - a corpuscular phenomenon, as evidenced by photons.
- In the 1920s, quantum mechanics developed by several scientists, and in particular Niels Bohr (1885-1962) who explained the microscopic world by probability amplitudes (wave functions) for particles. This mechanism deeply shocked Einstein and this controversy continued until their death.
- It was in 1923 that Louis de Broglie (1892-1987) extended wave-particle duality to material particles. He showed that all objects have a dual nature of wave and corpuscle, starting with the electron to which he assigned a wavelength (λ) called "de Broglie expressed by:

$$\lambda = \frac{h}{p} = \frac{h}{m\nu} = \frac{h}{\sqrt{2mE}} \text{…….(Eq.2)}$$

h is Planck's constant, p is the momentum. m, the mass, ν the velocity and E is the kinetic energy.

It can also be written as $\vec{p} = \hbar\vec{k}$ with $\hbar$ is the reduced Planck constant: $\hbar = \frac{h}{2\pi}$. We deduce that the kinetic energy of the particle is:

$$E_c = \frac{p^2}{2m} = \frac{\hbar^2 k^2}{2m} \text{…….(Eq.3)}$$

Louis de Broglie *: «My essential idea was to extend to all particles the coexistence of waves and particles discovered by Einstein in 1905 in the case of light and photons »*

In the theory of special relativity (used mainly for the velocities close to the velocity (C) of light in the vacuum, but valid for all the velocities, we introduce the Lorentz factor : $\gamma = \frac{1}{\sqrt{1-\frac{v^2}{c^2}}}$, Theodore :

$$\lambda = \frac{h}{mv}\sqrt{1-\frac{v^2}{c^2}} \quad \text{(Eq.4)}$$

However, the photon comes from an electromagnetic field and it represents a quantification of this field: one of the fundamental consequences of this duality is that there then exists for each particle a fundamental field whose excitation represents the particle itself, as we already do it for the photon.

2. Highlighting wave-corpuscle duality

2.1. Young's double slit experiment

While studying medicine at Göttingen in the 1790s, Thomas Young (1773-1829) wrote a thesis on the physical and mathematical properties of sound and in 1800, he presented a paper entitled "On the Theory of Light and Colours" which describes various interference phenomena. In 1803, he described his famous interference experiment. Unlike the modern double-slit experiment, Young's experiment reflects sunlight (using a steering mirror) through a small hole, and splits the thin beam in half using a paper card. He also mentions the possibility of passing light through two slits in his description of the experiment. His idea was greeted with a certain amount of skepticism because it contradicted Newton's corpuscular theory. Nonetheless, he continued to develop his ideas. He believed that a wave model could much better explain many aspects of light propagation than the corpuscular model.

2.1.1. Basic principles

Young's double slit experiment uses two coherent sources of light placed at a small distance apart. Usually, only a few orders of magnitude greater than the wavelength of light are used. Young's double slit experiment helped in understanding the wave theory of light, which is explained with the help of a diagram. As shown, a screen or photodetector is placed at a large distance (D), away from the slits.

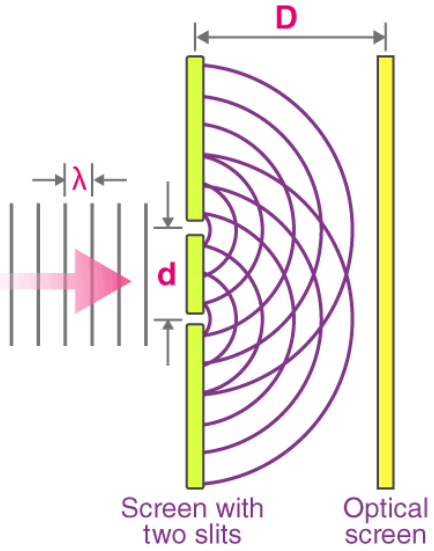
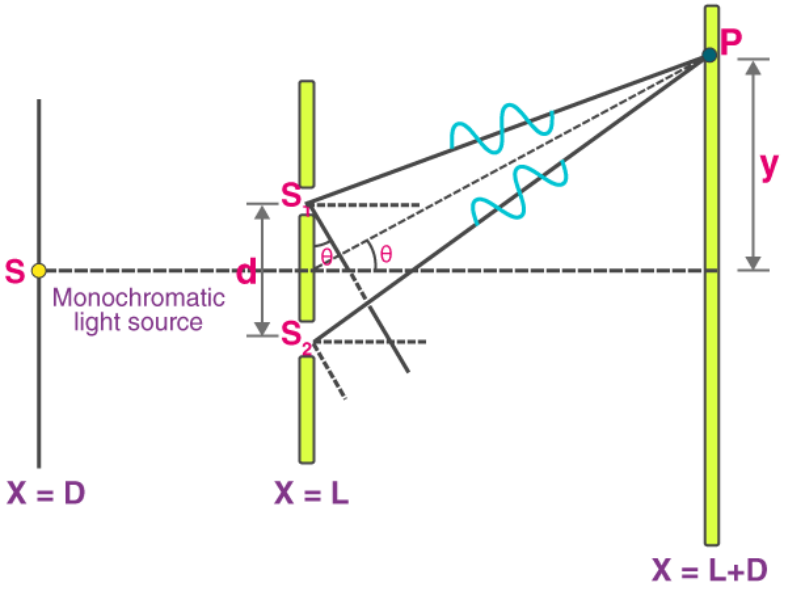


Figure.1. Principle of Young's Double Slit Experiment.

The original Young's double slit experiment used diffracted light from a single source passed into two more slits to be used as coherent sources. Lasers are commonly used as coherent sources in modern-day experiments.

2.1.2. Geometrical considerations

Consider a monochromatic light source 'S' kept at a considerable distance from two slits: S_1 and S_2. S is equidistant from S_1 and S_2. S_1 and S_2 behave as two coherent sources as both are derived from S.



The light passes through these slits and falls on a screen which is at a distance 'D' from the position of slits S_1 and S_2. 'd' is the separation between two slits. If S_1 is open and

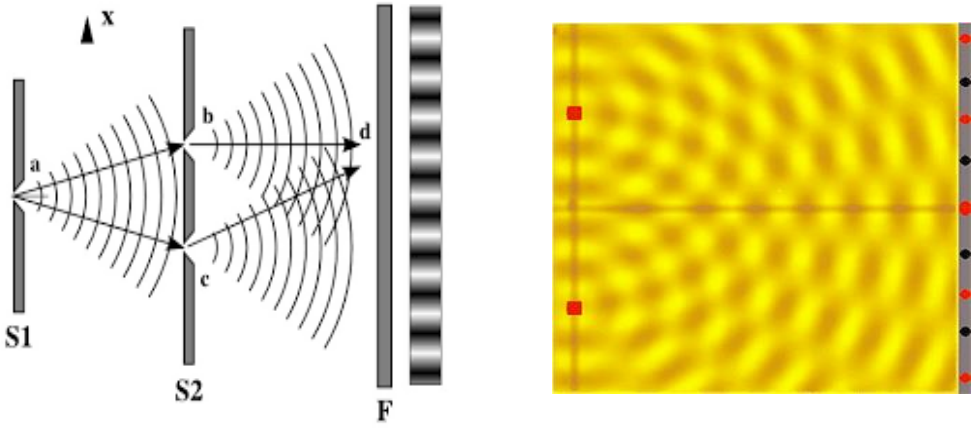
S_2 is closed, the screen opposite to S_1 is closed, and only the screen opposite to S_2 is illuminated. The interference patterns appear only when both slits S_1 and $S_2$are open. When the slit separation (d) and the screen distance (D) are kept unchanged, to reach P, the light waves from s1 and s2 must travel different distances. It implies that there is a path difference in Young's double slit experiment between the two light waves from

- ***Approximations in Young's double slit experiment S_1 and S_2.***
  - ***Approximation 1:*** $D >> d$: Since $D >> d$, the two light rays are assumed to be parallel.
  - ***Approximation 2:*** $d/\lambda >> 1$: Often, d is a fraction of a millimeter, and λ is a fraction of a micrometer for visible light.

Under these conditions, θ is small. Thus, we can use the approximation : $sin\,\theta = tan\,\theta \approx \theta = \lambda/d$. The path difference, $\Delta z = \lambda/d$.

Δz is the path difference between two waves meeting at a point on the screen. Due to this path difference in Young's double slit experiment, some points on the screen are bright, and some points are dark.

- ***Position of Fringes in Young's Double Slit Experiment***



Now, we will discuss the position of these light and dark fringes and fringe width.

- ***Position of Bright Fringes:***

For maximum intensity or bright fringe to be formed at P, Path difference:

$$\Delta z = n\lambda\ (n = 0, \pm1, \pm2, \ldots.)$$

$xd/D = n\lambda$ or $x = n\lambda D/d$

The distance of the nth bright fringe from the centre is :

$$x_n = n\lambda D/d$$

Similarly, the distance of the (n-1)th bright fringe from the centre is :

$$x_{n-1} = (n-1)\lambda D/d$$

Fringe width : $\beta = x_n - x_{n-1} = n\lambda D/d - (n-1)\lambda D/d = \lambda D/d$

(n = 0, ±1, ±2,….).

- ***Position of Dark Fringes***

For minimum intensity or dark fringe to be formed at P, Path difference :

$$\Delta z = (2n+1)(\lambda/2)\ (n = 0, \pm 1, \pm 2, \ldots.)$$

$$x = (2n+1)\lambda D/2d$$

The distance of the nth dark fringe from the centre is :

$$x_n = (2n+1)\lambda D/2d$$

Similarly, the distance of the (n-1)th bright fringe from the centre is :

$$x_{n-1} = (2(n-1)+1)\lambda D/2d$$

Fringe width:

$$\beta = x_n - x_{n-1} = (2n+1)\lambda D/2d - (2(n-1)+1)\lambda D/2d = \lambda D/d$$

$$(n = 0, \pm 1, \pm 2, \ldots.)$$

- ***Fringe Width***

The distance between two adjacent bright (or dark) fringes is called the fringe width.

$$\beta = \lambda D/d$$

If the apparatus of Young's double slit experiment is immersed in a liquid of refractive index (μ), then the wavelength of light and fringe width decreases 'μ' times.

$$\beta^1 = \frac{\beta}{\mu}$$

If white light is used in place of monochromatic light, then coloured fringes are obtained on the screen, with red fringes larger in size than violet.

- ***Angular Width of Fringes***

Let the angular position of nth bright fringe is θ_n, and because of its small value, $tan\ \theta_n \approx \theta_n, \tan\theta_n = \frac{\lambda n}{d} \Rightarrow \theta_n = \frac{n\lambda}{d}$

Similarly, the angular position of (n+1)th bright fringe is θ_{n+1}, then :

$$\theta_{n+1} = \frac{(n+1)\lambda}{d}$$

The angular width of a fringe in Young's double slit experiment is given by :

$$\theta = \theta_{n+1} - \theta_n = \frac{(n+1)\lambda}{d} - \frac{n\lambda}{d} = \frac{\lambda}{d}$$

$$\theta = \frac{\lambda}{d}$$

We know that : $\beta = \frac{\lambda D}{d} \Rightarrow \theta = \frac{\lambda}{d} = \frac{\beta}{D}$

Angular width is independent of 'n', i.e., the angular width of all fringes is the same.

2.2. Jönsson's double slit experiment

Young carried out his original double-slit experiment with light some time in the first decade of the 1800s, showing that the waves of light from the two slits interfered to produce a characteristic fringe pattern on a screen. In the early 1950s Ladislaus Laszlo Marton of the US National Bureau of Standards (now NIST) in Washington, DC demonstrated electron interference but this was in a Mach-Zehnder rather than a double-slit geometry. These were the early days of the electron microscope and physicists were keen to exploit the very short de Broglie wavelength of electrons to study objects that were too small to be studied with visible light. Doing gedanken or thought experiments in the laboratory was further down their list of priorities.

A few years later Gottfried Möllenstedt and Heinrich Düker of the University of Tübingen in Germany used an electron biprism, essentially a very thin conducting wire at right angles to the beam – to split an electron beam into two components and observe interference between them. (Möllenstedt made the wires by coating fibres from spiders' webs with gold – indeed, it is said that he kept spiders in the laboratory for this purpose). The electron biprism was to become widely used in the development of electron holography and also in other experiments, including the first measurement of the Aharonov-Bohm effect by Bob Chambers at Bristol University in the UK in 1960.

But in 1961 Claus Jönsson of Tübingen, who had been one of Möllenstedt's students, finally performed an actual double-slit experiment with electrons for the first time (Zeitschrift für Physik 161 454). Indeed, he demonstrated interference with up to five slits. The next milestone – an experiment in which there was just one electron in the

apparatus at any one time – was reached by Akira Tonomura and co-workers at Hitachi in 1989 when they observed the build up of the fringe pattern with a very weak electron source and an electron biprism (American Journal of Physics 57 117-120). Whereas Jönsson's experiment was analogous to Young's original experiment, Tonomura's was similar to G I Taylor's. (Note added on 7 May: Pier Giorgio Merli, Giulio Pozzi and GianFranco Missiroli carried out double-slit interference experiments with single electrons in Bologna in the 1970s; see Merli et al. in Further reading and the letters from Steeds, Merli et al., and Tonomura at the end of this article.)

Since then particle interference has been demonstrated with neutrons, atoms and molecules as large as carbon-60 and carbon-70. And earlier this year another famous experiment in optics – the Hanbury Brown and Twiss experiment – was performed with electrons for the first time (again at Tübingen!). However, the results are profoundly different this time because electrons are fermions – and therefore obey the Pauli exclusion principle – whereas photons are bosons and do not.

2.2.1. Basic principles

In order to verify de Broglie's hypothesis, in 1961, Claus Jönsson carried out for the first time a real Young-type experiment with electrons diffusing on slits. The electrons were accelerated by a source at 50 keV. The slits were very narrow (0.5 μm) and separated by approximately 0.1 μm. They were made on a copper foil. According to this experiment setup, Jönsson was able to show extraordinarily tight interference patterns, less than a 10^{th} of a μm apart, observed with an electron microscope.

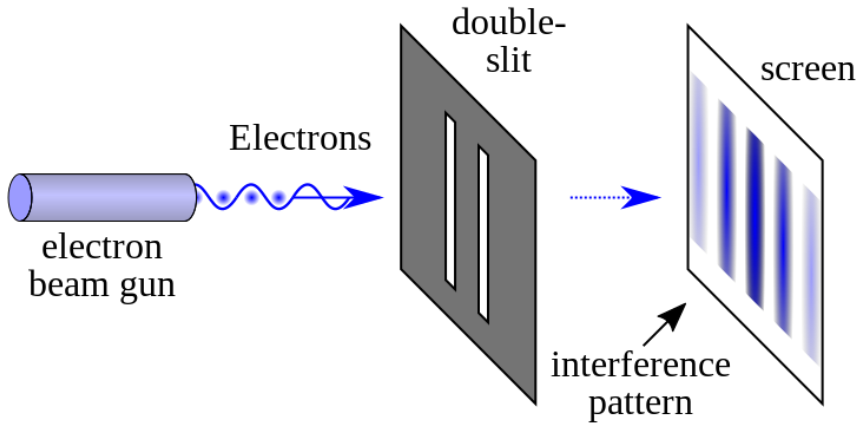


Figure.2. Jönsson's double slit experiment.

By the same geometric analysis as that of Young's experiment it is possible to deduce the wavelength which produced these interferences. We then obtain $\lambda = 0.05$ Å. Electrons behave like waves and their wavelength can be measured.

Jönsson's experiment requires that the electrons be isolated. Therefore, they pass through the device one by one, to avoid their reciprocal repulsion, which would confuse the result. This is the reason we take a very high voltage, so that they are ultra-fast (around 1/3 the light velocity). Furthermore, to avoid collisions with air molecules, the experiment must be carried out in a high vacuum. However, if the electrons pass one by one, we can ask which slit each passes through. This is a legitimate question, but without an answer. Any trick, or any mechanism for systematically revealing where an electron passes, has the effect of removing interference fringes. Clearly, nature clings to its quantum quirks and doesn't allow us to get around them.

3. X-ray diffraction (XRD)

Roentgen identified X–rays in 1895 as a by–product of experiments using high energy electron beams. The X-rays were produced via bremsstrahlung emission in the glass walls of the evacuation chamber. In the following decade, Charles Barkla demonstrated that X-rays demonstrated polarization phenomena – an important clue that they might be an electromagnetic wave. However, it was very difficult to produce diffraction or interference effects with X–rays – a null result that was understood only if X–rays had very short wavelengths, e.g. 10^{-10}m or 10^{-11}m.

Electromagnetic waves produce diffraction or interference patterns when the wavelength is of the order of or smaller than the size of the grating rulings (diffraction) or aperture in a screen (interference).

3.1. Max von Laue experiment

In 1912, Max Von Laue discovered that x-rays were di ffracted by a crystal, just like visible light is diffracted by a crystal lattice. This discovery proved both:

- The wave nature of X-rays: Waves like visible light, which were unknown at the time.
- The periodic structure of crystals: A crystal behaves like a network. The atoms are aligned regularly in a crystal structure, each atom diffracts the incident X-

rays and we observe a peak of intensity in the directions where the different diffracted waves interfere constructively (Figure. 4).

Max von Laue was the first to suggest that, as the interatomic spacing in certain crystals is of the order of 10^{-10}m, a suitably orientated crystal might act as a diffraction grating for X–rays. The experimental set–up that confirmed Laue's prediction is shown in the following figure.

The dots on the photographic screen are referred to as Laue dots and correspond to diffraction maxima produced by the three dimensional crystal structure.

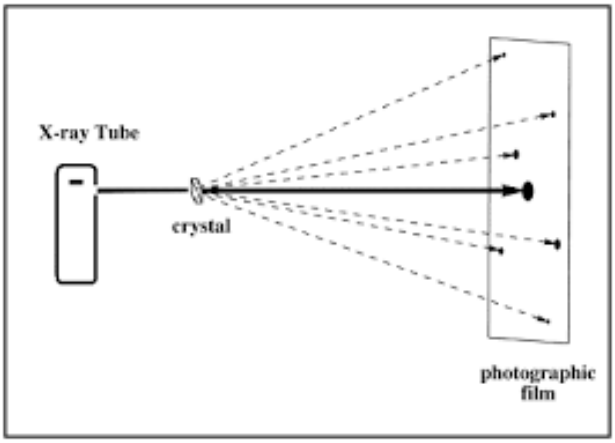


Figure.3. X-ray Laue diffraction experiment.

Laue's approach not only demonstrates the wave–like nature of X–rays but provides an important method for determining the structure of crystalline solids (and molecular material such as DNA.The geometry of X–rays scattering from a simple crystal is shown in the following figure.

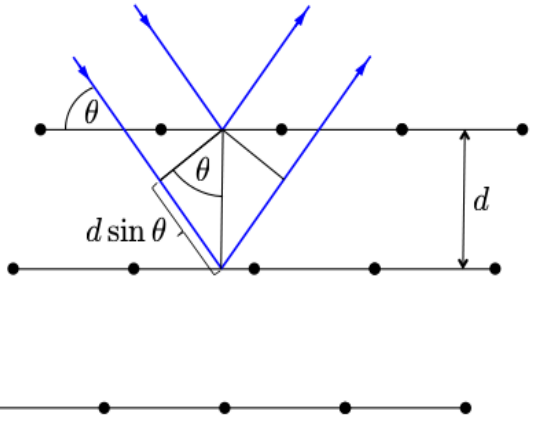


Figure.4. Bragg reflection from a particular family of lattice planes.

From this diagram and the above two conditions we derive Bragg's law

$$2d\ sin(\theta) = n\lambda \quad \text{(n integer)} \qquad \text{(Eq.5)}$$

$2d\ sin(\theta)$ is the path difference between the two shown rays.

The following figure shows the apparatus used in a Bragg spectrometer. The apparatus consists of a X-ray tube from which a narrow beam of X-rays is allowed to fall on the crystal mounted on a rotating table. The rotating table is provided with scale and vernier from which the angle of incidence θ can be measured.

An arm which is rotating about the same axis as the crystal table, carries an ionization chamber. The rays reflected from crystal enter into the ionization chamber and ionize the gas present inside. Due to the ionization, current produced is measured by electrometer. The current of ionization is a direct measure of intensity of reflected beam from the crystal. For different angles of incidence, the corresponding ionization current is measured from the electrometer. These values are plotted in the form of graph.

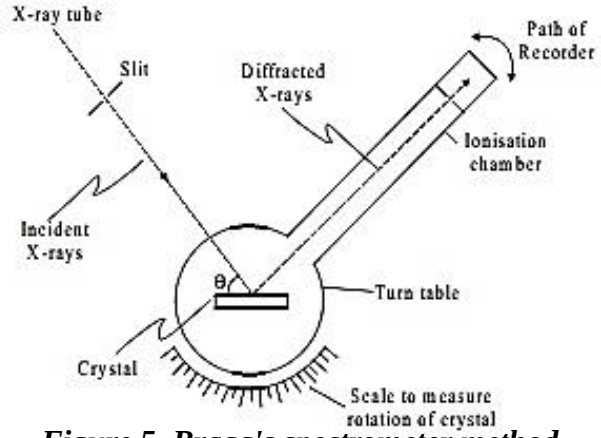
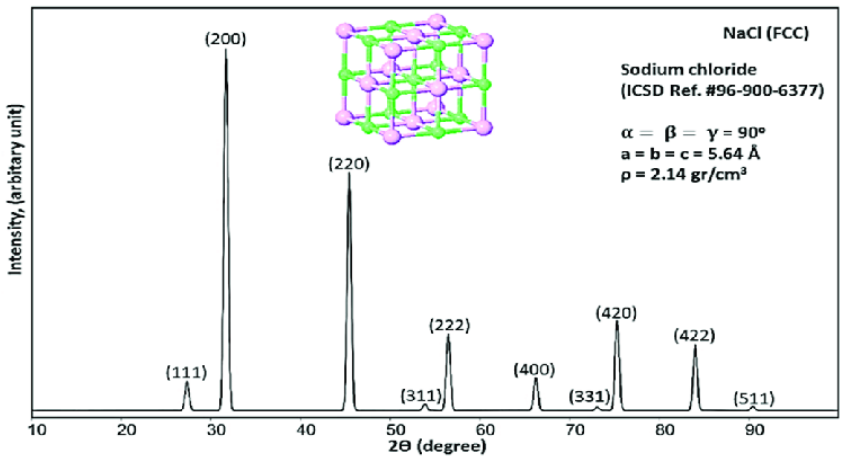


Figure.5. Bragg's spectrometer method.

Example :

The following figure presents XRD pattern of rock salt NaCl. We observed an intense diffraction maximum at an angle of 31.6° from the incident beam. Assuming $n = 1$, what is the wavelength of incident radiation?



Solution:

We see that the angle between the incident beam and the diffraction peak is 2θ.

We can then use basic chemical data to compute the interatomic spacing d, if we assume that the volume occupied with one atom is d^3.

The number of molecules per unit volume is :

$\frac{\text{number of molecules}}{\text{volume}} = \frac{N_A \rho}{M}$. Inserting the values for NaCl, we obtain

$$\frac{N_A \rho}{M} = \frac{\left(6.02 \times 10^{23} \frac{\text{molecules}}{\text{mol}}\right)\left(2.16 \times 10^{3} \frac{\text{kg}}{\text{m}^3}\right)}{58.5 \times 10^{-3} \frac{\text{kg}}{\text{mol}}}$$

$$= 2.22 \times 10^{28} \frac{\text{molecules}}{\text{m}^3}$$

$$= 4.45 \times 10^{28} \frac{\text{atoms}}{\text{m}^3}.$$

As NaCl has a simple, cubic structure, we may write $\frac{1}{d^3} = 4.45 \times 10^{28} \frac{\text{atoms}}{\text{m}^3}$

$$d = 2.82 \times 10^{-10}\,\text{m} = 0.282\,\text{nm}.$$

Now that we know d we can rearrange the Bragg law in terms of wavelength, i.e.

$$\lambda = \frac{2d\sin\theta}{n} = \frac{2 \times 0.282 \times \sin 15.8}{1} = 0.153\,nm = 1.53\,°A$$

This analysis demonstrates how crystals of known properties act as a X–ray diffraction spectrograph. Conversely, by using X–rays of known wavelength, one can probe the geometry of the Bragg planes and thus learn about new crystal structures.

4. Electron diffraction

4.1. Davisson and Germer experiment

In 1927, three years after the thesis of de Broglie, Clinton Davisson and Lester Germer have supposed that low energy electrons possess a De Broglie wavelength similar to X–rays. It is therefore reasonable to anticipate that they might generate diffraction effects in a similar fashion to X–rays. Davisson and Germer were in the process of studying electron scattering from metal surfaces during the period when De Broglie developed his concept of matter waves. Their experimental set up is shown in figure.6 and consisted of an electron beam of energy 40–70 eV directed at a nickel target. Under normal circumstances nickel exists

as a polycrystalline solid and the scattered electron beam shows a smooth variation of intensity versus angle φ.

However, a laboratory accident required the nickel target to be repeatedly heated and cooled in order to ensure a pure nickel sample, a process which created extended, uniform crystals of nickel on the surface. The electron scattering pattern now demonstrated a variable pattern as a function of beam energy, with a strong intensity peak evident at φ = 50◦ for a beam energy of 54 eV (figure.7).

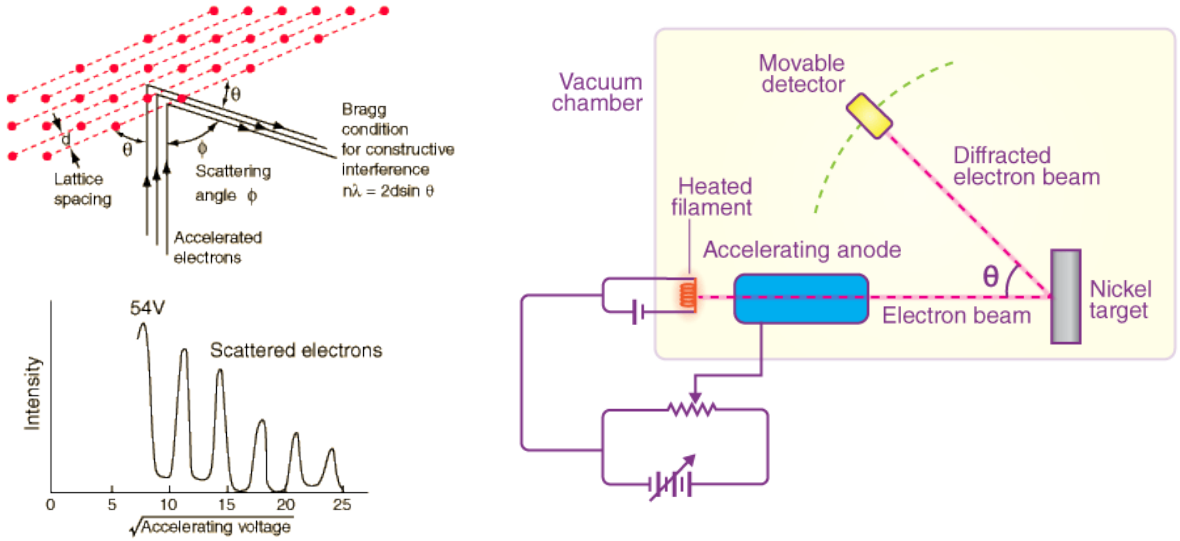


Figure.6. Davisson and Germer electrons diffraction experiment.

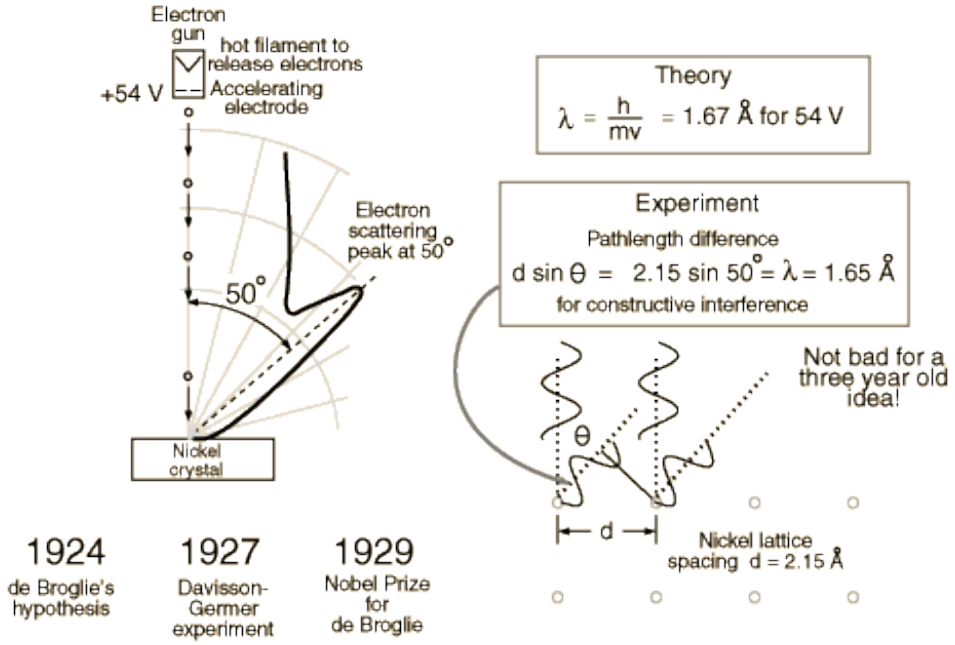


Figure.7. Davisson and Germer experiment conditions.

Davisson and Germer's insight was to apply the Bragg law to their data. Figure.7 shows the relationship between the incident electron beam and the nickel crystal. The angular

relationships are slightly different to the original Bragg case. The Bragg law states that $n\lambda = 2d\,sin\,\theta$ (where 2θ is the angle between the incident and exiting beams). However, from Figure.7, we have $\varphi = \pi - 2\theta = 2\alpha$. As $sin\,\theta = cos(\varphi/2) = cos\,\alpha$, we can rewrite the Bragg condition as $n\lambda = 2d\,cos\,\alpha$. However, d is the lattice plane spacing and is related to the interatomic distance D by $d = D\,sin\,\alpha$. Therefore, we can write :

$$n\lambda = 2d\sin\theta = 2d\cos\alpha = 2D\sin\alpha\cos\alpha$$

$$n\lambda = D\,sin\,2\alpha = D\,sin\,\varphi \text{……...……(Eq.6)}$$

Or:

$$\lambda = \frac{D\sin\varphi}{n} \text{……...…...……(Eq.7)}$$

For nickel, the interatomic distance is $D = 0.215\,nm$. Assuming that the electron scattering peak at 50◦ corresponds to n = 1, then the electron wavelength is

$$\lambda = (0.215\,nm)(sin\,50°) = 0.165\,nm \text{……(Eq.8)}$$

Example: Determine the de Broglie wavelengths for an electrons of 54 eV of kinetic energy.

Solution:

The De Broglie wavelength of an electron can be written in terms of the potential difference V_0 over which the electron is accelerated. For the kinetic energy of the electron we may write:

$$\frac{p^2}{2m} = eV_0 \rightarrow p = \sqrt{2meV_0}$$

Inserting this relationship into the expression for the De Broglie wavelength, we obtain:

$$\lambda = \frac{h}{p} = \frac{hC}{pC} = \frac{hC}{\sqrt{2(mC^2)eV_0}} = \frac{1240\,eV.nm}{\sqrt{2\times511\times10^3 eV(eV_0)}} = \frac{1.226nm\,V^{1/2}}{\sqrt{V_0}}$$

$$= \frac{1.226nm\,V^{1/2}}{\sqrt{54}} = 0.167\,nm$$

which is in very good agreement with the value for λ determined experimentally by Davisson and Germer. This first measurement was performed by scattering electrons off a metallic crystal target. Later experiments employed transmission electron diffraction.

The electron beam was fired through a material to produce diffraction patterns similar to X-ray images (Figure.8).

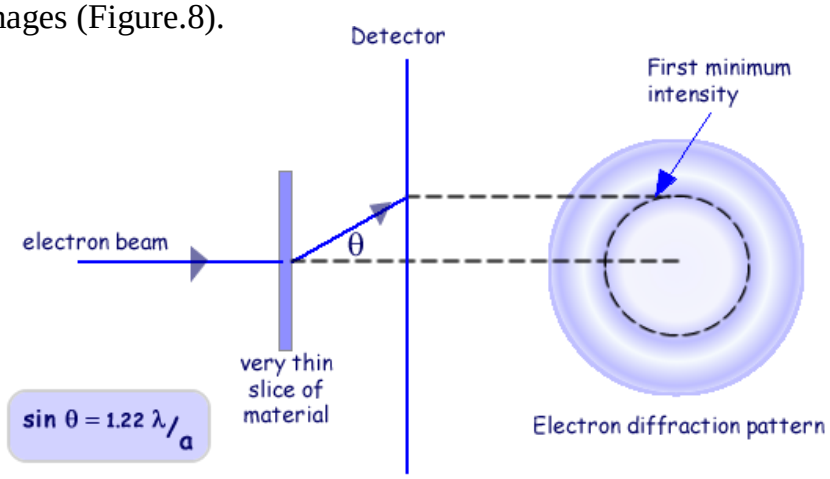


Figure.8. Transmission electron diffraction pattern.

5. Matter waves properties

The de Broglie theory, which states that light can have dual nature is governed by a set of properties which the matter waves are said to exhibit and hence the application of the concept of de-Broglie waves is required. The criteria under which the waves are said to be called de-Broglie waves need to be determined in order to state or list out the properties of matter waves. In fact, Light is capable of exhibiting a dual nature which means that it can obey both light and wave properties but not at the same time. According to de-Broglie a moving material particle is said to exhibit the wave nature at certain times and the particle nature at other times. The particle theory of light states that light travels through packets of energy also given by the corpuscular theory of light. When a moving particle is said to exhibit particle nature the wave was named after the person who stated this theory. Hence these waves were called matter waves or de-Broglie waves given by equation.2. The basic principle behind these matter waves is that they describe the relationship between the wave nature and the particle nature by relating the wave characteristic, that is, wavelength with the particle characteristic, that is, momentum and hence this is given by the de-Broglie wavelength. All matter at a subatomic level, that is, at a microscopic level is said to obey the wave nature and hence the wave-like motion of particles like electrons and protons can be significantly observed.

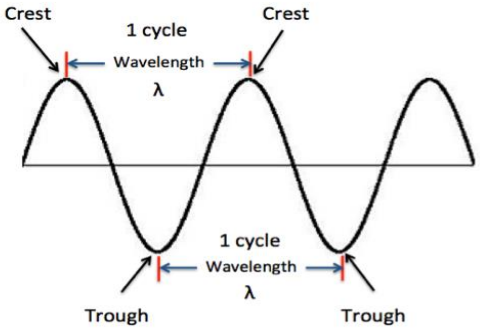
- ✓ Matter waves are not electromagnetic in nature because electromagnetic waves are only associated with accelerated charged particles but the matter waves need not have charge in its material.
- ✓ Matter waves' phase velocity could be larger than that of the speed of light.
- ✓ Matter waves are named so because they are independent of charges because as per the equation given by de-Broglie the motion of the particle is dependent only on its wavelength, mass, velocity and hence its momentum.
- ✓ The likelihood of locating a particle in spacetime is represented by a matter-wave.
- ✓ The charge of a material component has no effect on matter waves.
- ✓ Even though matter waves may travel throughout a vacuum, they are not mechanical waves.
- ✓ The electron microscope would be constructed on de-Broglie waves.

5.1. Concept of wave function

In quantum mechanics, we cannot use the notion of trajectory to describe the dynamics of material particles such as electrons. We are going to introduce a new mathematical tool, which will take into account the wave behavior of matter. Indeed, we associate with a particle a wave function denoted $\psi(\vec{r}\,,t)$ which depends on space and time, and which contains all the information available on the particle. The existence of the wave function is one of the postulates of quantum mechanics. However, before describing the relationship between the presence of a particle and its wave function, we will introduce some basic parameters about the wave function.

5.1.1. Wavelength

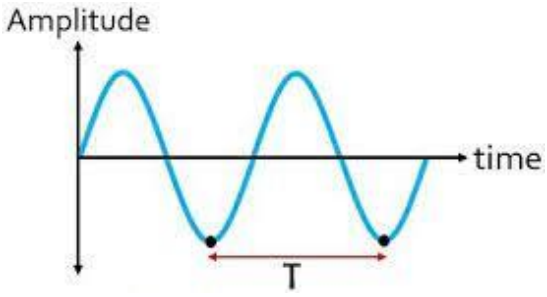
The wavelength noted λ, of a wave describes how long the wave is. In electromagnetism, the wavelength is distance traveled to complete one cycle (figure below). The distance from the "crest" (top) of one wave to the crest of the next wave is the wavelength. Alternately, we can measure from the "trough" (bottom) of one wave to the trough of the next wave and get the same value for the wavelength.



Crest, Trough and Wavelength

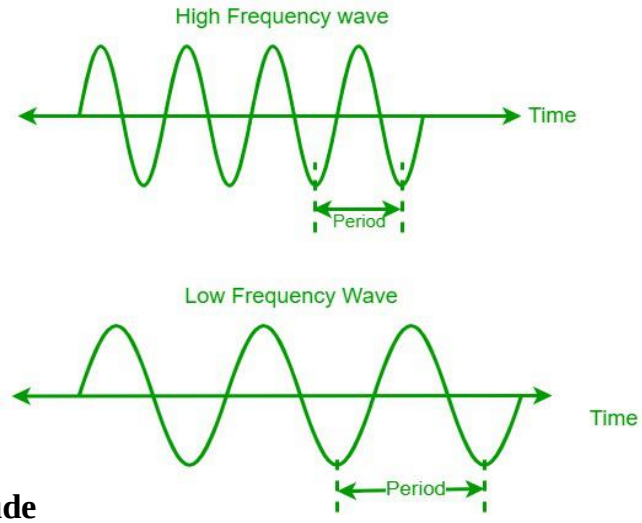
5.1.2. Wave period

The wave period, denoted T, is the length of time that it takes to complete one cycle. It presents the amount of time it takes for a wave to complete one cycle. To calculate the wave period, one must know the wave's frequency.



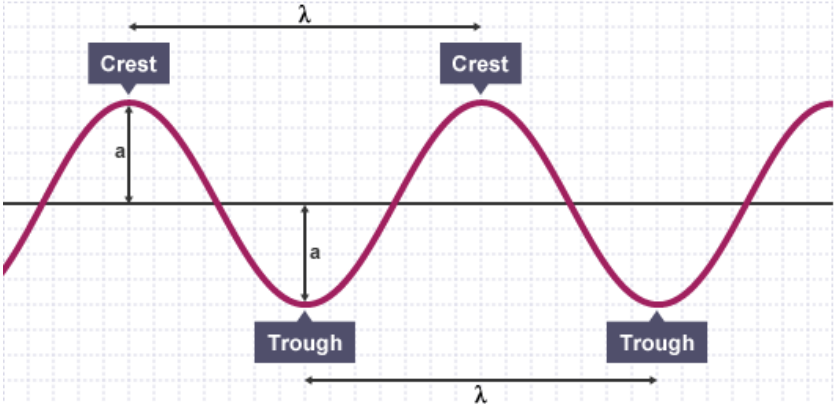
5.1.3. Wave frequency

The frequency of a wave denoted (f) or (ν) presents the number of cycles (waves) produced by a source each second. It is also the number of waves that pass a certain point each second. The unit of frequency is the hertz (Hz). It is common for kilohertz (kHz), megahertz (MHz) and gigahertz (GHz) to be used when waves have very high frequencies. The frequency (f) is the inverse of the period: $f = 1/T$ (Hz or s^{-1}).



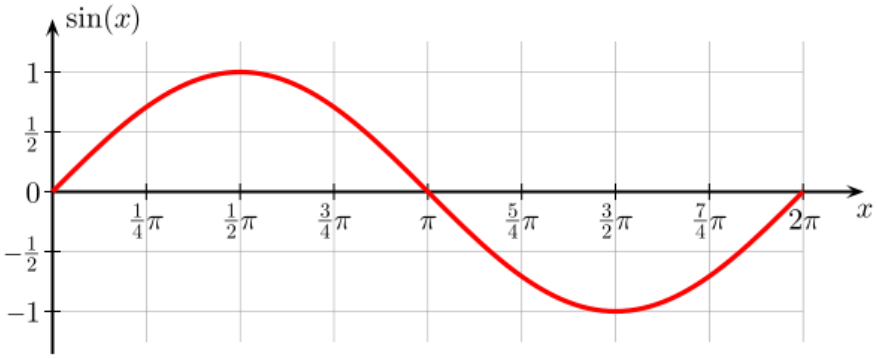
5.1.4. Wave amplitude

The amplitude (a) of a wave is the distance from the centre line (or the still position) to the top of a crest or to the bottom of a trough. Be careful with this quantity, the centre line is not always given in a diagram. Amplitude is measured in meters. The greater the amplitude of a wave then the more energy it is carrying.



5.1.5. Wave phase

The phase of a wave denoted φ or ϕ is the value representing a fraction of a wave cycle. In a wave, a complete cycle, from crest to crest or trough to trough, is equal to 2π rad. Every fraction of that length, therefore, is less than 2π rad. Half a cycle is π rad, while a quarter of a cycle is π/2 rad.



To calculate the wave phase in an arbitrary position, you need to identify how far this position is from the beginning of your wave cycle. In the simple case, if your wave can be approximated by a sine or cosine function, your wave equation can be simplified as:

$$y = A\sin(x) \quad \text{.....(Eq.9)}$$

Here, A is the maximum amplitude of the wave, x is the value on the horizontal axis, which repeats from 0 to 2π for sinus or cosinus functions, and y is the wave height at x. The phase of any point x can be determined using the equation below:

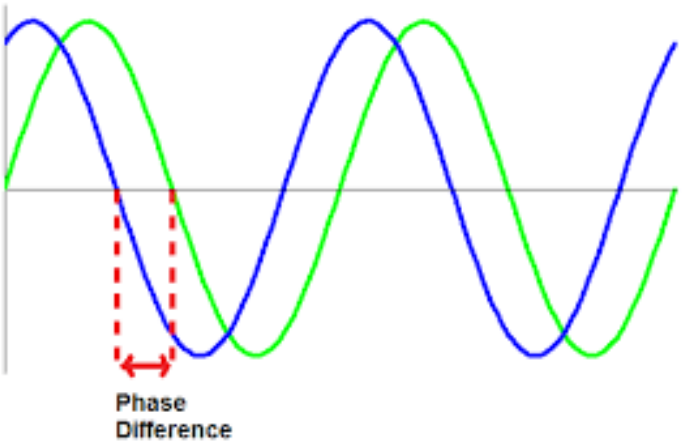
$$x = sin^{-1}y \quad \text{.....(Eq.10)}$$

The equation gives you the value of x in radians, so you need to convert to degrees to obtain the phase. This is done by multiplying x by 180 degrees and then dividing by π.

$$\phi(x) = x \cdot \frac{180^\circ}{\pi} \text{.....(Eq.11)}$$

❖ ***The phase difference in waves***

The phase difference of waves occurs when two waves move and their cycles do not coincide. The phase difference is known as the cycle difference between two waves at the same point. Overlapping waves that have the same cycle are known as waves in phase, while waves with phase differences that do not overlap are known as out-of-phase waves. Waves that are out of phase can cancel each other out, while waves in phase can amplify each other. If two waves have the same frequency/period, we can calculate their phase difference. We will need to calculate the difference in radians between the two crests that are next to each other, as in the following figure.



This difference is the phase difference: $\Delta\phi = \phi_1 - \phi_2$

Here is an example of how to calculate the wave phase and the wave phase difference.

Example:

A wave with a maximum amplitude A of 2 metres is represented by a sine function. Calculate the wave phase when the wave has an amplitude of y = 1. Using the $y = A \cdot \sin(x)$ relationship and solving for x gives us the following equation:

$$x = \sin^{-1}(\frac{y}{A}) = \sin^{-1}(\frac{1}{2})$$

This gives us: $x = 30^\circ$

Converting the result to radians, we get: $\phi(30) = 30^\circ \cdot \frac{\pi}{180^\circ} = \frac{\pi}{6}$

Now let's say another wave with the same frequency and amplitude is out of phase with the first wave, with its phase at the same point x being equal to 15 degrees. What is the phase difference between the two?

First, we need to calculate the phase in radians for 15 degrees.

$$\phi(15) = 15° \cdot \frac{\pi}{180°} = \frac{\pi}{12}$$

Subtracting both phases, we obtain the phase difference: $\Delta\phi = \phi(15) - \phi(30) = \frac{\pi}{12}$

In this case, we can see that the waves are out of phase by π / 12, which is 15 degrees.

5.1.6. Wave angular frequency

Angular frequency denoted ω is a fundamental concept in studying wave motion and oscillations. It measures the angular displacement of a particle per unit time. The formula for angular frequency, is given by:

$$\omega = 2\pi\nu = \frac{2\pi}{T} \text{.....(Eq.12)}$$

The angular frequency is measured in radians per second (rad/s).

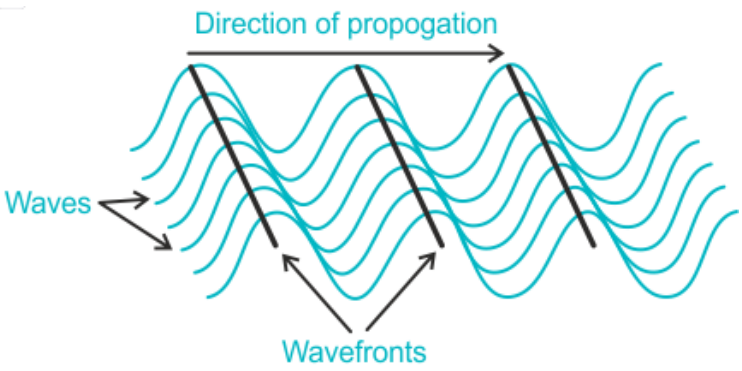
5.1.7. Wave vector

The wave vector, denoted $\vec{k}$ is a mathematical vector that represents the spatial and directional properties of a wave. It provides essential information about the wave's propagation direction, magnitude, wavelength, and phase. The wave vector is typically measured in m^{-1}. The magnitude of the wave vector is called the wave number measured by (rd. m^{-1}) and is given by:

$$\|\vec{k}\| = k = \frac{2\pi}{\lambda} \text{.....(Eq.13)}$$

Where λ is the wavelength.

The wave vector is always perpendicular to the wave fronts. In isotropic media, the wave vector has the same direction as the direction of wave propagation.



5.1.8. Wave Phase velocity

Phase velocity, denoted by v_p, is the speed at which a wave phase propagates in space. It is determined by dividing the wave's frequency (specifically, its angular frequency) by its wavenumber:

$$v_p = \frac{\omega}{k} \text{ ……..……..…...……(Eq.14)}$$

❖ **We note that:**

✓ A sinusoidal plane wave $\psi(x\,,t)$ is expressed mathematically by:

$$\psi(x,t) = \psi_0 \cdot \cos(\omega t - kx + \varphi_0) \text{……..……(Eq.15)}$$

ψ_0 is the maximum elongation or amplitude of the wave.

✓ The wave function $\psi(\vec{r},t)$can take complex values (which are really complex, and not a writing convenience, like the complex notations of electromagnetic fields for example). We can write equation (14) in the complex form /

$$\psi(x,t) = \psi_0\, e^{i(kx-\omega t)} \text{……..……(Eq.16)}$$

Or generally in 3D variation:

$$\psi(\vec{r},t) = \psi_0\, e^{i(\vec{k}.\vec{r}-\omega t)} \text{…….……(Eq.17)}$$

5.2. Wave function and probability of presence

The de-Broglie theory is only applicable for moving particles or particles in constant motion. The theory used the concept of matter waves to find the probability (P) of the location of a particle in space. This was done by using the square of the wave's amplitude known given by concept of probability density $dP(\vec{r}\,,t)$ in order to find out the whether the intensity of the matter wave is large or not.

$$dP(\vec{r}\,,t) = |\psi(\vec{r}\,,t)|^2\, d^3\vec{r} \text{…….……(Eq.18)}$$

The probability of finding a particle at any point in all of space must be equal to 1 at each moment. Thus the wave function $\psi(\vec{r}\,,t)$ must satisfy, for any instant t, the normalization condition:

$$P(\vec{r}\,,t) = \int dP(\vec{r}\,,t) = \int |\psi(\vec{r}\,,t)|^2\, d^3\vec{r} = 1 \text{……(Eq.19)}$$

We note that :

➢ Two wave functions $\psi_1(\vec{r}\,,t)$ and $\psi_2(\vec{r}\,,t)$ which differ only by a constant phase term describe the same physical state (since the phase term disappears when we take the module squared).

- There is no device that would give direct access to the values of $\psi(\vec{r}\,,t)$. It is a non-classical probabilistic description; it is the squared module of the wave function, which represents a physical probability for the particle to be in a place at a time. We can also calculate the average position of the particle from the following equation:

$$<\vec{r}>=\int \vec{r}.|\psi(\vec{r}\,,t)|^2\, d^3\vec{r} \quad \text{.....(Eq.20)}$$

5.3. Dynamics of the wave function

5.3.1. Momentum space wave function

So far, we have described the position of the particle. In classical physics, we'd only need to know about its velocity to know everything about it. Equivalently, we can focus on its momentum. Classically, the momentum denoted $\vec{p}$ is the velocity multiplied by the mass of the particle: $\vec{p}=m\vec{v}$. It's a much more significative concept in physics because of the law of conservation of momentum, which states that the momentum of a closed system is always conserved. This has been essential to explain the photoelectric effect, which boils down to a transfer of momentum from photons to electrons. For a photon or of an electron, Planck and Einstein showed that the momentum of light depends on the frequency of its wave and its direction of motion. What we usually mean by frequency of light is the time frequency of the wave, but since the speed of light is constant, we may equivalently consider the spatial frequency, also known as the wave vector ($\vec{k}$) . A similar definition occurs in quantum physics for all particles. So the momentum vector of a particle is related to the wave vector of its wave function. This corresponds to the relation :

$$\vec{p}=\hbar\vec{k}=\frac{h}{2\pi}\vec{k} \quad \text{.....(Eq.21)}$$

$\hbar$ is the reduced Planck constant

5.3.2. Heisenberg's Uncertainty Principle

Uncertainty principle, statement, articulated (1927) by the German physicist Werner Heisenberg, that the position and the velocity of an object cannot both be measured exactly, at the same time, even in theory. The very concepts of exact position and exact velocity together, in fact, have no meaning in nature.

Heisenberg's Uncertainty Principle states that there is inherent uncertainty in the act of measuring a variable of a particle. Commonly applied to the position and momentum of a particle, the principle states that the more precisely the position is known the more uncertain the momentum is and vice versa. This is contrary to classical Newtonian physics which holds all variables of particles to be measurable to an arbitrary uncertainty given good enough equipment. The Heisenberg Uncertainty Principle is a fundamental theory in quantum mechanics that defines why a scientist cannot measure multiple quantum variables simultaneously. Until the dawn of quantum mechanics, it was held as a fact that all variables of an object could be known to exact precision simultaneously for a given moment. Newtonian physics placed no limits on how better procedures and techniques could reduce measurement uncertainty so that it was conceivable that with proper care and accuracy all information could be defined. Heisenberg made the bold proposition that there is a lower limit to this precision making our knowledge of a particle inherently uncertain.

More specifically, if one knows the precise momentum of the particle, it is impossible to know the precise position, and vice versa. This relationship also applies to energy and time, in that one cannot measure the precise energy of a system in a finite amount of time. Uncertainties in the products of "conjugate pairs" (momentum-position) and (energy-time) were defined by Heisenberg as having a minimum value corresponding to the following inequality :

$$\Delta p.\Delta x \geq \frac{h}{4\pi} \quad \text{.....(Eq.22)}$$

$$\Delta E.\Delta t \geq \frac{h}{4\pi} \quad \text{.....(Eq.23)}$$

Where Δ refers to the uncertainty in that variable and h is Planck's constant (h).

5.3.3. Schrödinger equation

The Schrödinger equation is a linear partial differential equation that governs the wave function of a quantum-mechanical system. Its discovery was a significant landmark in the development of quantum mechanics. It is named after Erwin Schrödinger, who postulated the equation in 1925 and published it in 1926, forming the basis for the work that resulted in his Nobel Prize in Physics in 1933.

The Schrödinger equation is the quantum counterpart of Newton's second law in classical mechanics. Given a set of known initial conditions, Newton's second law makes a mathematical prediction as to what path a given physical system will take over time. The Schrödinger equation gives the evolution over time of a wave function, the quantum-mechanical characterization of an isolated physical system. The equation postulated by Schrödinger based on a postulate of Louis de Broglie that all matter has an associated matter wave. The equation predicted bound states of the atom in agreement with experimental observations.

$$i\hbar \frac{d\psi(\vec{r},t)}{dt} = \hat{H}\psi(\vec{r},t) \quad \text{.....(Eq.24)}$$

$\hat{H}$ is the Hamiltonian operator corresponding to the total energy of that system, including both kinetic energy and potential energy.

$$i\hbar \frac{\partial}{\partial t}\psi(\vec{r},t) = \left[\frac{-\hbar^2}{2m}\Delta + V(\vec{r},t)\right]\psi(\vec{r},t) \quad \text{.....(Eq.25)}$$

Where Δ denotes the Laplacian (in Cartesian coordinates): $\Delta = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$

The term in $\frac{-\hbar^2}{2m}$ is thus interpreted as a term of kinetic energy in the Schrödinger equation.

Schrödinger therefore discovered a partial differential equation describing a Hamiltonian mechanical system using a scalar field ψ propagating in the 6N-dimensional space of the generalized coordinates of this system. Applied to a particle in a field, it is very close to a wave equation in space and time, hence sometimes the name wave mechanics for this particular and restricted form of quantum mechanics. This also explains why the state vector $/\psi >$ is sometimes called the wave function $\psi\ (x)$ of the system. As its discoverer understood, it shows that the quantification of the energy of atomic systems results from a formulation in terms of the Sturm Liouville problem, or the problem of proper values for a linear differential operator H. Initially, it was not in a relativistic form for particles, but it was Dirac who found a generalization.

However, we show here how Schrödinger led to this relationship. Considering the wave function $\psi(\vec{r},t)$ given by:

$$\psi(\vec{r},t) = \psi_0\, e^{i(\vec{p}.\vec{r}-Et)} \quad \text{.....(Eq.26)}$$

reformulated using the relations proposed by de Broglie. Schrödinger then noticed that by diverting this wave in time, it became:

$$\frac{\partial}{\partial t}\psi(\vec{r},t) = -\frac{i}{\hbar}E\psi_0\, e^{i(\vec{p}.\vec{r}-Et)} = -\frac{i}{\hbar}E\psi(\vec{r},t) \text{.....(Eq.27)}$$

Similarly, the gradient of this wave function gives:

$$\nabla\psi(\vec{r},t) = \frac{i}{\hbar}p\psi(\vec{r},t) \text{.....(Eq.28)}$$

So we have, for every wave of this form, at every point and at every moment:

$$i\hbar\frac{\partial}{\partial t}\psi(\vec{r},t) = E\psi(\vec{r},t) \text{.....(Eq.29)}$$

For a particle, according to classical mechanics, the mechanical energy is given by:

$$E = E_c + E_p = \frac{1}{2}\, m\, v^2 += \frac{P^2}{2m} + V(r) \text{ .....(Eq.30)}$$

This quantity actually appears more naturally in the Hamiltonian formulation of classical mechanics: the sum of potential energy and kinetic energy is called Hameltonian, which here identifies itself with total mechanical energy. By multiplying by the wave function:

$$\frac{P^2}{2m}\psi(\vec{r},t) + V(r)\psi(\vec{r},t) = E\psi(\vec{r},t) \text{.....(Eq.31)}$$

And finally, using the previous results, we have:

$$\frac{(-i\hbar\nabla)^2}{2m}\psi(\vec{r},t) + V(r)\psi(\vec{r},t) = i\hbar\frac{\partial}{\partial t}\psi(\vec{r},t) \text{.....(Eq.32)}$$

Which can be written in the form of equation 25or as follows:

CHAPTER. II. INTRODUCTION TO ATOMIC SPECTROSCOPY

Introduction

Spectroscopy is the experimental study of the decomposition of a spectrum of a physical phenomenon on an energy scale, or on any other magnitude related to an energy (frequency, wavelength,..etc). It presents the study of interactions between matter and different forms of electromagnetic radiation; when practiced to quantitative analysis, the term spectrometry is used. It is an experimental characterization technique carried out using a measuring instrument called a spectroscope or spectrometer.

1. Atomic spectroscopy

Atomic spectroscopy is an experimental technique used for determining the elemental composition of the atoms and molecules by their electromagnetic or mass spectrums. It is used for qualitative and quantitative determination of perhaps 70 elements. Element concentrations of a millionth (ppm) or one billionth part (ppb) of the sample can be detected by using this technique. Atomic spectroscopy methods are speed, convenience, unusually high selectivity, and moderate instrument costs.

1.1. Atomic Spectroscopy types

Atomic Spectroscopy is of three types.

- Atomic absorption Spectroscopy (AAS)
- Atomic emission Spectroscopy (AES)
- Atomic Fluoroscence Spectroscopy (AFS) including X-ray fluorescence (XRF).

1.2. Basic principles

Every element has a characteristic atomic structure, with a small, positively charged nucleus surrounded by a sufficient number of electrons necessary to maintain neutrality. Electrons settle into orbitals within an atom and one of the electrons can also jump from one energy level to the higher level by acquiring the necessitated energy (Figure 1). This energy is provided by colliding with other atoms, such as heating (AES), photons derived from light (AAS and AFS), or high energy electrons (XRF). Possible transitions happen, when the required energy reaches to the difference between two energy states (ΔE). A neutral atom may exist at a low energy shell or ground state (E_0), or at any of

a group of excited states depending on how many electrons have been jumped to higher energy levels (E′) although it is normal to think for the first transition. Each element has a unique energy level and the ΔEs associated with transitions between those levels. The ΔE for movements of valence electrons in most elements meets the energy equal to UV orvisible radiation.

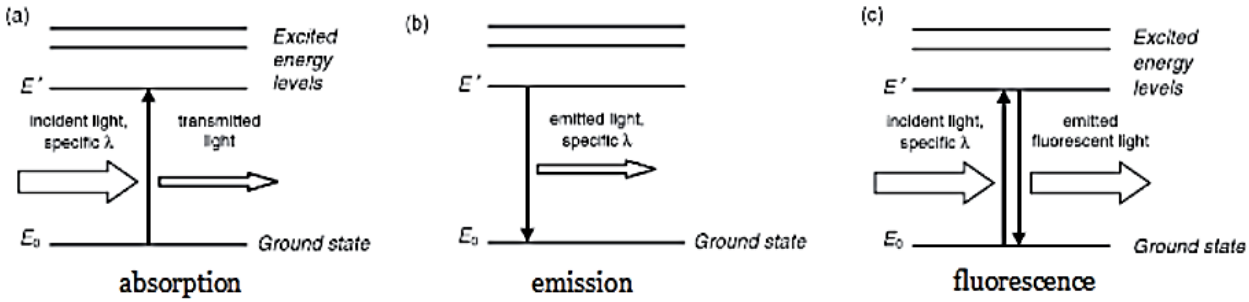


Figure.1. Energy level diagrams to show transitions associated with (a) AAS, (b) AES, and (c) AFS. The vertical arrows indicate absorption or emission of light.

The energy of a photon (E) is computed with the following equation:

$$E = h\upsilon \quad \text{.....(Eq.1)}$$

(where h is Planck's constant ($h = 6.63 \times 10 - 34\, J.s$) and υ the frequency of the wave form corresponding to that photon.

The relationship between wavelength and frequency is showed by the equation below:

$$\upsilon = \frac{C}{\lambda} \quad \text{.....(Eq.2)}$$

where C is the speed of light and λ the wavelength. Thus :

$$E = \frac{hc}{\lambda} \quad \text{.....(Eq.3)}$$

and a specific transition, ΔE, is associated with a unique wavelength.

When light of a specific wavelength enters an analytical system, outer shell electrons of the corresponding atoms will be excited as energy is absorbed. As a result, the amount of light transmitted from the system to detector will be reduced, this is understood as AAS (Figure 1a).Under appropriate circumstances, outer shell electrons of vaporized atoms maybe excited by heating. As these electrons return to the more stable ground state, energy is lost. As Figure1b shows, some of this energy is emitted as light, which can be measured with a detector, this is AES. Some of the radiant energy absorbed by ground state atoms can be emitted as light as the atom returns to the ground state i.e.

AFS (Figure.1c).When high-energy photons strike to a massive particle, it can excite an inner shell electron of the atom. The forming inner orbital vacancy can be filled with an outer shell electron. The transition is created by an emission of an X-Ray photon. This process is called X-ray fluorescence (XRF).The energy of the emission i.e. the wavelength is characteristic of the atom(element) from which it originated while the intensity of the emission is related to concentration of the atoms in the sample. The high temperature inductively coupled plasma has been successfully used as an effective ion source for a mass spectroscopy, the type of method of inductively coupled plasma-mass spectroscopy (ICP-MS) is routinely used for measurements of trace elements in clinical and biological samples. It follows from equations 1 and 3 that the wavelengths of the absorbed or emitted light are unique to a given element.

1. 3. Atomic spectroscopy instrumentation

The first step in all atomic spectroscopic procedures is atomization i.e. Formation of the atomic vapor. It consists the major principle of emission, absorption, and fluorescence techniques. The most critical component of instruments used in atomic spectroscopy is the atomization sources and sample introduction devices with an associated spectrometer for wavelength selection and detection of light.

Atomization involves the several key (the basic) steps:

- ✓ Solvent removal,
- ✓ Separation from anion and other elements of the matrix,
- ✓ Reduction of ions to the ground state atom.

The design of an AFS instrument is similar to those for AAS and AES except that the light source and the detector are located at a right angle (Figure 2).

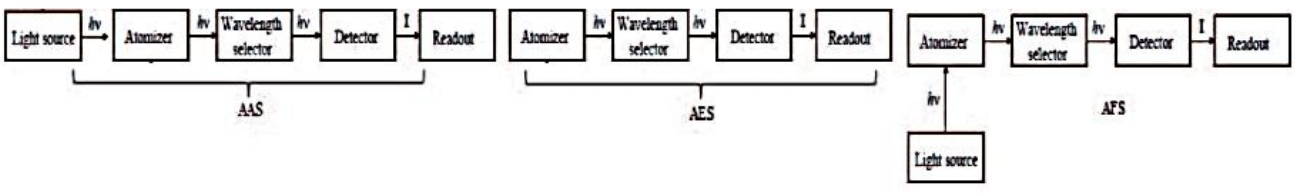


Figure.2. Schematic diagram of an AAS, AES, and AFS instrument.

1.3.1. Light sources of atomic spectra

A light source which emits the sharp atomic lines of the element to be determined is selected. There are two types of light sources used in these instruments: continuous

sources and line sources. A continuous source, also called to as a broad-band source, emits radiation over a broad range of wavelengths. A line source, on the other hand, emits radiation at specific wavelengths, but this source of radiation is not as pure as radiation from a laser. Table 1 provides a list of most common kinds of lamps considered to be light sources.

Source	Wavelength Region	Useful for...
H_2 and D_2 lamp	continuum source from 160–380 nm	molecular absorption
tungsten lamp	continuum source from 320–2400 nm	molecular absorption
Xe arc lamp	continuum source from 200–1000 nm	molecular fluorescence
nernst glower	continuum source from 0.4–20 μm	molecular absorption
globar	continuum source from 1–40 μm	molecular absorption
nichrome wire	continuum source from 0.75–20 μm	molecular absorption
hollow cathode lamp	line source in UV/Visible	atomic absorption
Hg vapor lamp	line source in UV/Visible	molecular fluorescence
laser	line source in UV/Visible/IR	atomic and molecular absorption, fluorescence, and scattering

Table.1. The most common kinds of light sources.

1.3.2. Atomizer

Atomizer is the most critical component of instruments used in atomic spectroscopy. The atomizer is any device which will produce ground state atoms as a vapor into the light path. Many atomizers utilized for AFS are similar to those used for AAS and AES. The atomizers most commonly used in these techniques are flames and electrothermal atomizers.

a). Flame atomizer

In a flame atomizer, a solution of the sample is nebulized by a flow of gaseous oxidant, mixed with a gaseous fuel, and carried into a flame where atomization occurs. As shown in the following figure, a complex set of interconnected processes then occur in the flame. The first step is desolvation, in which the solvent evaporates to produce a finely divided solid molecular aerosol. The aerosol is then volatilized to form gaseous molecules. Dissociation of most of these molecules produces an atomic gas. Some of the atoms in the gas ionize to form cations and electrons. Other molecules and atoms are produced in the flame as a result of interactions of the fuel with the oxidant and with the

various species in the sample. As indicated in Figure, a fraction of the molecules, atoms, and ions are also excited by the heat of the flame to yield atomic, ionic, and molecular emission spectra. With so many complex processes occurring, it is not surprising that atomization is the most critical step in flame spectroscopy and the one that limits the precision of such methods. Because of the critical nature of the atomization step, it is important to understand the characteristics of flames and the variables that affect these characteristics.

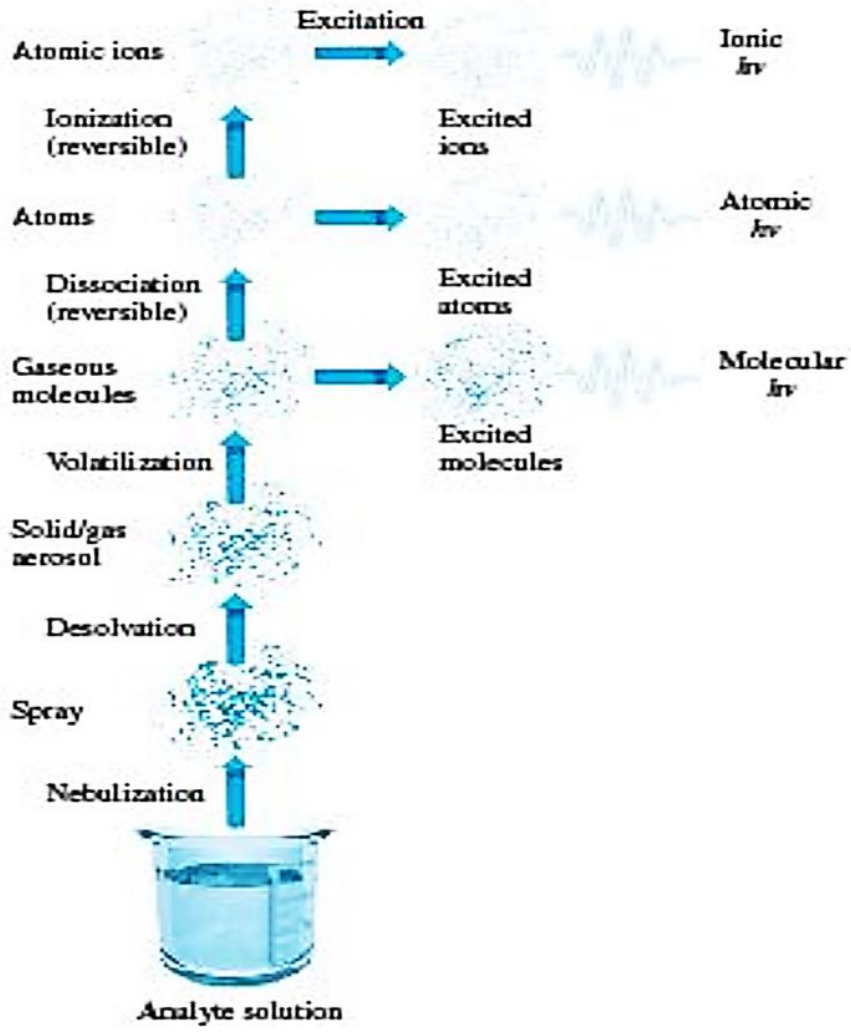


Figure. 3. Processes occurring during atomization.

Table.2. lists the common fuels and oxidants used in flame spectroscopy and the approximate range of temperatures realized with each of these mixtures. Note that temperatures of 1700°C to 2400°C occur with the various fuels when air is the oxidant. At these temperatures, only easily decomposed samples are atomized, so oxygen or nitrous oxide must be used as the oxidant for more difficult to atomize samples (refractory samples). These oxidants produce temperatures of 2500°C to 3100°C with

the common fuels. The burning velocities listed in the fourth column of Table.2 are important because flames are stable only in certain ranges of gas flow rates. If the gas flow rate does not exceed the burning velocity, the flame propagates back into the burner, giving *flashback.* As the flow rate increases, the flame rises until it reaches a point above the burner where the flow velocity and the burning velocity are equal. This region.

Fuel	Oxidant	Temperature, °C	Maximum Burning Velocity, $cm\ s^{-1}$
Natural gas	Air	1700–1900	39–43
Natural gas	Oxygen	2700–2800	370–390
Hydrogen	Air	2000–2100	300–440
Hydrogen	Oxygen	2550–2700	900–1400
Acetylene	Air	2100–2400	158–266
Acetylene	Oxygen	3050–3150	1100–2480
Acetylene	Nitrous oxide	2600–2800	≃285

Table.2. Properties of flames.

Flame atomizers are used for atomic absorption, fluorescence, and emission spectroscopy.Figure.4 is a diagram of a typical commercial laminar-flow burner that uses a concentric tube nebulizer.

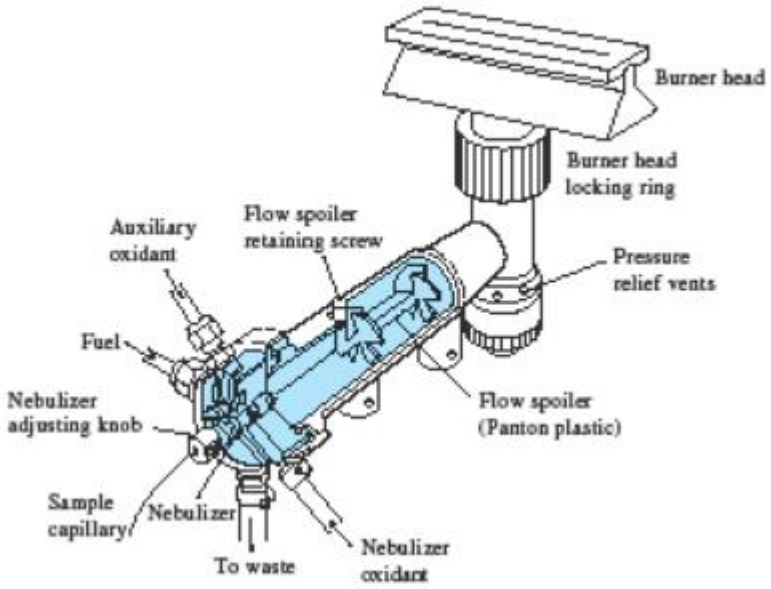


Figure.4. A laminar-flow burner (Courtesy of Perkin-Elmer Corporation, Norwalk, CT.).

The aerosol, formed by the flow of oxidant, is mixed with fuel and passes a series of baffles that remove all but the finest solution droplets. The baffles cause most of the sample to collect in the bottom of the mixing chamber where it drains to a waste container. The aerosol, oxidant, and fuel are then burned in a slotted burner to provide a 5- to 10-cm high flame. Laminar-flow burners produce a relatively quiet flame and a long path length for maximizing absorption. These properties tend to enhance sensitivity and reproducibility in AAS. The mixing chamber in this type of burner contains a potentially explosive mixture that can flash back if the flow rates are too low.

b). Electrothermal atomizer

Electrothermal atomizers, which first appeared on the market in the early 1970s, generally provide enhanced sensitivity because the entire sample is atomized in a short period, and the average residence time of the atoms in the optical path is a second or more. Electrothermal atomizers are used for atomic absorption and atomic fluorescence measurements but have not been generally applied for direct production of emission spectra. They are also used for vaporizing samples in inductively coupled plasma emission spectroscopy, however. In electrothermal atomizers, a few microliters of sample is first evaporated at a low temperature and then ashed at a somewhat higher temperature in an electrically heated graphite tube similar to the one in Figure.5 or in a graphite cup.

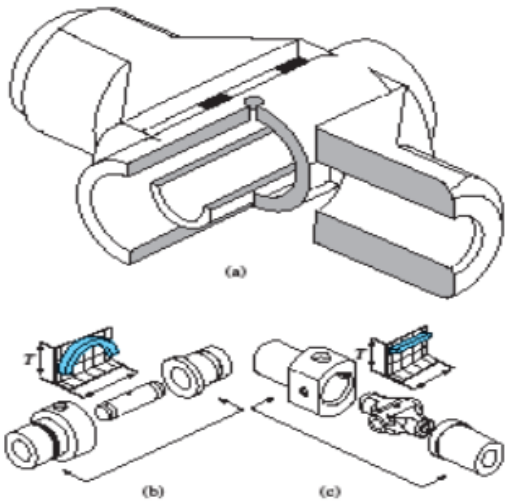


Figure.5. Cross section view of a graphite furnace with integrated L'vov platforme. (b) Longitudinal configuration, the temperature varies continuously along the path, reaching a maximum at the center. (c) Transverse configuration of the furnace. The temperature profile is relatively constant along the path. (Courtesy of Perkin-Elmer Life Analytical Sciences, Shelton, CT.).

After ashing, the current is rapidly increased to several hundred amperes, which causes the temperature to rise to 2000°C to 3000°C; atomization of the sample occurs in a period of a few milliseconds to seconds. The absorption of the atomic vapor is then measured in the region immediately above the heated surface.

Electrothermal atomizers offer the advantage of unusually high sensitivity for small volumes of sample. Typically, sample volumes between 0.5 and 10 μL are used; under these circumstances, absolute detection limits typically lie in the range of 10-10 to 10-13 g of analyte. The relative precision of electrothermal methods is generally in the range of 5% to 10% compared with the 1% or better that can be expected for flame or plasma atomization. Furthermore, because of the heating-cooling cycles, furnace methods are slow, typically requiring several minutes per element. A final disadvantage is that the analytical range is relatively narrow, usually less than two orders of magnitude. As a result, electrothermal atomization is the method of choice only when flame or plasma atomization provides inadequate detection limits.

1.3.3. Wavelength selector

An ideal wavelength selector has a high throughput of radiation and a narrow effective bandwidth. There are two major types of wavelength selectors : filters and monochromators.

a). Filter

A simple example of an absorption filter is a piece of colored glass. Absorption filters provide effective bandwidths of 30–250 nm, although the throughput can be only 10% of the source's emission intensity at the low end of this range. Interference filters constructed of a several optical layers deposited on a glass or transparent material. Typically, effective bandwidth is 10^{-20} nm, with maximum throughputs of at least 40%.

b). Monochromator

A monochromator is used to convert a polychromatic source of radiation at the entrance slit to a monochromatic source of restricted effective bandwidth at the exit slit. These devices are classified as either fixed-wavelength or scanning. The wavelength selects by manually rotating the grating in a fixed-wavelength monochromator. A scanning monochromator includes a drive mechanism that continuously rotates the grating, allowing sequential wavelengths to exit from the monochromator (Figure.6).

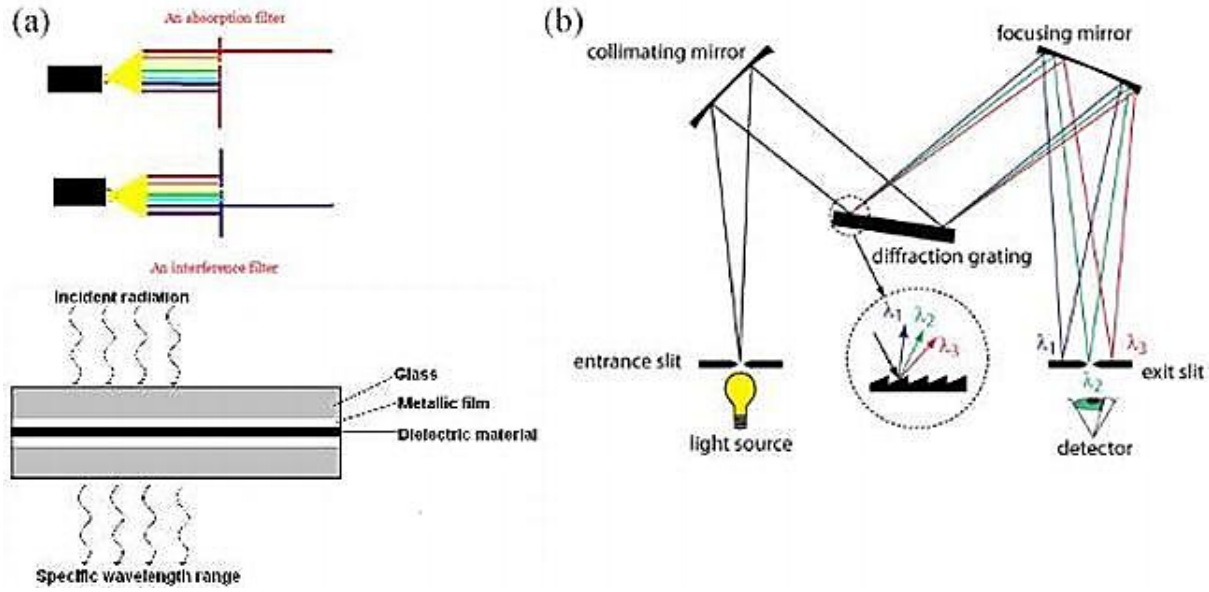


Figure.6. Schematic diagram of wavelength selectors: (a) filters and (b) a diffraction grating monochromator.

c). Detectors

Detectors use a sensitive transducer that converts a signal comes from light energy into electrons An ideal detector produces signal, S, is a linear function of the electromagnetic radiation's power, P:

$$S = kP + D$$

where k s the detector's sensitivity and D is the detector's dark current, or the background current when no radiation of source reached to the detector. Phototubes and photomultipliers include a photosensitive surface that absorbs radiation in the UV-visible, or near-IR, generating an electrical current proportional to the number of photons reaching the transducer (Figure.7).

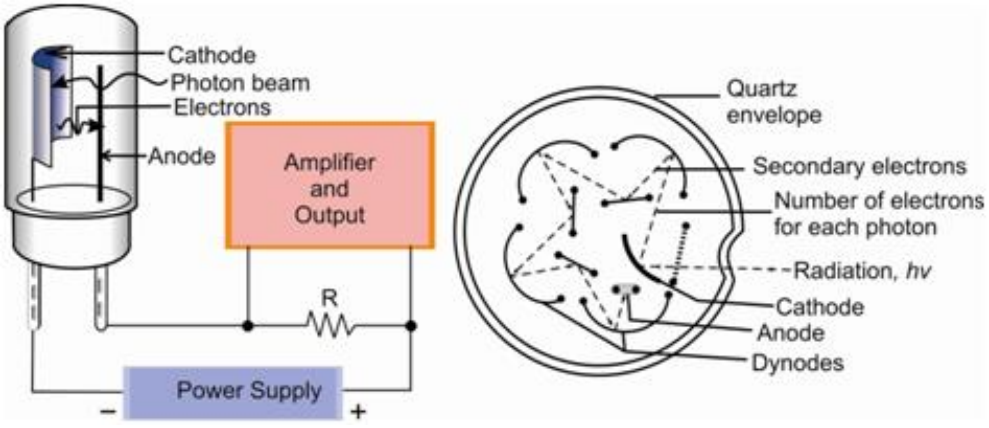


Figure.7. Diagram of a phototube and a photomultiplier tube.

Detectors use a semiconductor compound as the photosensitive surface. One advantage of the Si photodiode manufactured utilizing semiconductor process is that it is easy to miniaturize. Infrared photons do not have enough heat to generate a measurable current with a photon transducer. A transducer's electrical signal is sent to a signal processor where it is displayed in a form that is more convenient to explain. The analog meters, digital meters, recorders, and computers equipped with data acquisition boards are good examples of signal processors. A signal processor is used in calibrating the detector's response, amplificating the transducer's signal, removing noise by filtering, or mathematically transforming the signal (Table.3).

Detector	Class	Wavelength Range	Output Signal
phototube	photon	200–1000 nm	current
photomultiplier	photon	110–1000 nm	current
Si photodiode	photon	250–1100 nm	current
photoconductor	photon	750–6000 nm	change in resistance
photovoltaic cell	photon	400–5000 nm	current or voltage
thermocouple	thermal	0.8–40 μm	voltage
thermistor	thermal	0.8–40 μm	change in resistance
pneumatic	thermal	0.8–1000 μm	membrane displacement
pyroelectric	thermal	0.3–1000 μm	current

Table.3. Examples of detectors for spectroscopy.

1.4. Sample preparation

An ideal sample preparation should remove interfering components from the matrix and to adjust of analyte to facilitate the actual measurement. Methods for destruction of the organic matrix by simple heating or by acid digestion have been developed and are thoroughly approved. Microwave heating is used for this purpose, with the specifically designed a compatible equipment to avoid dangerous of excessive pressure within reaction flask. Although the number of samples that can be processed is not large, microwave heating affords rapid digestion and low reagent blanks. More recent developments include continuous flow systems for automated digestion which has a direct link with the instrument. Liquid-liquid portioning has been widely applied for preconcentration procedure. Analyte atoms in a large volume of aqueous solution are complexed with a suitable agent and collected into a small volume of solvent. Vapor generation procedures permit the rapid introduction of 100% of the sample into the

atomizer and are used for AAS, AES, AFS, and ICP-MS. Certain elements such as arsenic, selenium, and bismuth readily evolve gaseous hydrides and transferred by a flow of inert gas to an AES, and ICP-MS or to a heated silica tube positioned in the light path for AAS, AFS. The tube can be heated using the air-acetylene flame or an electric current. The obtained heat is enough to cause decomposition of the hydride and atomization of the analyte. Thus, there is no loss off analyte, which in all the atoms flow the light path with in few seconds and they are trapped within the silica tube that was retarded their dispersion. Any sample volume added to the reaction container, hydride generation AAS has detection limits a few nanograms of analyte. Mercury can quickly form a vapor in the ambient temperature, and this property is the basis for cold vapor generation. When a reducing agent is added to sample solution, Hg^{2+} converts to the elemental mercury. Agitation or bubbling of gas through the solution is used to enhance rapid vaporization of the atomic mercury and to improve the transfer of mercury to a flow through cell located in the light path. As with hydride generation, the detection limit is a few nanogram and some manufacturers have been developed common instrumentation to accomplish both procedures. Chromatographic or electrophoretic techniques have been also developed that are coupled directly to the atomic spectroscopic instrument to develop integrated analytical arrangements.

2. Atomic spectra

The spectrum of electromagnetic radiation produced or absorbed by an electron during transitions between different levels of energy within an atom. As the electron is excited from one energy level to another, it either emits or absorbs light from a particular wavelength. Collection of all these wavelengths of the atom in a given range of conditions, such as pressure, temperature, etc., is the atomic spectra of atoms.

2.1. Characteristics of atomic spectra

There are various characteristics of atomic spectra, such as:

- The atomic spectra should be a pure line spectrum.
- It should be an emission band spectrum.
- It should be an absorption line spectrum.
- Also, it should be the absorption band spectrum

The atomic spectrum is also called line spectrum because it contains only certain frequencies, unlike the continuous spectrum of light. The atomic spectrum is the identity card of the atom. Each atom has its own spectrum.

2.2. Types of atomic Spectra

There are three kinds of atomic spectra, namely:

- Continuous spectra
- Emission spectra
- Absorption spectra.

2.2.1. Continuous Spectrum

A rainbow is an example of a continuous spectrum. Here, the colors displayed are within the visible spectrum (between 380-760 nm). Light in this wavelength range is visible to the naked eye. Unlike the visible spectrum, light that is of different wavelengths (see the electromagnetic spectrum below) is not visible. The following figure presents the different areas of the light (or electromagnetic spectrum).

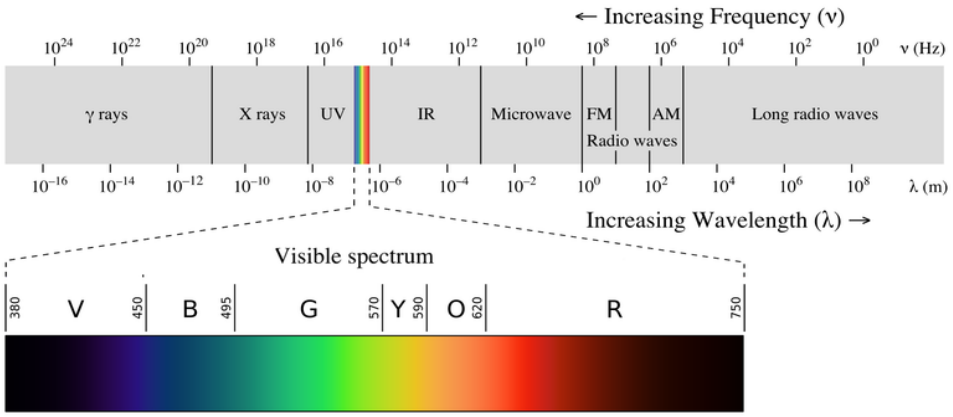


Figure.8. The electromagnetic spectrum is an example of a continous spectrum. It contains various frequencies (cycle/time) and wavelengths.

Areas of light that possess short wavelengths are located on the left of the spectrum. All wavelengths from UV (ultraviolet) to γ (gamma) range have the potential to ionize tissues and/or DNA. As a result, individuals who have been exposed to large amounts of these types of radiation in acute time periods could develop cancer. In contrast, visible light (see the rainbow area in Figure.9) and radiation on the right side of the spectrum has longer wavelengths and does not have the potential to ionize tissues and/or DNA. Visible, infrared (labeled IR), microwave, and radio waves are classified as being nonionizing radiation and have not been linked to cancer. Note that, lower frequency,

lower-energy electromagnetic radiation is nonionizing, and higher frequency, higher energy electromagnetic radiation is ionizing (Figure.9).

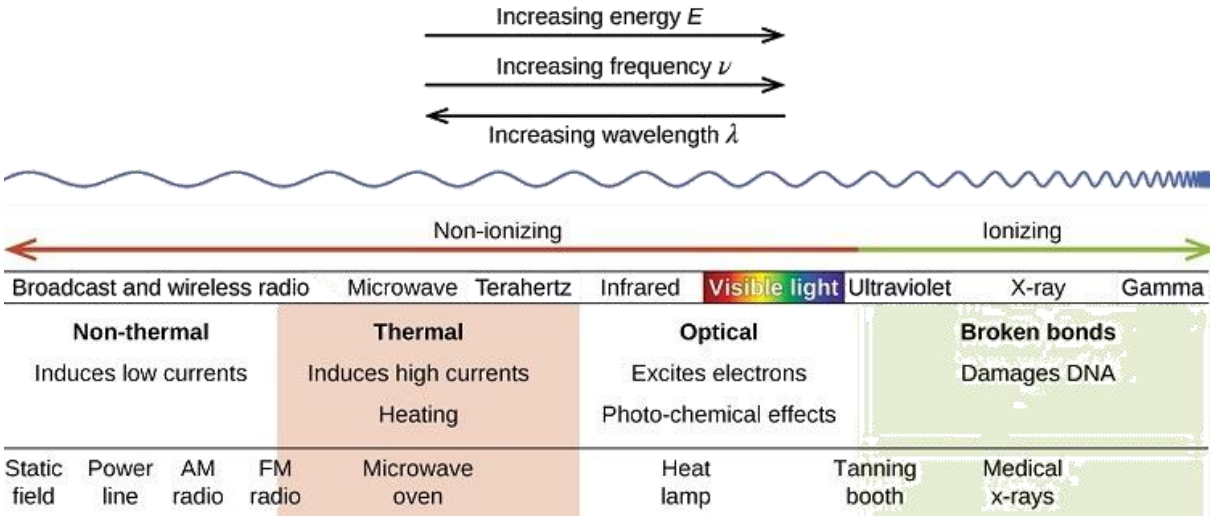


Figure.9. Classification of ionizing and non-ionizing radiation in electromagnetic spectrum.

2.2.2. Discontinuous Spectra

If the light emitted from the excited atoms is viewed through a prism, then individual patterns of lines will be produced. These lines are called spectra and correspond to fingerprint wavelengths (λ) for a specific element. Figure.11 illustrates how the light from excited electrons can be diffracted to produce line spectra for the elements of hydrogen, helium, and iron. The specific elements produce wavelengths within the visible spectrum (between 400-700 nm) and can be seen by the naked eye. In order to obtain the numerical wavelengths (in nanometers), one would need to employ some type of detector.

When light from a hydrogen gas discharge tube is passed through a prism, the light is split into four visible lines. Each of these spectral lines corresponds to a different electron transition from a higher energy state to a lower energy state. Every element has a unique atomic emission spectrum, as shown by the examples of helium (He) and iron (Fe) (Figure.10).

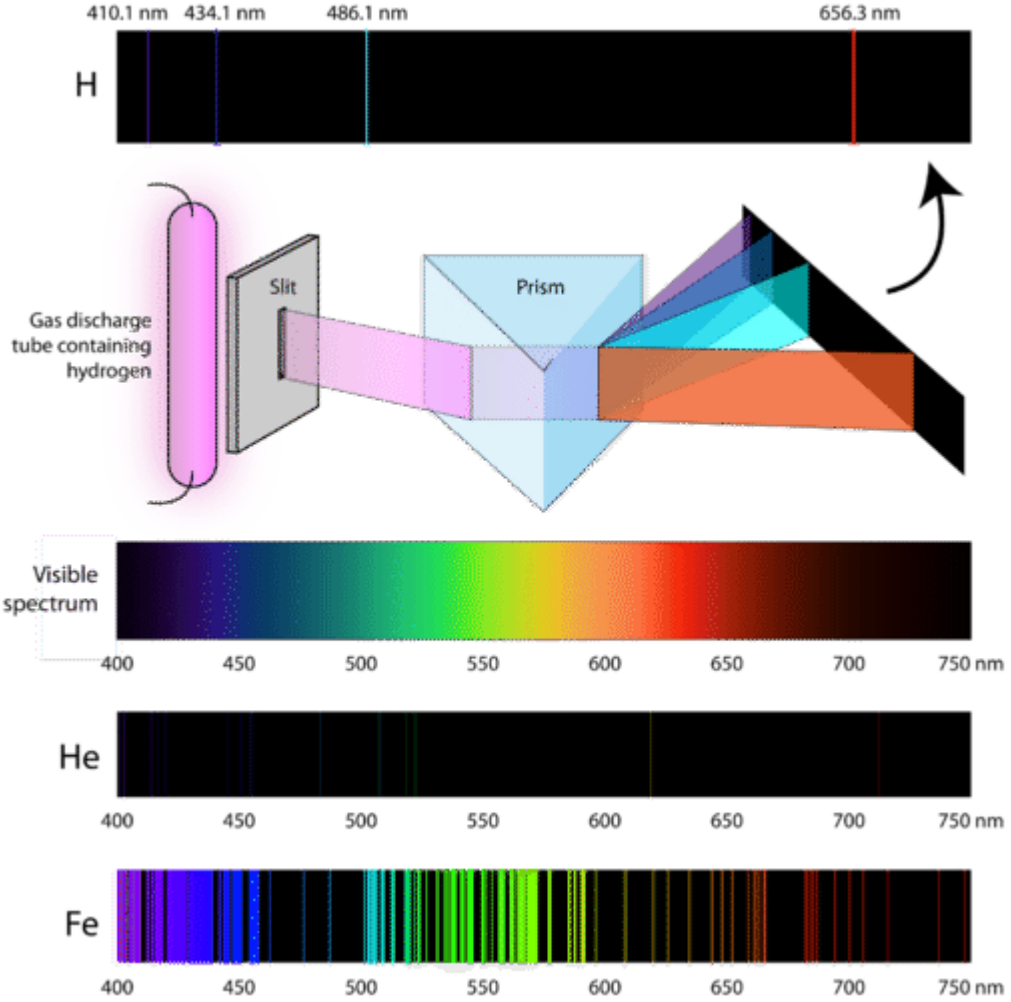


Figure.10. Emission spectrum of helium (He) and iron (Fe) obtained using a dispersion prism.

3. Atomic Absorption Spectra

The electrons in an atom tend to be arranged in such a way that the energy of the atom is as low as possible. The ground state of an atom is the lowest energy state of the atom. When those atoms are given energy, the electrons absorb the energy and move to a higher energy level. These energy levels are called excited levels. An excited state of an atom is a state where its potential energy is higher than the ground state. These energy levels of the electrons in atoms are quantized, meaning again that the electron must move from one energy level to another in discrete steps rather than continuously. Noting the energy changes from ground to excited states, we can obtain another type of discontinuous spectrum (Figure.12). Once again, a fingerprint wavelength pattern is produced that can be used to identify an atom.

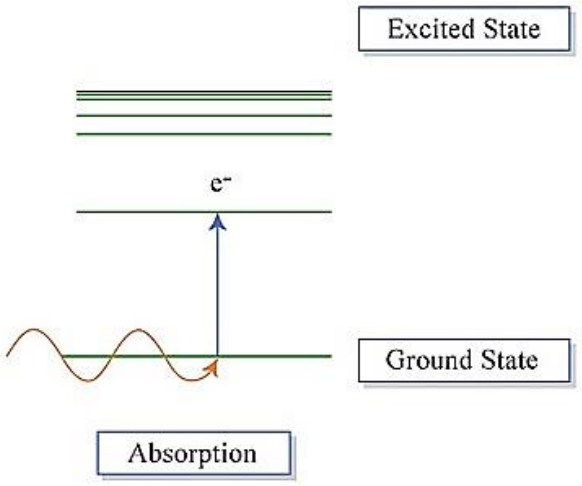


Figure.11. Atomic absorption mechanism from ground state to an excited state.

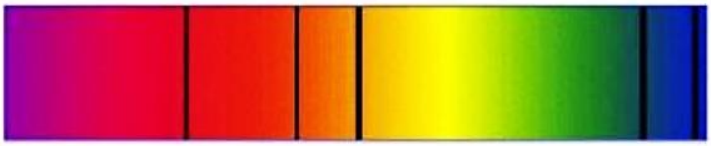


Figure.12. absorption spectrum of the mercury (Hg) atom.

4. Atomic Emission Spectra

The emission of light can occur spontaneously, by losing of energy from the excited atom. The atom passes from an excited level to a ground level more stable energy level by releasing the energy that it had previously gained often in the form of electromagnetic radiation (although it can be released via heat).

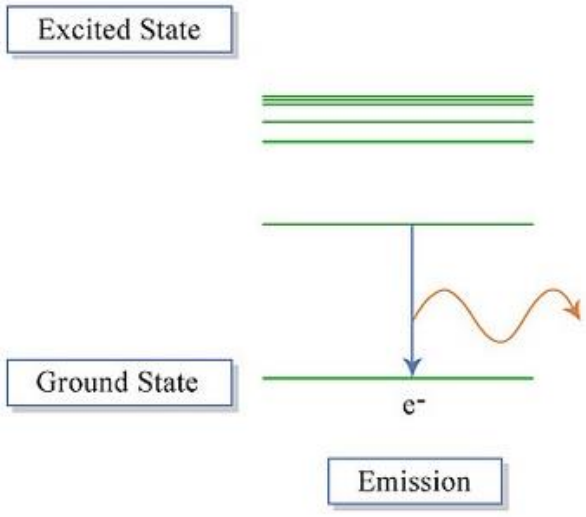


Figure.13. Atomic emission mechanism from the excited state to the ground state.

Atoms can gain energy to induce these transitions from various sources. The gases in the image below have been excited with the use of electrical current. The atoms in each of these noble gases produce distinctive colors that can be used to identify the elements (Figure.14). Each of these species contains a different number of electrons that can undergo different types of excitations. In turn, each gas produces a signature color. Indeed, Gas discharge tubes are enclosed glass tubes filled with a gas at low pressure through which an electric current is passed. Electrons in the gaseous atoms first become excited, and then fall back to lower energy levels, emitting light of a distinctive color in the process (Figure.13).

Figure.13. Gas discharge tubes of helium, neon, argon, krypton, and xenon.

Flames can be utilized to excite atoms as well. During a flame test experiment, metal chlorides are directly placed into a flame. The intense heat will promote the metal's electrons to an excited state. Upon emission, this extra energy is released in the form of visible light. If a reference panel is provided, the flame color can be used to identify a metal atom (Table. 4).

Metal Ion	Flame Color		Metal Ion	Flame Color
Li	Red		K	Light Purple
Na	Orange		Ba	Light Green
Ca	Orange-Red		Cu	Blue

Table.4. Flame colors of some metals ions.

We note that the wavelengths of absorption and emission are identical.

5. Resonance line

Resonance line is the spectral line that corresponds to the electronic transition from the ground state to the first excited state.

5.1. Choice of resonance line

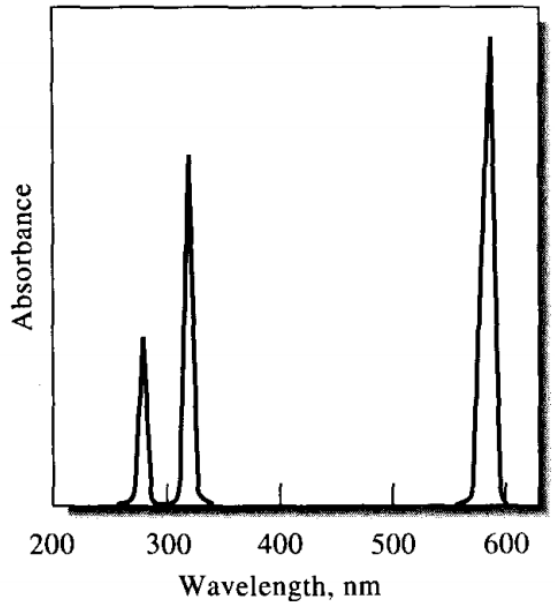
• Resonance line is the best

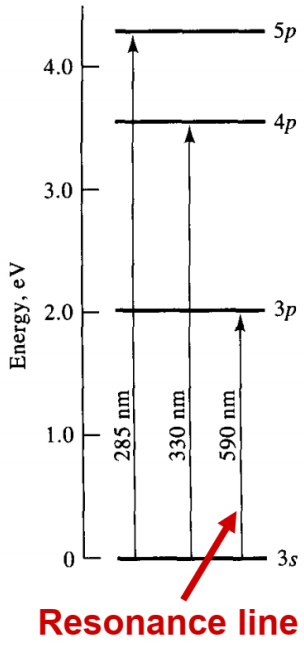
• Resonance line is the line that corresponds to the transition of outermost electron from the ground state to the first excited state.

• Resonance line is always more intense than other lines i.e, more sensitive for analysis.

• Resonance line is used always for small concentrations

• Most elements require from 6 to 9 electron volts for ionization to occur. Thus using appropriate excitation, the spectra of all metals can be obtained simultaneously.





Partial absorption spectrum for sodium vapor

We note that :

There are some exceptions for choosing other line than the resonance ones, like :

• Line from the light source lies close to the most sensitive atomic line

• High background absorbance at the resonance line

• Non resonance line from analyte or light source may be close to the resonance line

• Presence of atoms or molecules which may absorb at the same wavelength as resonance line.

6. Rydberg Formula

Johannes Rydberg was a Swedish physicist who found the mathematical relationship between one spectral line and the wavelenghs of certain elements. He discovered that there was an integer relationship between the wavenumbers of successive lines. Following is the formula:

$$\frac{1}{\lambda} = \frac{m_e\, e^4}{8\, h^3 \varepsilon_0{}^2\, C}\left(\frac{1}{n^2} - \frac{1}{m^2}\right) = R_H Z^2 \left(\frac{1}{n\prime^2} - \frac{1}{n^2}\right) \text{……..…..……...(Eq.4)}$$

R_H is the Rydberg constant $R_H = 1.097 \cdot 10^7\, m^{-1}$

Z is the atomic number

n is the upper energy level

n' is the lower energy level

λ is the wavelength of light or spectral line.

His findings were combined with Bohr's model of the atom to create this formula.Using the Rydberg formula, it becomes easy to calculate the spectral lines.

CHAPTER. III. HYDROGEN AND HYDROGEN-LIKE ATOMS

Introduction

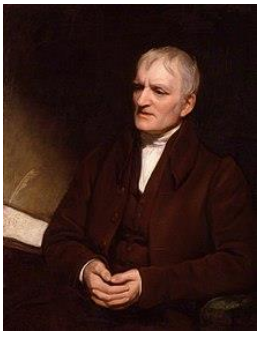
Hydrogen is a chemical element; it has symbol H and atomic number 1. It is the lightest element and, at standard conditions, is a gas of diatomic molecules with the formula H_2, sometimes called dihydrogen, but more commonly called hydrogen gas, molecular hydrogen or simply hydrogen. It is colorless, odorless, tasteless, non-toxic, and highly combustible. Constituting approximately 75% of all normal matter, hydrogen is the most abundant chemical substance in the universe. Stars, including the Sun, primarily consist of hydrogen in a plasma state, while on Earth, hydrogen is found in water, organic compounds, and other molecular forms. The most common isotope of hydrogen (symbol 1H) consists of one proton, one electron, and no neutrons.

1. History of atomic structure

Because of its simple atomic structure, consisting only of a proton and an electron, the hydrogen atom, together with the spectrum of light produced from it or absorbed by it, has been central to the development of the theory of atomic structure.

The basic idea that matter is made up of tiny indivisible particles is an old idea that appeared in many ancient cultures. The word atom is derived from the ancient Greek word atomos,[a] which means "uncuttable". This ancient idea was based in philosophical reasoning rather than scientific reasoning. Modern atomic theory is not based on these old concepts. Indeed, the structure of atoms is a recent discovery. Various models of atoms were postulated and discarded. In this chapter, we will present the most famous atomic models that were postulated and discarded until the final one was accepted.

1.1. Dalton’s atomic model



In 1804, Dalton explained his atomic theory to his friend and fellow chemist Thomas Thomson, who published an explanation of Dalton's theory in his book A System of Chemistry in 1807. The main points of Dalton's atomic theory, as it eventually developed, are:

- Elements are made of extremely small particles called atoms.
- Atoms of a given element are identical in size, mass and other properties; atoms of different elements differ in size, mass and other properties.
- Atoms cannot be subdivided, created or destroyed.
- Atoms of different elements combine in simple whole-number ratios to form chemical compounds.
- In chemical reactions, atoms are combined, separated or rearranged.

In his first extended published discussion of the atomic theory (1808), Dalton proposed an additional (and controversial) "rule of greatest simplicity". This rule could not be independently confirmed, but some such assumption was necessary in order to propose formulas for a few simple molecules, upon which the calculation of atomic weights depended. This rule dictated that if the atoms of two different elements were known to form only a single compound, like hydrogen and oxygen forming water or hydrogen and nitrogen forming ammonia, the molecules of that compound shall be assumed to consist of one atom of each element. For elements that combined in multiple ratios, such as the then-known two oxides of carbon or the three oxides of nitrogen, their combinations were assumed to be the simplest ones possible. For example, if two such combinations are known, one must consist of an atom of each element, and the other must consist of one atom of one element and two atoms of the other.

Dalton’s atomic theory successfully explained the Laws of chemical reactions, namely, the Law of conservation of mass, Law of constant properties, Law of multiple proportions, and Law of reciprocal proportions. Discovery of subatomic particles electrons, protons, and neutrons discarded the indivisible nature of the atom proposed by John Dalton.

1. 2. Thomson’s atomic model

Thomson's atomic model was proposed by Joseph John Thomson, who discovered the electron in 1897. It was proposed in 1904 before the discovery of the simplified nucleus. According to this model, an atom possesses a spherical shape in which the positive charge is uniformly distributed. This model can be visualized as a pudding with plums or watermelon of

positive charge with seeds (electrons) embedded into it. Hence, it is also called plum pudding, raisin pudding, or watermelon model.

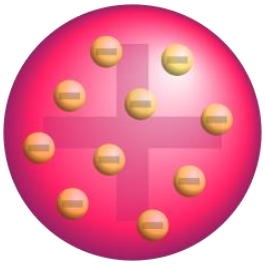
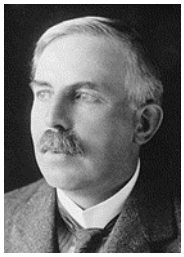


Figure.1. The plum pudding atomic model.

1. 3. Rutherford's atomic model



In the early 20th century, in 1909, the scientist Ernest Rutherford discovered the presence of the nucleus of the atom by looking at the findings from experiments conducted by two scientists working in his laboratory. These two scientists were Hans Geiger and Ernest Marsden, and they had been conducting experiments looking at the behavior of alpha particles.

1.3.1. Alpha Ray Scattering Experiment

Construction :

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

Observations :

- Most of the rays just went through the gold foil, making scintillations (bright spots) in the ZnS screen.
- A few rays got reflected after hitting the gold foil.
- One in 1000 rays got reflected by an angle of 180° (retraced path) after hitting the gold foil.

Conclusions :

- Since most rays passed through, Rutherford concluded that most of the space inside the atom is empty.
- A few rays got reflected because of the repulsion of its positive with some other positive charge inside the atom.

- 1/1000th of the rays got strongly deflected because of a very strong positive charge in the centre of the atom. He called this strong positive charge "nucleus".
- He said most of the charge and mass of the atom resides in the nucleus.

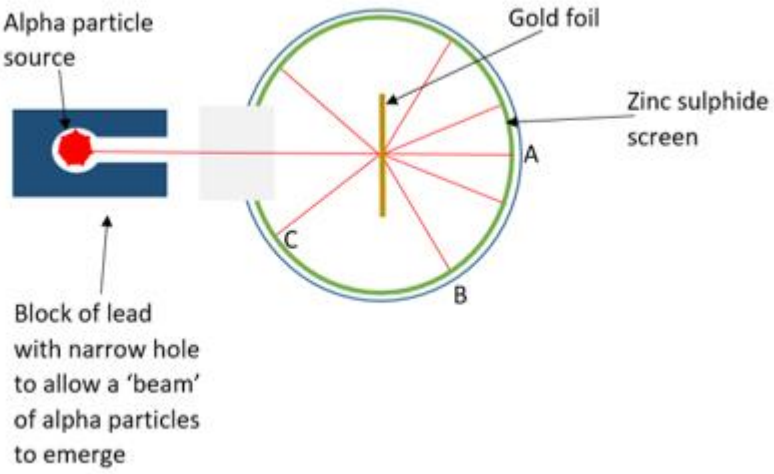


Figure.2. Geiger and Marsden's experiment set-up (Gold foil).

If Thompson's model of atomic structure was correct, the alpha particles should either pass straight through the gold foil or be only slightly deflected.

Based on the above observations and conclusions, Ernest Rutherford proposed his own atomic structure called "planetary model", in 1911, which is as follows.

- The nucleus is at the centre of an atom, where most of the charge and mass is concentrated.
- The atomic structure is spherical.
- Electrons revolve around the nucleus in a circular orbit, similar to the way planets orbit the sun.

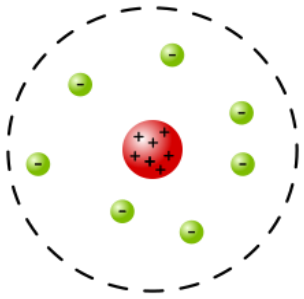


Figure.3. The Rutherford's atomic model.

1.3.2. Limitations of the Rutherford Atomic Model

- If electrons have to revolve around the nucleus, they will spend energy and that too against the strong force of attraction from the nucleus, a lot of energy will be spent by the electrons, and eventually, they will lose all their energy and will fall into the nucleus so the stability of atom is not explained.
- If electrons continuously revolve around the 'nucleus, the type of spectrum expected is a continuous spectrum. But in reality, what we see is a line spectrum.

Indeed, Rutherford had previously considered a "planetary model" with a positively charged nucleus at the centre with orbiting electrons. As we will later see this is very close in structure to early quantum mechanical models, but it could easily be shown to be untenable according to classical physics. If we take for example the hydrogen atom composed of a proton nucleus and a single orbiting electron, then we can calculate the Coulomb force binding the electron to the proton with

$$\vec{F} = -\frac{e^2}{4\pi\varepsilon_0 r^2}\overrightarrow{e_r} \text{.....(Eq.1)}$$

where $\overrightarrow{e_r}$ is the unit vector directed from the proton to the electron. For the atom to be in equilibrium, this force must be counteracted by the centrifugal acceleration (times the electron mass m) due to the orbital motion of the electron.

or, for the electron kinetic energy:

$$E_c = \frac{1}{2}mv^2 = \frac{1}{2}\frac{e^2}{4\pi\varepsilon_0 r} = -\frac{1}{2}E_p \text{ .....(Eq.2)}$$

with E_p the potential energy due to the Coulomb interaction. It therefore follows that the total energy $(E_{tot})$of the electron is negative with:

$$E_{tot} = E_c + E_p = -\frac{1}{2}\frac{e^2}{4\pi\varepsilon_0 r} < 0 \text{ .....(Eq.3)}$$

This negative value indicates that the electron is on a bound orbit about the nucleus.

But we also know from Maxwell's laws that the electron must radiate electromagnetic energy as it is accelerating on its orbit (to constantly change its direction of motion and stay on a circular orbit). From the conservation of energy its total orbital energy must become more negative, and we see from equation.3 that the size of its orbit (r) decreases accordingly. This is shown schematically in Figure 4. This scenario is

evidently flawed as the electron would eventually collapse on the proton and the atom would cease to exist. This was another spectacular failure for classical physics…

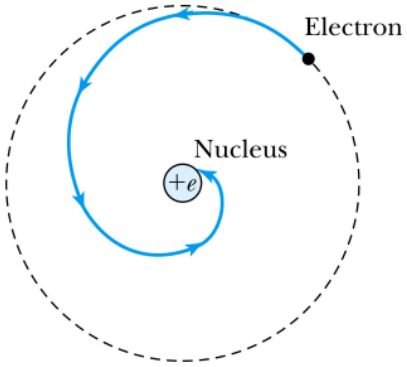


Figure. 4. The orbit of the electron about a proton for a classical hydrogen atom.

Exercise

The radius of a hydrogen nucleus is believed to be about 1.2 $\times 10^{-15}$m, according to Thomson and Rutherford scattering experience .

1. If an electron rotates around the nucleus at that radius, what would be its speed according to the planetary model?
2. What would be the total mechanical energy?
3. Are these reasonable ?

Solution

1. According to equation.2, we have :

$$v = \sqrt{\frac{e^2}{m 4\pi\varepsilon_0 r}} = \sqrt{\frac{e^2}{4\pi\varepsilon_0}} \cdot \frac{c}{\sqrt{mc^2 r}}$$
$$= \frac{c\sqrt{1.44\times10^{-9}\ \text{eV}\cdot\text{m}}}{\sqrt{(511\ \text{keV})(1.2\times10^{-15}\ \text{m})}}$$
$$= 1.53c.$$

2. According to equation.3, we write :

$$E = -\frac{1}{2}\frac{e^2}{4\pi\varepsilon_0 r}$$
$$= -\frac{1.44\times10^{-9}\,\text{eV}\cdot\text{m}}{2\cdot1.2\times10^{-15}\,\text{m}}$$
$$= -600\ \text{keV}.$$

Clearly the speed calculated in (1) is impossible as it is greater than the speed of light, and the energy in (2) is far too great compared to the ionization potential of hydrogen (i.e., 13.6 eV).

1.4. The Bohr model of the Hydrogen atom

Niels Bohr (1885-1962) was certainly one of the greatest physicists of the twentieth century, and arguably one of the best ever. Like Einstein he was one of the first to recognize the importance of Planck's quantum hypothesis, but he also pushed it further and with more far-reaching consequences than anybody else. He was a bold thinker who could see through the challenges classical physics faced and came up with imaginative solutions based on the nascent quantum theory. When considering the failure of the atomic classical model Bohr proposed four general assumptions or postulates, which he could then use to explain much of the experimental data known at the time;

1.4. 1. Postulates of Bohr's model

- To avoid the in-spiral motions of electrons orbiting a nucleus, Bohr postulated that stationary states existed in atoms where electrons could stay on stable orbits. The electrons would therefore not radiate electromagnetic energy when occupying a stationary state.
- The emission or absorption of radiation can only occur when an electron makes a transition between two stationary states. If we denote these states by the subscripts '1' and '2', then Bohr asserted that the difference in the energy of the two states is quantized :

$$E = E_1 - E_2 = h\nu \quad \text{.....(Eq.4)}$$

where h is the Planck constant and ν the frequency of the radiation emitted or absorbed. This hypothesis is then consistent with Einstein's earlier work on the quantization of radiation (i.e., the notion of the photon) and the photoelectric effect.

- The classical laws of physics only apply to stationary states, not to the transitions between them.
- Finally, not only is the energy between stationary states quantized but so is the angular momentum of the electron-nucleus system, with levels that are multiples of $\hbar = \frac{h}{2\pi}$.

- The angular momentum of the orbiting electron and equate it to the quantized level of the system's stationary state (the nucleus is much more massive than the electron and we will neglect its contribution at present.

$$\|\vec{L}\| = mvr = n\hbar \quad n = 1,2,3, \ldots \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\text{(Eq.5)}$$

with r the radius of the orbit (assumed circular), v the speed of the electron, and n the principal quantum number.

Using this relation and equation.2 we find that /

$$v^2 = \frac{e^2}{4\pi\varepsilon_0 mr} = \frac{n^2\hbar^2}{m^2r^2}\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\text{(Eq.6)}$$

This relation, in turn, allows us the define the Bohr radius when $n = 1$.

$$a_0 = \frac{4\pi\varepsilon_0\hbar^2}{me^2} = 0.53 \times 10^{-10}m\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\text{(Eq.7)}$$

from which we determine the other permitted orbital radii for stationary states.

$$r_n = \frac{4\pi\varepsilon_0 n^2\hbar^2}{me^2} = n^2a_0\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\text{(Eq.8)}$$

Bohr was thus able to determine a fundamental a_0 for the hydrogen atom, entirely based on fundamental constants, that was in excellent agreement with the experimental data already existent at the time (in 1913). This size, i.e., the Bohr radius, corresponds to the ground state of the hydrogen atom (when n = 1), while stationary states for n >1 are called excited states.

The energy associated with stationary states are given, from equations.3 and .8 :

$$E_n = -\frac{e^2}{8\pi\varepsilon_0 r_n} = -\frac{e^2}{8\pi\varepsilon_0 a_0 n^2} = -\frac{E_0}{n^2}\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\text{(Eq.9)}$$

with the energy of the ground state :

$$E_0 = \frac{e^2}{8\pi\varepsilon_0 a_0} = \frac{m}{2\hbar^2}\left(\frac{e^2}{4\pi\varepsilon_0}\right)^2 = 13.6\ eV\ldots\ldots\ldots\ldots\ldots\ldots\ldots\text{(Eq.10)}$$

We can also use the second of Bohr's four assumptions to calculate the frequency or the wavelength of the radiation emitted as a result of a transition between two stationary states of principal quantum numbers n and n′ with :

$$\frac{1}{\lambda} = \frac{E_n - E_{n\prime}}{hC} = -\frac{E_0}{hC}\left(\frac{1}{n^2} - \frac{1}{n'^2}\right) = R\left(\frac{1}{n'^2} - \frac{1}{n^2}\right)\ldots\ldots\ldots\ldots\text{(Eq.11)}$$

with $R = \frac{E_0}{hC} = \frac{m}{4\pi C\hbar^3}\left(\frac{e^2}{4\pi\varepsilon_0}\right)^2 = 1.097373 \times 10^7\, m^{-1}$

Bohr had thus succeeded in theoretically deriving the Rydberg equation, established experimentally in 1890, and confirming the value of the Rydberg constant:

$$R_H = 1.097373 \times 10^7\, m^{-1}\ .$$

The small discrepancy between Bohr's theoretical value and the experimental determination of Rydberg can be explained by taking into account the mass of the proton. Furthermore, Bohr's theory could be used to predict the presence of then unknown spectral lines, which were eventually verified experimentally.

Finally, another fundamental parameter can be established by considering the orbital speed of the electron. Using equations 6 and 8 we find that :

$$v_n = \frac{1}{n}\frac{\hbar}{ma_0} = \frac{1}{n}\frac{e^2}{4\pi\varepsilon_0\hbar} \text{.....(Eq.12)}$$

Focusing on the speed of the ground state at n = 1 and dividing it by the speed of light we get a unit-less parameter :

$$\alpha \equiv \frac{v_1}{C} = \frac{\hbar}{ma_0 C} = \frac{e^2}{4\pi\varepsilon_0\hbar C} \cong \frac{1}{137} \text{ .....(Eq.13)}$$

which is the so-called fine structure constant

1.4. 2. The Correspondence Principle

It was highly difficult for several physicists at the start of the twentieth century to accept the new quantum physics at face value and equally troubling that it should be assigned with any kind of physical reality. On the one hand, classical physics was incredibly successful in describing the macroscopic world as we see and feel it, while on the other it appeared that the new experiments could only be "explained" within the context of the theories of Planck, Einstein, and Bohr. This apparent paradox was lessened by the fact that the classical and quantum realms dealt with scales that were worlds apart. For example, consider the scale of the Bohr radius (i.e., on the order of 10−10m) to those we experience on a daily basis. Although such could be the hope that both worlds would "coexist independently" in this manner, common sense would also dictate that there must exist a domain where the two realities must merge. After all, nature cannot be both classical and quantum at the same time, in view of their very different characters.

Bohr was acutely aware of this issue and proposed The *Correspondence Principle* as a guideline:

In the limits where classical and quantum theories should agree, the quantum theory must reduce to the classical result.

This is not to be interpreted as a "concession" made by the new generation of physicists. to make the quantum theory more palatable… But it should be understood in the context where one transitions from the quantum to the classical domain. Alternatively the Correspondence Principle could be stated such that *the behaviour of quantum systems must reproduce the results of classical physics in the large-quantum-number limit.* This will be made clearer with the following example :

According to equations.4 and 9, the angular frequency of the radiation resulting from an atomic transition between two adjacent stationary states can be calculated with

$$\omega_q = -\frac{E_0}{\hbar}\left[\frac{1}{(n+1)^2} - \frac{1}{n^2}\right] = \frac{E_0}{\hbar}\left[\frac{2n+1}{n^2(n+1)^2}\right] \text{.....(Eq.14)}$$

To find the large-quantum-number limit, we choose an arbitrarily large value for n such that we can approximate equation (13) to :

$$\omega_q = -\frac{2E_0}{n^3\hbar} \cong \frac{m}{n^3\hbar^3}\left(\frac{e^2}{4\pi\varepsilon_0}\right)^2 \text{.....(Eq.15)}$$

This equation should reproduce the corresponding classical result as for such a large value for the principal quantum number the difference in energy associated with the two stationary states is much smaller than that of the ground state (i.e. $E_{n+1} - E_n = E_0$)

Classically, the frequency of the radiation ω_C is the same as that of the acceleration of the electron responsible for the emission of electromagnetic waves. We therefore write:

$$\omega_C = \frac{v}{r} \text{.....(Eq.16)}$$

which is simply the reciprocal of the time taken to complete one orbit (i.e., the period). The classical relation for the orbital speed is obtained with equation.2 (or equivalently through the first of Eq. 6)

$$v = \left(\frac{e^2}{4\pi\varepsilon_0 mr}\right)^{1/2} \text{.....(Eq.17)}$$

such that :

$$\omega_C = \left(\frac{e^2}{4\pi\varepsilon_0 mr^3}\right)^{1/2} \text{.....(Eq.18)}$$

As can be verified by examining the different quantities composing it, this equation is

entirely classical in nature, i.e., the Planck constant is not part of it.

To establish the correspondence between equations. 18 and 14, we note that the quantity $n\hbar$ present (to the third power) in the quantum mechanical equation is nothing more than the angular momentum of the electron. We therefore first establish the following correspondence :

$$n\hbar \rightarrow mvr = \left(\frac{mre^2}{4\pi\varepsilon_0}\right)^{1/2} \text{.....(Eq.19)}$$

Inserting this result in equation.14, we have :

$$\omega_q \rightarrow m\left(\frac{4\pi\varepsilon_0}{mre^2}\right)^{3/2}\left(\frac{e^2}{4\pi\varepsilon_0}\right)^2 \rightarrow \left(\frac{e^2}{4\pi\varepsilon_0 mr^3}\right)^{1/2} = \omega_C \text{.....(Eq.20)}$$

which is what we sought to establish in agreement with the Correspondence Principle

1. 4. 3. Limitations of the Bohr Model

Bohr's biggest contribution in his model was to introduce quantum principles to classical physics, but his model had a few limitations:

1- Spectra of Large atoms. The Bohr model could only successfully explain the hydrogen spectrum. It could not accurately calculate the spectral lines of larger atoms. The model only worked for hydrogen-like atoms, if the atom had only one electron.

2- Relative Spectra Intensity. Bohr's model could not explain why the intensity of the spectra lines were NOT all equal.

3- Hyperfine spectral lines with better equipment and careful observation, it was found that there were previously undiscovered spectral lines. These were named hyperfine lines and they accompanied the other more visible lines. Bohr's model could not explain why this was the case due to the lack of equipment and development in quantum physics.

4- The Zeeman effect; It was found that, when hydrogen gas was excited in a magnetic field, the produced emission spectrum was split. Bohr's model could not account for this. Solved by accounting for the existence of a tiny magnetic moment of each electron.

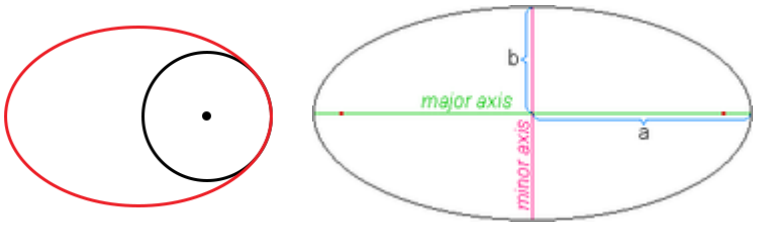
1. 5. Bohr-Sommerfeld atomic model

The Bohr-Sommerfeld model (also known as the Sommerfeld model or Bohr Sommerfeld theory) was an extension of the Bohr model to allow elliptical or bits of electrons around an atomic nucleus. It was proposed in 1916 by Arnold Sommerfeld to try to cover the deficiencies that the

Bohr model presented. Therefore, it is a relativistic version of the Rutherford-Bohr model and was based, in part, on Albert Einstein's relativistic postulates. Bohr's atomic model with electrons circular orbits characterized by a principal quantum number (n) describes the spectral lines of the hydrogen atom, but does not successfully describe the atomic spectra of multi-electrons atoms. Furthermore, when the hydrogen atom is placed in a magnetic or electric field, we observe new lines not predictable by Bohr's theory. Therefore, Sommerfeld asserted a number of corrections to the model.

1.5. 1. Postulates of Sommerfeld's model

- Orbits may be both circular and elliptical. When path is elliptical, then there are two axis, major axis and minor axis. When length of major & minor axis becomes equal then orbit is circular.



- **Elliptical minor axis (in purple)**
- **Major axis (in grren)**
- **b half minor axis distance**
- **a half major axis distance.**

- Sommerfeld introduced a new quantum number called Orbital or azimuthal quantum number (l) which determines the orbital angular momentum of electron $(\vec{L})$. Therefore, the angular momentum $(\vec{L})$ of the electron moving in an elliptical orbit is quantified and given by:

$$\|\vec{L}\| = \frac{nh}{2\pi} = \sqrt{l(l+1)}\,\hbar. \qquad l = 0,1,2, \ldots \ldots n-1. \ldots\ldots\ldots\ldots\ldots\text{(Eq.21)}$$

n is the principal quantum number.

l is the azimuthal quantum number.

We note that, with increase in value of the azimuthal quantum number (l), ellipticity of the orbit decreases. When $n = l$, then orbit is circular (Figure.5).

Sommerfeld introduced another quantum number denoted (m) which presents electron magnetic momentum placed in the magnetic field of other charges. It determines orbital orientation. It is an integer number taken in $-l \leq m \leq +l$ range.

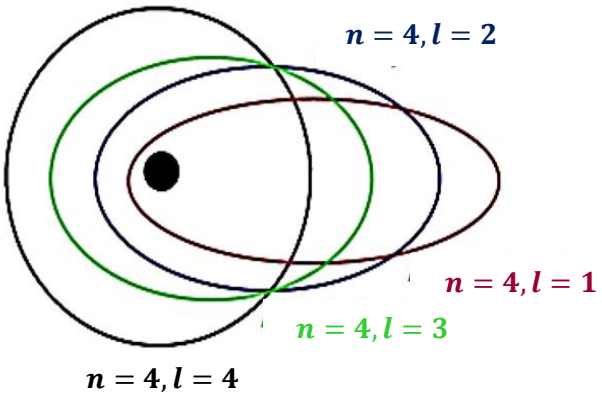


Figure.5. Sommerfeld's elliptical orbits.

- Sommerfeld suggested that orbits characterized by principal quantum number n, are made up of sub energy levels. These are s,p,d,f. These sub shells possess slightly different energies.

  For, $= 1$; $l = 0$; 1s sub shell

  $n = 2$; $l = 0,1$; $2s$, $2p$ sub shell

  $n = 3$; $l = 0,1,2$; $3s$, $3p$, $3d$ sub shell

  $n = 4$; $l = 0, 1, 2, 3$; $4s$, $4p$, $4d$, $4f$ sub shell

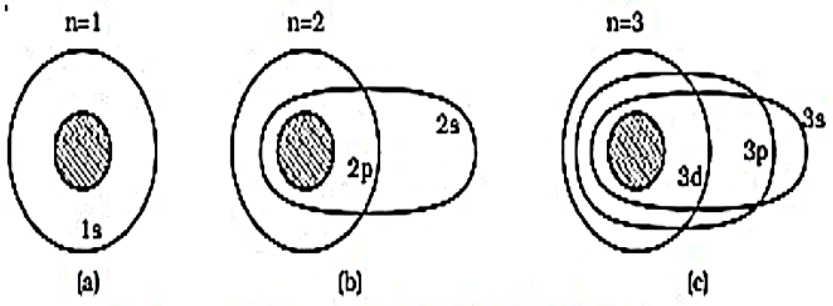


Figure.6. sub shells identifided according to Sommerfeld's model.

- When an electron jumps from one orbit to another orbit, the difference of energy (ΔE) depends upon sub energy levels.

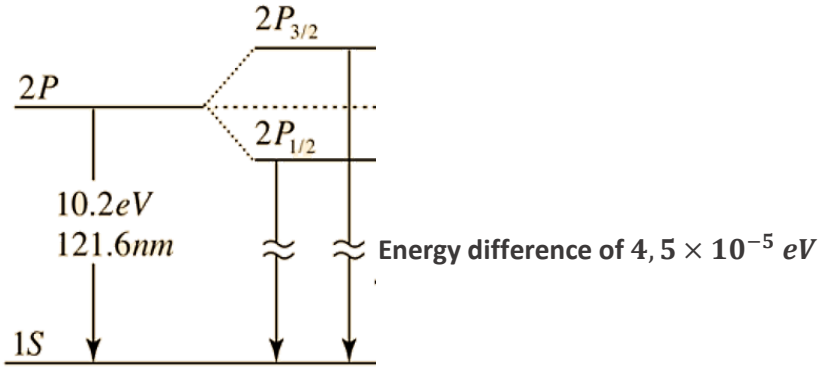


Figure.7. Individual spectral lines present in fine spectrum of hydrogen.

This can explain the splitting of individual spectral lines of hydrogen and thus fine spectrum. It could not predict the exact number of lines which are actually present in the fine spectrum.

- Unlike the Bohr model, in the Sommerfeld's model, the nucleus of the atom is not point-like and it moves relative to a center of gravity.

1. 5.2. Limitations of Sommerfeld atomic model

1- This model does not explain the Zeeman & Stark effect. This model does not take into account the interaction between the angular momentum and the magnetic moment of the electron: Spin-orbit interaction.

2- This model does not explain the behavior of system having more than one electron. It was ultimately, abandoned and replaced by the quantum model of the wave function of an electron (Schrodinger's model).

2. Hydrogen atom line spectrum

Another piece of strange behavior observed at about the same time is the so called "line spectrum" of the hydrogen atom. You are already familiar with the fact that a prism can be used to disperse (separate) the colors of white light (like light from the sun or a light bulb) into its component colors: red, orange, yellow, Green, blue, indigo and violet (ROYGBIV). The rainbow that results from dispersion by a prism is called the spectrum of the sun. We know that our sun is made up of many elements, everything, in fact, from hydrogen (most abundant) to Iron (0.003% of all atoms in the sun). Although sunlight consists of more of some colors and less of others, we refer to its light as white light because it contains all colors visible to humans. However, if we look at the emission spectrum of only hot, glowing hydrogen gas (e.g. by putting H_2 gas in a fluorescent bulb), dispersing it with a prism in just the same way, we see a completely different result (figure below). Now instead of a rainbow, we see only four distinct "lines" or "bands" of colored light with nothing in between; thus the term "line spectrum."

2.1. Hydrogen emission spectrum

In 1859, Julius Plücker identified the H_α and H_β lines of Hydrogen emission with Fraunhofer's C and F lines in sunlight. In 1862, Angström discovered that Fraunhofer's f and h lines in the solar spectrum corresponded to the H_γ and H_δ lines of hydrogen. He deduced that Hydrogen is present in the solar atmosphere, as well as other elements.

Fraunhofer's lines	Hydrogen lines	Wavelengh (Å)	Color
C		6562,10	red
F		4860,74	blue
f		4340,10	blue
h		4101,20	Violet

Table.1. Wavelengths of hydrogen lines determined in Angstroms.

John Herschel (1826): shine light from heated gas through spectroscope, and you will observe monochromatic lines of pure color on a dim/dark background. Herschel's discovery of emission spectra from heated gas was studied extensively in the 1800's. It was realized that a heated gas emits a unique combination of colors, called emission spectrum, depending on its composition.

2.1.1. Discharge Hydrogen tube experiment

We put an H_2 gas under the effect of a very intense alternating electric field by using a hydrogen discharge lamp (Balmer lamp) which contains a water vapor (Figure.8). The electric discharge (alternating electric field) causes the dissociation of H_2O molecules to H+OH. The hydrogen atoms produced are electronically excited.

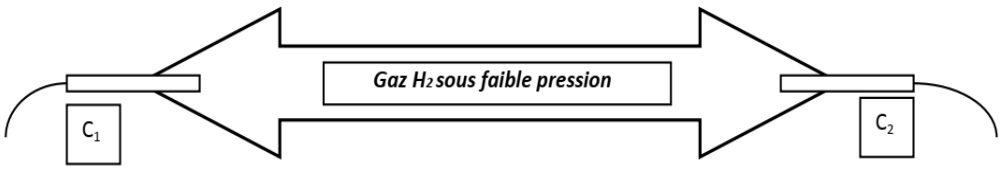


Figure.8. Hydrogen Gas Discharge tube.

When an electric current is passed through a glass tube that contains hydrogen gas at low pressure the tube gives off blue light. When this light is passed through a prism (as shown in the figure below), five narrow bands of bright light are observed against a black background.

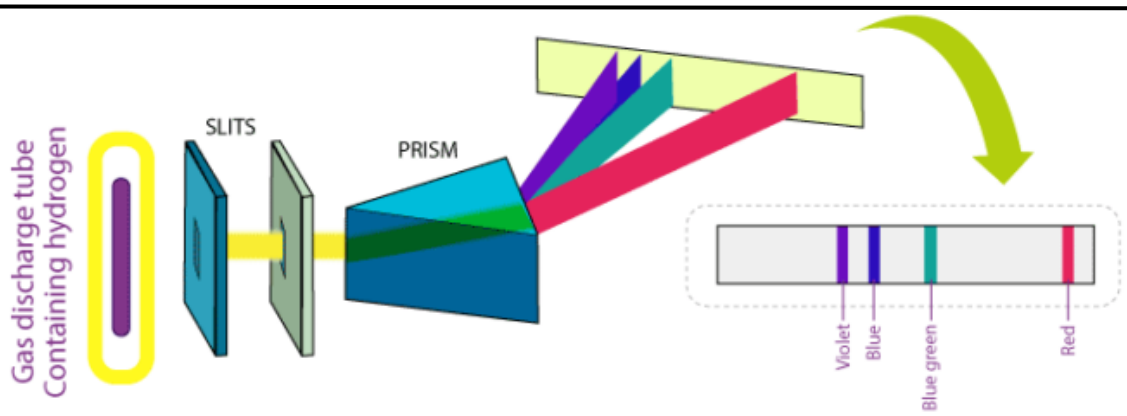


Figure.9. Hydrogen emission spectrum experiment.

These narrow bands have the characteristic wavelengths and colors. The lines absorption and emission spectra for hydrogen atom are shown below :

Figure.10. Visible wavelength lines absorption and emission spectra of hydrogen atom (wavelengths are in nanometers).

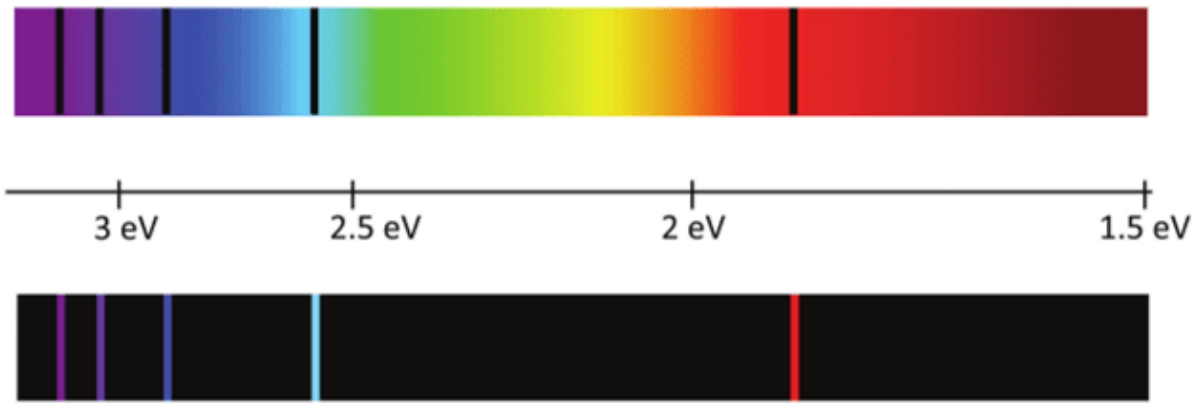


Figure.11. Visible energy lines of absorption and emission spectra of hydrogen atom

2.1.2. Energy Levels of Hydrogen atom

The calculation of the energy levels $E_1, E_2, \ldots \ldots$ etc, of an atom can only be done in a simple and explicit manner for the hydrogen atom H, the ions He^{+}, Li^{++}, etc. or for atoms/ions having an external electron sufficiently far from all the other electrons (case

of alkalis, vapors of Na, K,..etc.). In these simplest cases, the energy levels are given by following formula (Eq. 9) :

$$E_n = -\frac{13.6\ eV}{n^2} \text{.....(Eq.22)}$$

This remarkably simple formula provides a wonderfully compact way of remembering everything that is shown in the energy-level diagram of hydrogen. The formula applies only to the hydrogen atom; indeed, it is not possible to summarize all the energy levels of any other atom in a simple formula.

- When a hydrogen atom (or in fact any other atom) sits in the lowest energy level, it is said to be in its **ground state**. This is the "normal" state in which an atom might be found. It will correspond to a situation in which the electron is likely to be close to the proton, with a minimum value of electrical energy. The energy value corresponding to the ground state of the hydrogen atom is the minimum value : $n = 1 \Rightarrow E_1 = -13{,}6\ eV$.
- Above this energy, when the atom sits in its second, third, fourth, etc., level, it is said to be in an **excited state**. In principle there is an infinite number of energy levels, and the topmost one corresponds to a situation in which the electron and proton are widely separated, with a maximum value of electrical energy.
- All bound states of atoms, therefore, correspond to negative values of energy levels, as these energy levels sit below the topmost energy level. So, the ground-state energy is 13.60 eV below that, namely at -13.60 eV. Furthermore, each of the excited levels can then be associated w'ith some negative value of energy between -13.60 eV and 0 eV. Note that this is not implying that the atom has a "negative energy" when it is in one of the bound states shown, simply that it has less energy than if the electron and proton were separated.
- The next point to note is that although an energy-level diagram may contain an infinite number of levels there is still only a finite difference in energy between the lowest energy level and the highest energy level. This shows that there is a limit to the amount of energy that a hydrogen atom can absorb without the electron and proton being split apart. If the atom is initially in its ground state and it absorbs a photon with an energy greater than the difference between the ground state and the uppermost energy level, the electron is freed completely from its bondage to the proton at the

core of the atom (the nucleus). The removal of an electron from a hydrogen atom leaves a charged particle which is written H+ and is called an ion. (In fact, the hydrogen ion is simply a proton.) The technical term for such removal of an electron from an atom is therefore ionization. The energy difference between the topmost energy level and the ground state is called the **ionization energy**, which in the case of hydrogen is about 13.60 eV.

- There is a continuous range of possible energies above the ionization energy, and this is generally referred to as the continuum. The continuum corresponds to situations in which the electron and proton move around separately, with a combined kinetic energy that is greater than the topmost energy level. The electron is no longer bound to the proton, and the particles can have any value of energy.
- Now for a rather subtle point. We have already seen that the energies of the levels are not really known. However, there is no such doubt about the differences in energy between the levels. These differences are very well defined, and, as you have already seen, they can be determined quite simply from atomic spectra. The energy of any of the energy levels is not known, but it makes life simpler for everyone if it is agreed, as a matter of convention, that the energy of the topmost energy level is 0 eV : ($n \rightarrow +\infty$ et $E_n = E_\infty = 0\ eV$). This corresponds to the energy of a separated electron and proton.

Scientists have indeed produced such a list, and this allows the complete energy- level diagram for the hydrogen atom to be drawn, in which the energy values are illustrated in a conventional and convenient way (Figure.12).

What matters here is the vertical spacing of the energy values; neither the horizontal extent of the lines nor their thickness is of any significance whatsoever. One important thing to notice about this energy-level diagram is its simplicity: the pattern is one in which the energy levels gradually come closer together. The higher energy levels of hydrogen become so densely packed that it becomes impossible to draw them as distinct lines and the best that an illustrator can do is to indicate that the lines gradually get closer and closer together. The energy-level diagram for hydrogen is in fact the simplest of all atomic energy-level diagrams, just as you might have supposed.

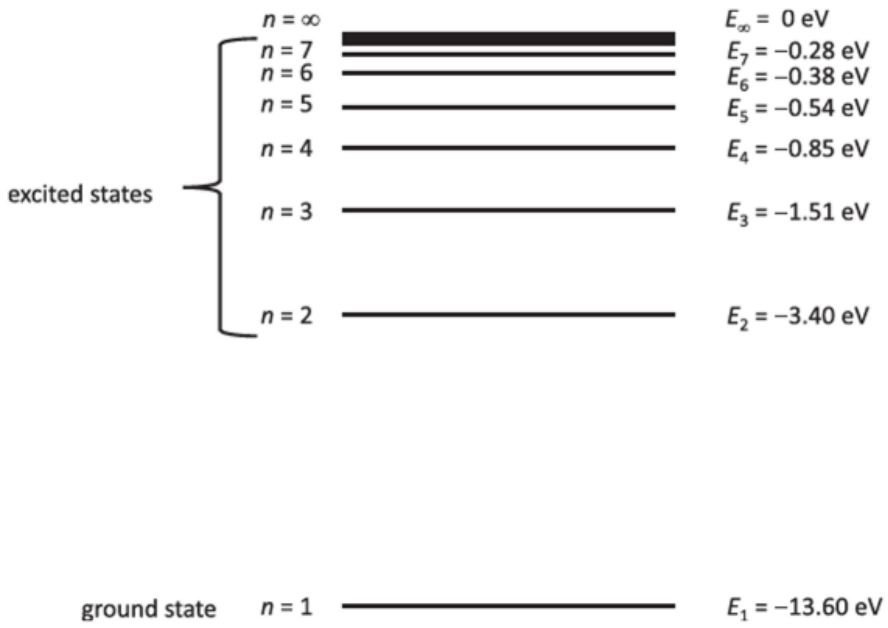


Figure.12.The hydrogen energy-level diagram.

2.1.3. Line spectral series in hydrogen atom

Given the full range of hydrogen energy levels, it is possible to identify all possible transitions between energy levels $(\Delta E = h\nu)$ in the hydrogen atom using the following mathematical formula (Eq.11), suggested by J. Balmer (1885) and J. Rydberg (1888):

$$\nu = \frac{1}{\lambda} = R_H \left(\frac{1}{{n_f}^2} - \frac{1}{{n_i}^2}\right) \text{.....(Eq.22)}$$

where ν is the frequency of an emission line, n_i and n_f are orbital principal quantum numbers $(n_i > n_f)$ and $R_H = 1.097373 \times 10^7\, m^{-1}$ is Rydberg's constant.

Therefore all the possible spectral lines. In the case of the hydrogen atom these transitions are grouped into series, named after the scientists w'ho discovered them.

a). Lyman Series :

The series with $n_f = 1$ is known as the Lyman series and lies in the ultraviolet part of the spectrum.

$$\nu_L = \frac{1}{\lambda_L} = R_H \left(\frac{1}{1^2} - \frac{1}{{n_i}^2}\right) \; n_i = 2,3,4, \text{.....(Eq.23)}$$

The lines are labeled as $L_\alpha, L_\beta, L_\gamma, \ldots\ldots$ in order of decreasing wavelengths.

L_α, line: $n_f = 1$ and $n_i = 2$; λ = 1216 °A

L_β, line: $n_f = 1$ and $n_i = 3$; λ = 1026 °A

L_γ, line: $n_f = 1$ and $n_i = 3$; λ = 973 °A

While the Lyman series limit ($n_i \to \infty$) λ = 912 °A.

b). *Balmer Series* :

The series with $n_f = 2$ is known as the Balmer series and lies in the ultraviolet part of the spectrum.

$$\nu_B = \frac{1}{\lambda_B} = R_H \left(\frac{1}{2^2} - \frac{1}{{n_i}^2}\right) \; n_i = 3,4,5,\ldots\ldots\ldots\ldots\ldots\ldots\text{(Eq.24)}$$

The lines are labeled as $H_\alpha, H_\beta, H_\gamma, \ldots\ldots$ in order of decreasing wavelengths.

H_α, line: $n_f = 2$ and $n_i = 3$; λ = 6563 °A

H_β, line: $n_f = 2$ and $n_i = 4$; λ = 4861 °A

H_γ, line: $n_f = 2$ and $n_i = 5$; λ = 4340 °A

While the Balmer series limit ($n_i \to \infty$) λ = 3646 °A. The H_α is an important line used in the detection of hydrogen presence.

c). Paschen Series:

Paschen series was observed by Friedrich Paschen in 1908 corresponds to the transition between the states with ($n_f = 3$) and successive higher states and lies in the near Infrared region of the spectrum.

$$\nu_P = \frac{1}{\lambda_P} = R_H \left(\frac{1}{3^2} - \frac{1}{{n_i}^2}\right) \; n_i = 4,5,6, \ldots\ldots\ldots\ldots\ldots\ldots\text{(Eq.25)}$$

The Paschen series starts with a line at λ = 18751°A and ends at λ = 8204 °A (wavelength of Paschen series limit).

c). Brackett Series:

In the Brackett series electron transition takes place from any higher principle quantum state to ($n_f = 4$) and it is obtained in the far infrared region.

$$\nu_B = \frac{1}{\lambda_B} = R_H \left(\frac{1}{4^2} - \frac{1}{{n_i}^2}\right) \; n_i = 5,6,7, \ldots \ldots\ldots\ldots\ldots\ldots\text{(Eq.26)}$$

The Brackett series start at 40500 °A whereas the series limit lies at 14580 °A . The shortest or high frequency lines of Brackett series overlap with the Paschen series lines.

d). Pfund Series:

This series was discovered by A.H. Pfund in 1924 which corresponds to transition between the states with ($n_f = 5$) and successive higher states and lies in Infrared region of the spectrum.

$$\nu_F = \frac{1}{\lambda_F} = R_H \left(\frac{1}{5^2} - \frac{1}{n_i{}^2}\right) n_i = 6,7,8 \ldots \ldots \ldots \ldots \ldots \ldots \text{(Eq.27)}$$

The Pfund series start at 74600 °A whereas the series limit lies at 22790 °A.

e). Humphreys Series:

The sixth series in the spectrum of hydrogen atom was observed by C.J. Humphreys in 1953 and lies in the infrared region of the spectrum. This series originates in transition to the sixth orbit from those of greater quantum numbers.

$$\nu_H = \frac{1}{\lambda_H} = R_H \left(\frac{1}{6^2} - \frac{1}{n_i{}^2}\right) n_i = 7,8,9 \ldots \ldots \ldots \ldots \ldots \text{(Eq.28)}$$

The series with higher orders is unnamed but it follows the same rule given by J. Rydberg formula.

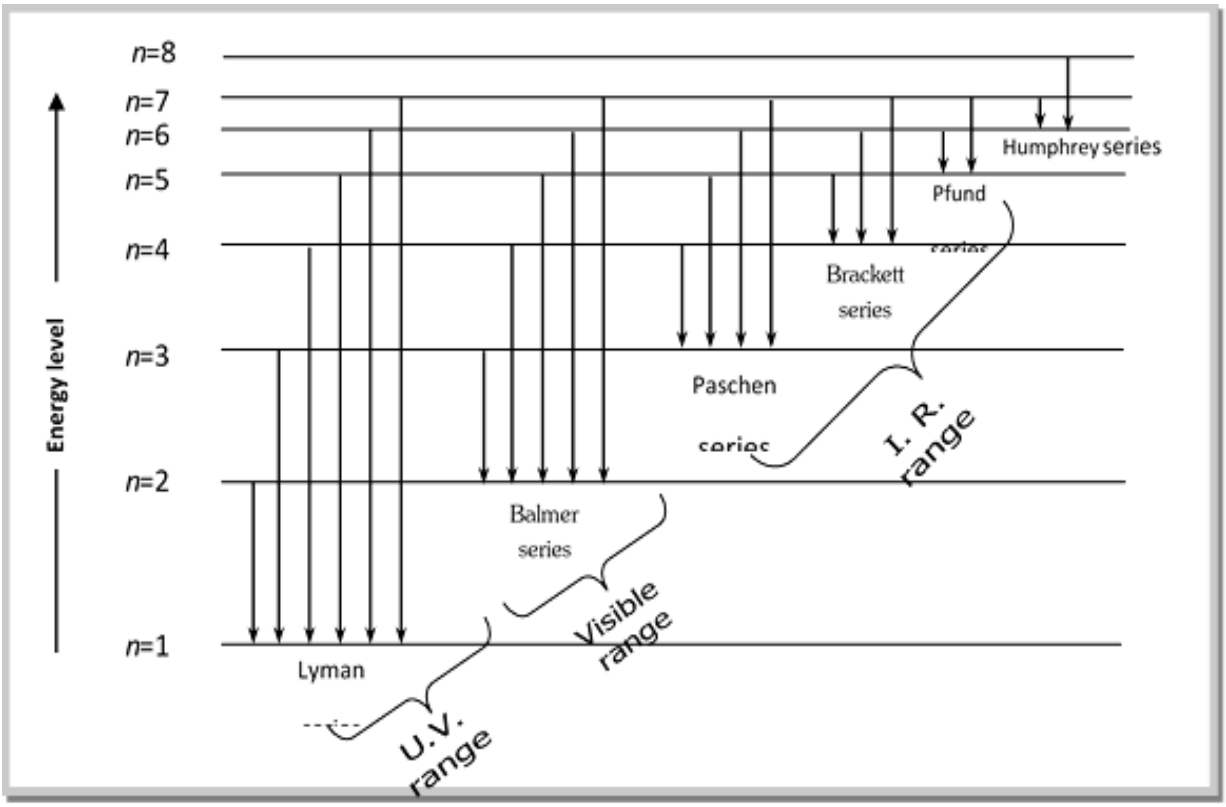


Figure.13. Spectral lines series diagram of hydrogen atom.

3. Hydrogen atom according to Schrödinger's quantum model

In 1925, Erwin Schrödinger proposed the quantum mechanical model of the atom, which treats electrons as matter waves. he used de Broglie's matter wave theory to develop a probabilistic model of the atom based on the following formula:

$$\hat{H}\psi = E\psi \ldots\ldots\ldots\

What is known in this equation is the Hamiltonian operator ($\hat{H}$) of the system, which is equivalent to the mechanical energy (sum of the kinetic energy E_c and the potential energy of the system: V) used in classical mechanics .

$$\hat{H} = -\frac{h^2}{8\pi^2 m}\Delta + \hat{V} \quad \text{.....(Eq.30)}$$

The Laplacian operator in Cartesian coordinates: $\Delta = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$

Schrödinger's equation can be solved to yield a series of wave function (ψ), each of which is associated with an electron binding energy. Orbitals are regions in which an electrons can be found. Inside an orbital, the probability (P) of finding an electron is the square of the wave function (ψ) :

$$P = |\psi|^2 \quad \text{.....(Eq.31)}$$

P represents the probability of finding an electron in a given region within the atom. While 'orbits' and 'orbitals' seem to share similarities, they are very different concepts. Different types of orbitals have different shapes and therefore electron density patterns. Appreciate the evident increase in probability of finding an electron with proximity to the nucleus (Figure.14).

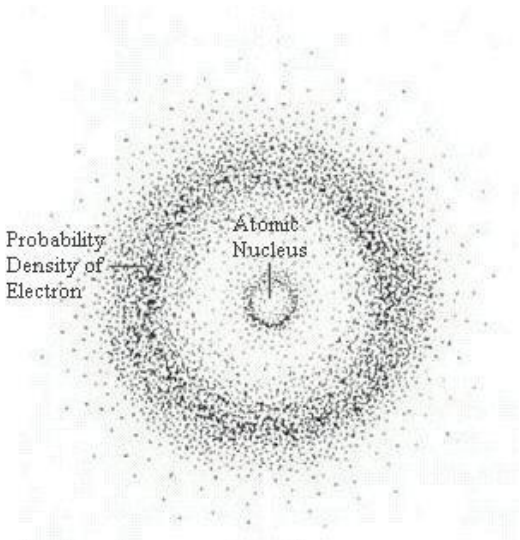


Figure.14. Atom according to the quantum model of Schrodinger.

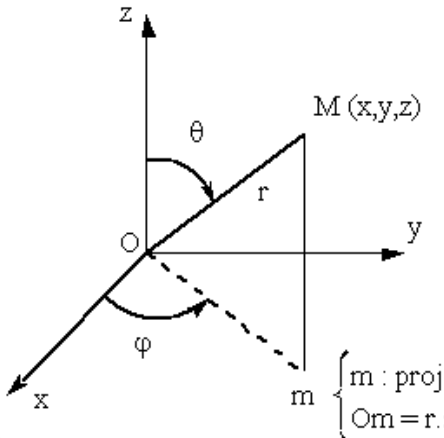
The hydrogen atom is constituted of a proton and an electron. The system studied is limited to the interaction between these two charges separated by a distance r. The potential energy V(r) of the H atom is given by:

$$V(r) = -\frac{1}{4\pi\varepsilon_0}\frac{e^2}{r}. \quad \text{.....(Eq.32)}$$

In three dimensions the Schrodinger equation generalizes to :

$$\left[-\frac{\hbar^2}{2m}\Delta - \frac{1}{4\pi\varepsilon_0}\frac{e^2}{r}\right]\psi = E\psi \text{.....(Eq.33)}$$

The interaction potential $V(r)$ has a radial variation. It will be preferred to write the wave equation $\psi(r)$ in terms of spherical coordinates (r, θ, φ). The proton is placed at the origin of the spherical reference and the electron at point M with Cartesian coordinates (x, y, z).



$$\begin{cases} x = r.\sin\theta.\cos\varphi \\ y = r.\sin\theta.\sin\varphi \\ z = r.\cos\theta \end{cases} \quad \begin{cases} r \in [0, \infty[\\ \theta \in [0, \Pi] \text{ (co-latitude)} \\ \varphi \in [0, 2\Pi] \text{ (longitude)} \end{cases}$$

$$\begin{cases} m : \text{projeté orthogonal de M dans le plan [xOy] (plan équatorial)} \\ Om = r.\sin\theta \end{cases}$$

$$-\frac{\hbar^2}{2m}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2 sin\theta}\frac{\partial}{\partial\theta}\left(sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{r^2 sin^2\theta}\frac{\partial^2}{\partial\varphi^2} - \frac{e^2}{4\pi\varepsilon_0 r}\right]\psi(r,\theta,\varphi) =$$

$$E\psi(r,\theta,\varphi) \text{ .....(Eq.34)}$$

In spherical coordinates $\psi(r, \theta, \varphi)$ and the plan is to look for a variables separable solution such that:

$$\psi_{n,m,l}(r,\theta,\varphi) = R_{n,l}(r)\Theta_{l,m}(\theta)\Phi_m(\varphi) = R_{n,l}(r)\mathrm{Y}_{l,m}(\theta,\varphi) \text{ .....(Eq.35)}$$

$\psi_{n,m,l}$ depends on three numbers n, m, l.

We will in fact find such solutions where $\mathrm{Y}_{l,m}(\theta, \varphi)$ are the spherical harmonic functions which represents the angular part corresponding to the quantum number of the orbital moment (l) and the magnetic quantum number (m_l).

$R_{n,l}(r)$ is expressible in terms of associated Laguerre functions. It represents the radial wave functions corresponding to the state designated by the principal quantum number (n) and the quantum number of the orbital moment (l).

Such wave functions describe the stationary state of the system specified by the combination (n, l, m_l) with a quantified energy E_n given by (Eq.9) and an orbital angular momentum $\overrightarrow{L}$ with amplitude $\|\overrightarrow{L}\|$ is given by (Eq.21).

We note that:

- ✓ Quantum numbers (n, l, m_l) are to specify and display to complete information about size, shape and orientation of the orbital.
- ✓ Quantum numbers (n, l, m_l) obey very precise relationships.
- ✓ In addition to the electron orbital angular momentum (m_l), it exist a fourth quantum number denoted (m_s) called the spin quantum number. This number was identified by two physicists, George Uhlenbeck and Samuel Goudsmit, in 1925. They discovered that electrons possess an intrinsic angular momentum, known as spin. Unlike $n, l,$ and m_l, the electron spin quantum number (m_s) does not depend on another quantum number. It designates the direction of the electron spin and may have a spin of +1/2, represented by↑, or –1/2, represented by ↓. This means that when (m_s) is positive the electron has an upward spin, which can be referred to as "spin up." When it is negative, the electron has a downward spin, so it is "spin down." The significance of the electron spin quantum number is its determination of an atom's ability to generate a magnetic field or not. (Electron Spin.) : $m_s = \pm\frac{1}{2}$.

3.1. Variations of radial wave function

3.1.1. Plots of radial wave function against the distance *r*

The variation of the radial part $R_{n,l}(r)$ of the orbital wave funcitons $\psi_{n,m,l}(r, \theta, \varphi)$for 1s, 2s and 2p orbitals. The radial function value changes form positive to zero then to negative. The region where this function reduces to zero is called nodal surfaces or simply nodes.

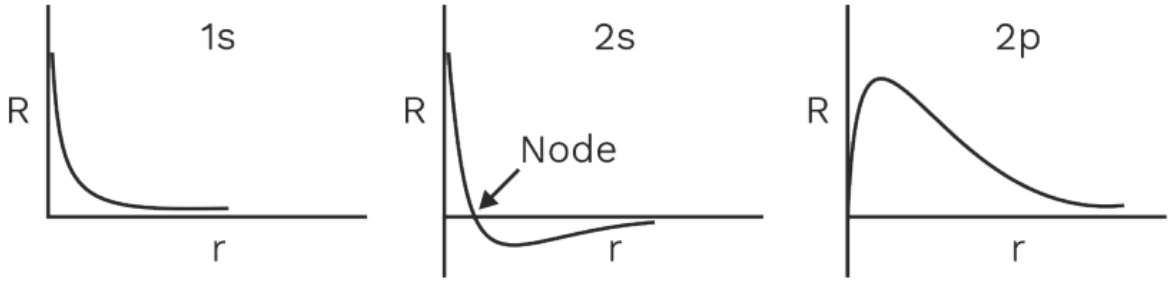
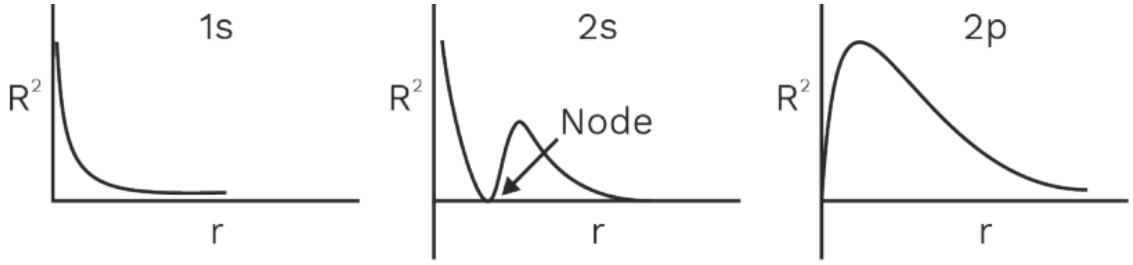


Figure. 15. Plots of radial wave function against the distance r

3.1.2. Radial probability density

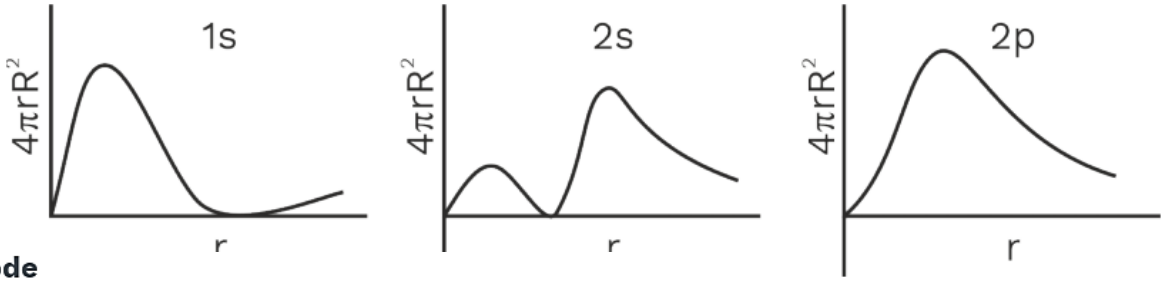
Square of radial wave function, $R^2(r)$ is the measure of the radial probability $P(r)$ of finding the electron in a unit volume around a particular point and is called probability density:

$$P(r) = R^2(r) \text{.....(Eq.36)}$$



3.1.3. Radial distribution function $4\pi r^2 R^2$

Probability density of finding electron at a point at a distance r form the nucleus. Since the atoms have spherical symmetry, it is more useful to discuss the probability of finding the electron in a spherical shell between the spheres of radii $r + dr$ and r.



Node

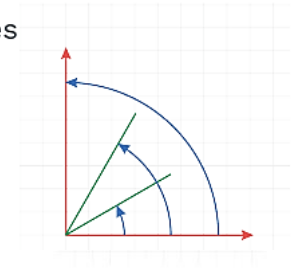
Nodal point (ϕ=0)

Nodal plane — Nodal plane / Angular Node = l

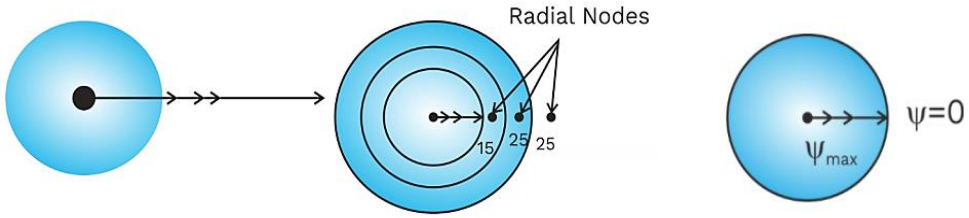
Nodal surface — Nodal surface / Radial Nodes = n – l – 1

Radial Nodes — Radial Nodes →→→→→→→

Angular Nodes



s- Subshell



4. Hydrogen-like atoms

A hydrogen-like atom (or hydrogenic atom) is any atom or ion with a single valence electron. Then, it has a structure similar to that of the hydrogen atom, except that the charge of its nucleus is Ze where Z is the atomic number of the chemical element and e is the electron charge. These atoms are isoelectronic with hydrogen.

Examples : A singly ionized helium atom (He^{+}), double ionized Lithium atom (Li^{++}), triple Beryllium ionized atom (Be^{+++}). All alkali metals such as Rb and Cs, singly ionized alkaline earth metals such as Ca^{+} and Sr^{+}.

Notation:

In the general case, these atoms carry the positive charge e(Z-1),. For example: Lead (^{82}Pb), its hydrogenic is written $^{82}Pb^{81+}$.. Uranium (^{92}U), its hydrogenic is written $^{92}U^{91+}$.

4.1. Extension of Bohr's model to hydrogen-like atoms

The model proposed in 1913 by the Danish physicist Niels Bohr (and later further developed by Arnold Sommerfeld) to describe the hydrogen spectrum was of great importance in the historical development of atomic theory. Even though it is very different from the modern description of an atom, it is difficult to avoid a summary of it in any introductory description of spectroscopy. In the simplest form, we could describe a model of an electron moving around a proton in a circular orbit. Here, however, we shall include in the theory such hydrogenlike atoms as He^{+}, Li^{++}, Be^{+++}…etc. Furthermore, we shall not suppose that the electron moves around the nucleus; rather we assume that the nucleus has a charge Ze (Z is the atomic number) and mass (M), and the electron has a mass (m), and the electron and nucleus move around their common centre of mass.

In Bohr's original model it was assumed that the electron could move round only in certain circular orbits (he and Sommerfeld later included the possibility of elliptic orbits in order to explain fine structure) such that the angular momentum $\|\vec{L}\| = n\hbar$ (Eq.20).This was an empirical assumption made only because it correctly predicted the appearance of the hydrogen spectrum.

Let us suppose that the hydrogen-like atom has a nucleus of charge $(+Ze)$ and mass (M), and the electron has charge $(-e)$ and mass (m), and that the distance between them is (a). The distance of the nucleus from the centre of mass is $ma/(M+m)$ and

the distance of the electron from the centre of mass is $Ma/(M+m)$. We'll suppose that the speed of the electron in its orbit around the centre of mass is (v). It may not be immediately obvious, and the reader should take the trouble to derive it, that the angular momentum of the system $\vec{L} = mva$. Bohr's first assumption, then is that :

$$\|\vec{L}\| = mva = n\hbar \quad \text{.....(Eq.37)}$$

The Coulomb force on the electron is equal to its mass times its centripetal acceleration:

$$\frac{Ze^2}{4\pi\varepsilon_0 a^2 \hbar} = \frac{mv^2}{Ma/(M+m)} \quad \text{.....(Eq.38)}$$

If we eliminate v from these, we obtain an expression for the radius of the nth orbit:

$$a_n = \frac{4\pi\varepsilon_0 n^2 \hbar^2}{Ze^2\mu} \quad \text{.....(Eq.39)}$$

Where: $\mu = \frac{mM}{m+M}$ represents the reduced mass of the electron. It is slightly less than the actual mass of the electron. In the hydrogen atom, in which the nucleus is just a proton, the ratio M/m is about 1836, so that $\mu = 0.99946\, m$. For heavier hydrogen-like atoms it is closer to m. Note that the radius depends on n^2, so that, for example, the radius of the $n = 2$ orbit is four times that of the $n = 1$ orbit. We should now calculate the radius of the first Bohr orbit for hydrogen. It should come to about $0.053\, nm$, so that the diameter of the hydrogen atom in its ground state is a little over one angstrom. Logically, we suppose, the symbol a_1 should be used for the first Bohr orbit, but in practice the usual symbol used is a_0. If we wish to calculate the radius of the first Bohr orbit for some other hydrogen-like atom, such as D, or He^+, or muonic hydrogen, note that for such atoms the only things that are different are the masses or charges or both, so there is no need to repeat the tedious calculations that we have already done for hydrogen.

By eliminating a rather than v from equations 37 and 38, we could get an explicit expression for the speed of the electron in its orbit. Alternatively we can simply calculate v from equation.38? now that we know a. We should, for interest, calculate v, the speed of the electron in the first Bohr orbit, and see how large a fraction it is of the speed of light and hence to what extent our nonrelativistic analysis so far has been. We should also calculate the frequency of the orbital electron - i.e. how many times per second it orbits the nucleus. The explicit expression for v is :

$$v_n = \frac{MZe^2}{4\pi\varepsilon_0 (M+m)\hbar n} \quad \text{.....(Eq.40)}$$

The energy of the atom is the sum of the mutual potential energy between nucleus and electron and the orbital kinetic energies of the two particles. That is:

$$E = -\frac{Ze^2}{4\pi\varepsilon_0 a} + \frac{1}{2}mv^2 + \frac{1}{2}M\left(\frac{mv}{M}\right)^2 \text{……..…….....(Eq.41)}$$

If we make use of equation 38 this becomes :

$$E = -\frac{m(M+m)v^2}{M} + \frac{1}{2}mv^2 + \frac{1}{2}\frac{m^2}{M}v^2 = -\frac{1}{2}m\left(\frac{M+m}{M}\right)v^2 \text{…. (Eq.42)}$$

Then, making use of equation.40, we obtain for the energy :

$$E_n = -\frac{\mu Z^2 e^4}{2(4\pi\varepsilon_0)^2\hbar^2}\left(1-\frac{1}{n^2}\right) \text{…….....(Eq.43)}$$

The expression before the large parentheses is called the Rydberg constant (R_H) for the atom. For hydrogen (^{1}H : Z=1), it has the value 1.09679×107 m^{-1}.

Energy (E_n) is proportional to the square of the atomic number (n^2). An orbital of a given quantum number has a lower energy as the atomic nucleus is charged.

If we put $Z = 1$ and $\mu = m$ the resulting expression is called the Rydberg constant for a hydrogen nucleus of infinite mass; it is the expression one would arrive at if one neglected the motion of the nucleus. It is one of the physical constants whose value is known with greatest precision, its value being : $R_\infty = 1.0973731534 \times 10^7 m^{-1}$

The term value equal to 1.097 373 153 4×107m^{-1}, or the corresponding energy, which is 2.1799×10^{-18}J or 13.61 eV, is called a rydberg. Therfore, Eq.43 becomes:

$$E_n = -13.6\frac{Z^2}{n^2}\ eV \text{……..…..……..….....(Eq.44)}$$

The spectral lines of hydrogen-like atoms are given through Rydberg formula which works for hydrogen. Thus, the wavelength of the photon emitted or absorbed is calculated by the Ritz formula:

$$\frac{1}{\lambda} = \frac{m_e e^4}{8h^3\varepsilon_0{}^2 C}Z^2\left(\frac{1}{{n_f}^2}-\frac{1}{{n_i}^2}\right) = Z^2 R_H\left(\frac{1}{{n_f}^2}-\frac{1}{{n_i}^2}\right) \text{……..……....(Eq.45)}$$

4.2. Extension of Schrodinger's model to hydrogen-like atoms

We consider a hydrogen-like atom composed of a nucleus with charge $+Ze$ and an electron with charge $-e$ interacting through the Coulomb potential:

$$V(r) = -\frac{1}{4\pi\varepsilon_0}\frac{Ze^2}{r} \text{…….……..……..…....(Eq.46)}$$

where r is the distance between electron and nucleus. From eq. 46, we can see that $V(r)$ depends only on r. Therefore, It is considered as a symmetrical radial potential. The relative momentum (electron-nucleus) is denoted ($\vec{p}$) while $\vec{p}$ will present the total momentum associated to the movement of the mass's centre (M) of the atom. The energy of the atom is composed of two parts: the kinetic energy of the mass's centre given by: $p^2/(M+m)$ and the potential energy $V(r)$ given in Eq.46. Therfore,the Hamiltonian operator is given by :

$$\hat{H} = \frac{P^2}{2\mu} - \frac{Ze^2}{4\pi\varepsilon_0 r} \text{.....(Eq.47)}$$

In the mass's centre reference (where $p = 0$) and in the position representation, the physical description of the nucleus-electron system amounts to solving the stationary Schrödinger equation (independent of time) which results in the equation:

$$\left[\frac{-\hbar^2}{2\mu}\Delta - \frac{Ze^2}{4\pi\varepsilon_0 r}\right]\psi(r) = E\,\psi(r) \text{.....(Eq.48)}$$

The energies E correspond to the eigenvalues of the Hamiltonian operator ($\hat{H}$). The interaction potential given by Eq. 46 being radial. So, it will be appropriate to write the wave equation $\psi(r)$ in spherical coordinates terms : $\psi(r) = \psi(r,\theta,\varphi)$.

In this coordinate system, the radial and angular variables of the wave function can be separated and can take the following form:

$\psi_{n,m,l}(r,\theta,\varphi) = R_{n,l}(r)\mathrm{Y}_{l,m}(\theta,\varphi)$ depended on three numbers n, 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).

$\mathrm{Y}_{l,m}(\theta,\varphi)$ is the angular part corresponding to the quantum number of the orbital moment (l) and the magnetic quantum number (m).

CHAPTER. IV. MULTI-ELECTRON ATOMS

Introduction

Unlike the Hydrogen and Hydrogen-like atoms having a single electron, it is impossible to obtain an exact analytical solution of Schrödinger equation for atoms having a nucleus and two or more electrons (system with more than two particles). Approximation methods can be used in the case of atoms with two electrons (Helium) or three electrons (Lithium). However, these methods become insufficient for a great number of electrons.

1. Multi-electron atoms according to Schrödinger's quantum model

A detailed analysis according to the quantum atomic model proposed by Schrödinger requires some considerations like :

- The kinetic energy of electrons and their potential energies in the attractive Coulomb electrostatic field of the nucleus.
- Coulomb electrostatic repulsion between electrons.
- The magnetic interaction of electron spins with their orbital moments (spin-orbit interaction).
- Other effects such as spin-spin interaction between electrons, different attractive corrections, radiative and nuclear corrections due to the finite mass of the nucleus, its finite size, the magnetic dipole momentum…..etc.

In the following, we will neglect, initially the spin-orbit interaction as well as all the small effects mentioned in the last point. Thus, we will only take into consideration the attractive Coulomb interactions between each electron and the nucleus (which we assume to be of infinite mass) in addition to the mutual forces of repulsion between the electrons.

For the quantum analysis multi-electron atoms, we will use the helium atom as a specific example of a multi-electron atom. Figure. 1 shows a schematic representation of a helium atom with two electrons whose coordinates are given by the vectors $\overrightarrow{r_1}$ and $\overrightarrow{r_2}$. The electrons are separated by a distance $r_{12} = |\overrightarrow{r_1} - \overrightarrow{r_2}|$. The origin of the coordinate system is fixed at the nucleus. As with the hydrogen atom, the nuclei for multi-electron atoms are so much heavier than an electron that the nucleus is assumed to be the center

of mass. Fixing the origin of the coordinate system at the nucleus allows us to exclude translational motion of the center of mass from our quantum mechanical treatment.

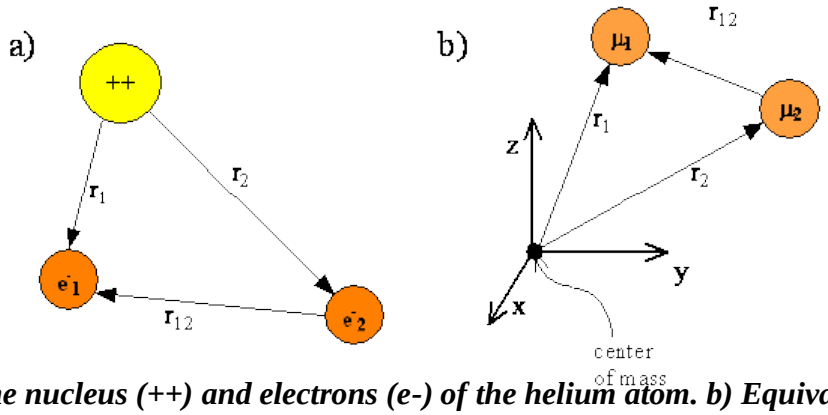


Figure.1. a) The nucleus (++) and electrons (e-) of the helium atom. b) Equivalent reduced particles with the center of mass (approximately located at the nucleus) at the origin of the coordinate system. Note that $\mu_1 \approx m_e$ and $\mu_2 \approx m_e$.

The Hamiltonian operator for the hydrogen atom serves as a reference point for writing the Hamiltonian operator for atoms with more than one electron. Start with the same general form we used for the hydrogen atom Hamiltonian :

$$\hat{H} = \hat{T} + \hat{V} \text{.....(Eq.1)}$$

$\hat{T}$ represents the kinetic energy operator and $\hat{V}$ is the potential energy operator of the particles system.

Include a kinetic energy term for each electron and a potential energy term for the attraction of each negatively charged electron for the positively charged nucleus and a potential energy term for the mutual repulsion of each pair of negatively charged electrons. The He atom Hamiltonian is :

$$\hat{H} = -\frac{\hbar^2}{2m_e}(\nabla_1^2 + \nabla_2^2) + V(r_1) + V(r_2) + V(r_{12}) \text{ .....(Eq.2)}$$

$$V(r_1) = -\frac{2e^2}{4\pi\epsilon_0 r_1}$$

$$V(r_2) = -\frac{2e^2}{4\pi\epsilon_0 r_2}$$

$$V(r_{12}) = +\frac{e^2}{4\pi\epsilon_0 r_{12}}$$

Equation. 2 can be extended to any atom or ion by including terms for the additional electrons and replacing the He nuclear charge +2 with a general charge Z :

$$V(r_1) = -\frac{Ze^2}{4\pi\varepsilon_0 r_1} \text{.....(Eq.3)}$$

Equation .2 then becomes:

$$\hat{H} = -\frac{\hbar^2}{2m_e}\sum_i \nabla_i^2 + \sum_i V(r_i) + \sum_{i\neq j} V(r_{ij}) \text{.....(Eq.4)}$$

Each electron has its own kinetic energy term in Equations.2 and 4. For an atom like sodium there would be $\nabla_1^2, \nabla_2^2, \nabla_{11}^2$. The other big difference between single electron systems and multi-electron systems is the presence of the $V(r_{ij})$ terms which contain $1/r_{ij}$, where r_{ij} is the distance between electrons i and j. These terms account for the electron-electron repulsion that we expect between like-charged particles.

Given what we have learned from the previous quantum mechanical systems we have studied, we predict that exact solutions to the multi-electron Schrödinger equation in Equation.4, would consist of a family of multi-electron wave functions, each with an associated energy eigenvalue. These wave functions and energies would describe the ground and excited states of the multi-electron atom, just as the hydrogen wave functions and their associated energies describe the ground and excited states of the hydrogen atom. We would predict quantum numbers to be involved, as well. The fact that electrons interact through their Coulomb repulsion means that an exact wave function for a multi-electron system would be a single function that depends simultaneously upon the coordinates of all the electrons; i.e., a multi-electron wave function, $\psi\,(r_1, r_2, \ldots . r_i)$. The modulus squared of such a wave function would describe the probability of finding the electrons (though not specific ones) at a designated location in the atom. Alternatively, ne|ψ|2 would describe the total amount of electron density that would be present at a particular spot in the multi-electron atom. All of the electrons are described simultaneously by a multi-electron wave function, so the total amount of electron density represented by the wave function equals the number of electrons in the atom.

$$\psi(r_1, r_2, \cdots, r_i) \approx \varphi_1(r_1)\varphi_2(r_2)\cdots\varphi_i(r_i) \text{.....(Eq.5)}$$

By writing the multi-electron wave function as a product of single-electron functions, we conceptually transform a multi-electron atom into a collection of individual electrons located in individual orbitals whose spatial characteristics and energies can be, separately identified. For atoms these single-electron wave functions are called atomic orbitals. For molecules, as we will see in the next chapter, they are called molecular

orbitals. While a great deal can be learned from such an analysis, it is important to keep in mind that such a discrete, compartmentalized picture of the electrons is an approximation, albeit a powerful one.

1.1. Solution of the Schrödinger Equation for multi-electron atoms

In this section we will see a useful method for approaching a problem that cannot be solved analytically and in the process we will learn why a product wave function is a logical choice for approximating a multi-electron wave function.

The helium atom Hamiltonian is re-written below with the kinetic and potential energy terms for each electron followed by the potential energy term for the electron-electron interaction. The last term, the electron-electron interaction, is the one that makes the Schrödinger equation impossible to solve.

$$\hat{H} = -\frac{\hbar^2}{2m}\nabla_1^2 - \frac{2e^2}{4\pi\epsilon_0 r_1} - \frac{\hbar^2}{2m}\nabla_2^2 - \frac{2e^2}{4\pi\epsilon_0 r_2} + \frac{e^2}{4\pi\epsilon_0 r_1 2} \quad \text{(Eq.6)}$$

To solve the Schrödinger Equation using this Hamiltonian, we need to make an assumption that allows us to find an approximate solution.

1.1.1. Independent-electron approximation

Analytically solving the electron Schrödinger equation is very difficult and approximations must be used. The simplest is the independent-electron approximation. While this approximation might seem very drastic, it is worth trying since it also presents a straightforward path to a solution. A general strategy when solving difficult problems is to make an assumption and see how the results turn out. In this case we can compare the results we obtain using the assumption to what is known experimentally about the quantum states of helium, like the ionization energies. The latter result would probably indicate that we have hit a dead end with this method, while the former might indicate a method worth refining.

Neglecting the electron repulsion term simplifies the helium atom Hamiltonian to a sum of two hydrogen-like Hamiltonians that can be solved exactly.

$$\hat{H}(r_1, r_2) = \hat{H}(r_1) + \hat{H}(r_2) \quad \text{(Eq.7)}$$

The variables (the positions of the electrons, $\vec{r_1}$ and $\vec{r_2}$.) in the Schrödinger equation separate, and we end up with two independent Schrödinger equations that are exactly

the same as that for the hydrogen atom, except that the nuclear charge is +2e rather than +1e.

$$\hat{H}(r_1)\varphi(r_1) = E_1\varphi(r_1)$$
$$\hat{H}(r_2)\varphi(r_2) = E_2\varphi(r_2) \quad \text{…..…..…..……(Eq.8)}$$

Using our previous experiences with separation of variables, we realize that the wave function can be approximated as a product of two single-electron hydrogen-atom wave functions with a nuclear charge Z=+2e :

$$\psi(r_1, r_2) \approx \varphi(r_1)\varphi(r_2) \quad \text{…..…..…..……(Eq.9)}$$

We note that, there is other approximation methods used to solve Schrodinger equation for multi-electron atoms such us the variational method, the Self-Consistent Field Approximation (Hartree-Fock Method) and perturbation theory.

2. Electronic structure of multi-electron atoms

To discuss the electronic structure of multi-electron atoms, we need a system of notation for multi-electron wave functions in ground or lowest-energy states.

2.1. Electron configuration

The electron configuration of an atom is the representation of the arrangement of electrons distributed among the orbital shells and subshells. Commonly, the electron configuration is used to describe the orbitals of an atom in its ground state, but it can also be used to represent an atom that has ionized into a cation or anion by compensating with the loss of or gain of electrons in their subsequent orbitals. Many of the physical and chemical properties of elements can be correlated to their unique electron configurations. The valence electrons, electrons in the outermost shell, are the determining factor for the unique chemistry of the element.

Before assigning the electrons of an atom into orbitals, one must become familiar with the basic concepts of electron configurations .

3. Rules for Assigning Electron Orbitals

There are certain rules to follow when assigning electrons to different orbitals.

3.1. Pauli Exclusion Principle

By analyzing spectroscopic data of multi-atoms with several electrons, Wolfgang Pauli states, in 1924, that in an atom or molecule, no two electrons can have the same four electronic quantum numbers. As an

orbital can contain a maximum of only two electrons, the two electrons must have opposing spins. This means if one electron is assigned as a spin up (+1/2) electron, the other electron must be spin-down (-1/2) electron. Electrons in the same orbital have the same first three quantum numbers, e.g., $n = 1\ , l = 0, m_l = 0$ for the 1s subshell. Only two electrons can have these numbers, so that their spin moments must be either $m_s = -1/2$ or $m_s = +1/2$. If the 1s orbital contains only one electron, we have one ms value and the electron configuration is written as 1s1 (corresponding to hydrogen). If it is fully occupied, we have two ms values, and the electron configuration is $1s^2$ (corresponding to helium). Visually these two cases can be represented as

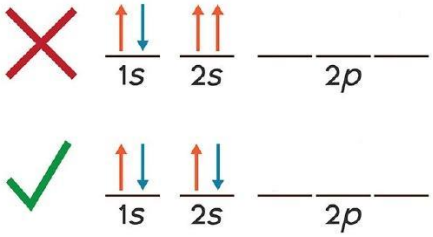
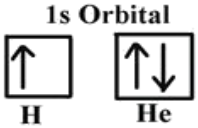


Figure.2. Electrons configuration through Pauli Exclusion Principle.

As we can see, the 1s and 2s subshells for beryllium atoms can hold only two electrons and when filled, the electrons must have opposite spins. Otherwise they will have the same four quantum numbers, in violation of the Pauli Exclusion Principle.

Example : Hydrogen and Helium

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



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

We note that:

- In the independent electron model, the state of each electron is specified by a combination of the quantum numbers $(n, l, m_l\ , m_s\ )$.

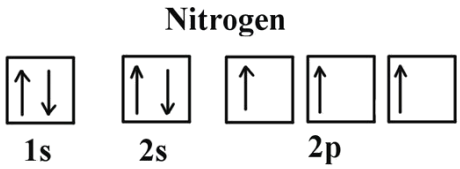
- Electrons with the same n quantum number, occupy the same electron shell. The different electronic shells are designated by capital letters depending on the value of the quantum number n.
- Value of n: 1 2 3 4
- Shell letter: K L M N

3.2. Hund's Rule

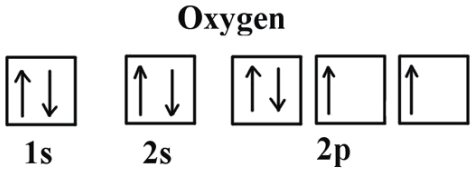
When assigning electrons in orbitals, each electron will first fill all the orbitals with similar energy (also referred to as degenerate) before pairing with another electron in a half-filled orbital. Atoms at ground states tend to have as many unpaired electrons as possible. When visualizing this processes,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

Example 2: Oxygen and Nitrogen

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



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



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

3.3. Klechkowski's rule (Occupation of orbitals)

Electrons fill orbitals in a way to minimize the energy of the atom. Therefore, the electrons in an atom fill the principal energy levels in order of increasing energy (the electrons are getting farther from the nucleus). The relative energy of the orbitals is shown in Figure.3.

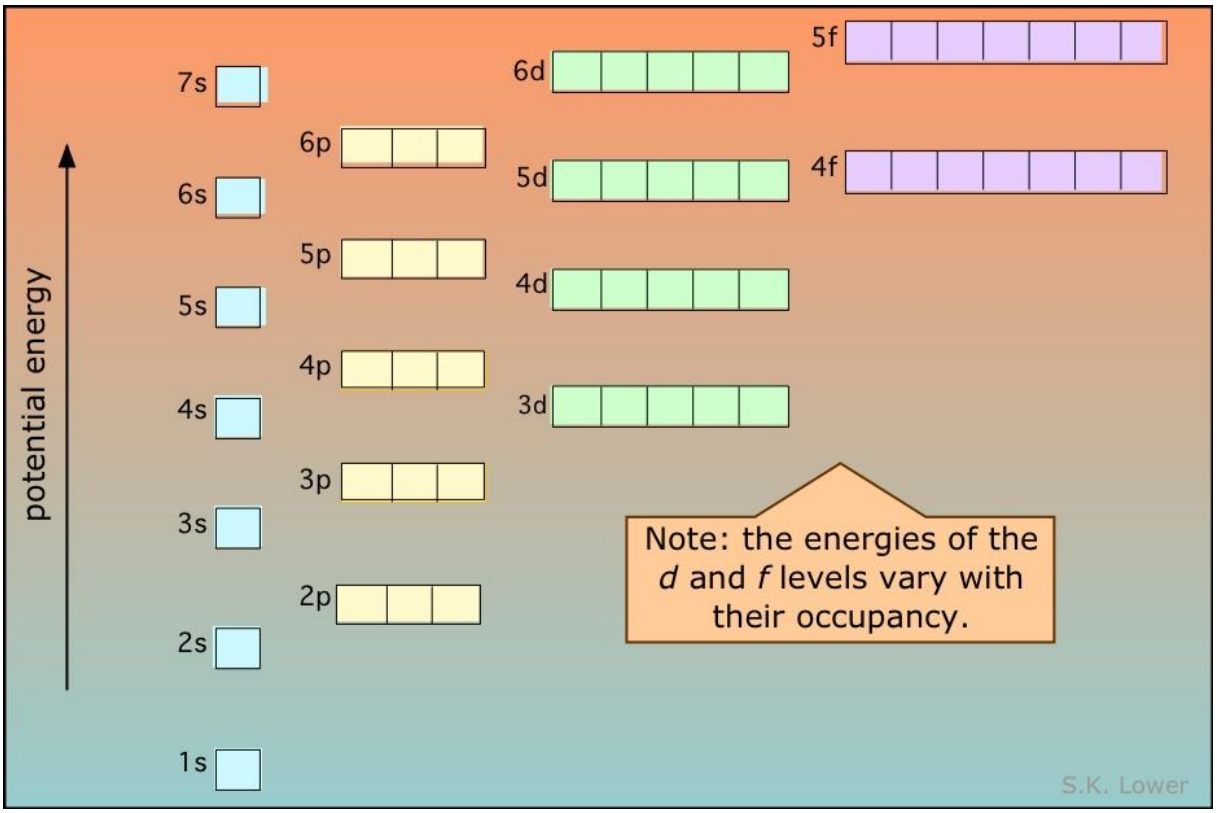


Figure.3. The relative potential energy of atomic orbitals.

The order of levels filled is then:

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

The general order in which orbitals are filled is depicted in Figure.4. Subshells corresponding to each value of n are written from left to right on successive horizontal lines. The order in which the orbitals are filled is indicated by the diagonal lines running from the upper right to the lower left. Accordingly, the 4s orbital is filled prior to the 3d orbital because of shielding and penetration effects. Consequently, the electron configuration of potassium, which begins the fourth period, is [Ar]4s1, and the configuration of calcium is [Ar]$4s^2$. Five 3d orbitals are filled by the next 10 elements, the transition metals, followed by three 4p orbitals. Notice that the last member of this row is the noble gas krypton (Z = 36), [Ar]$4s^2 3d^{10} 4p^6$ = [Kr], which has filled 4s, 3d,

and 4p orbitals. If you write the subshells for each value of the principal quantum number on successive lines, the observed order in which they are filled is indicated by a series of diagonal lines running from the upper right to the lower left (Figure.4).

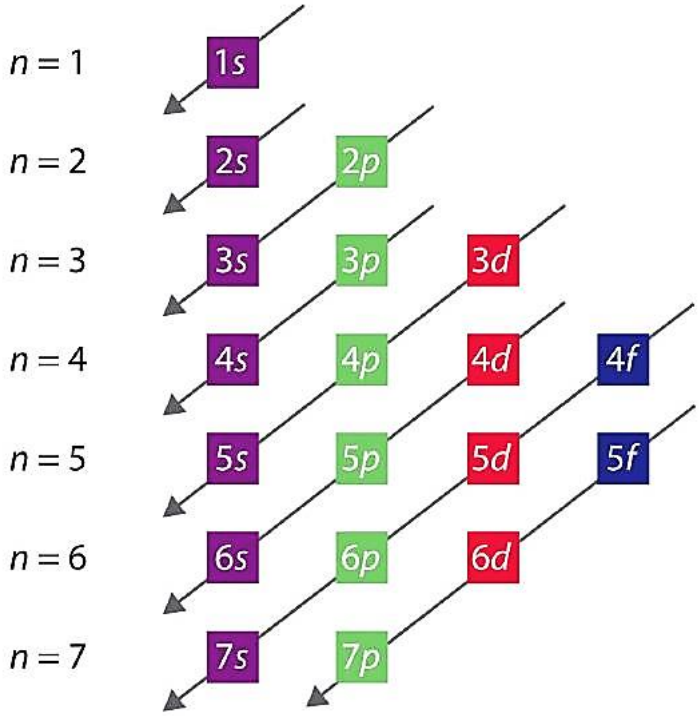


Figure.4. Predicting the order in which orbitals are filled in multi-electron atoms according to Klechkowski rule.

3.4. Aufbau process

Aufbau comes from the German word "aufbauen" meaning "to build." The Aufbau principle states that electrons fill the lowest energy levels first before moving to higher energy levels. This principle helps to explain the observed electronic configurations of atoms and the periodic trends in the properties of elements. Indeed, electrons in an atom follow the rules of quantum mechanics, which dictate that they must occupy the lowest available energy levels before filling higher ones. This principle is known as the Aufbau principle. There are a few reasons why electrons tend to occupy the lowest energy levels first:

- Stability: Electrons are negatively charged particles that are attracted to the positively charged nucleus of an atom. By occupying the lowest energy levels closest to the nucleus, electrons are in a more stable configuration because they are closer to the positive charge of the nucleus.
- Energy Minimization: Electrons exist in specific energy levels around the nucleus of an atom. Lower energy levels are closer to the nucleus and are associated with

lower energy states. Electrons naturally seek to occupy these lower energy levels to minimize their energy and achieve a more stable configuration.

- Quantum Mechanical Rules: Quantum mechanics governs the behavior of electrons in an atom. The Pauli exclusion principle states that no two electrons in an atom can have the same set of quantum numbers. Electrons must therefore fill the available energy levels in a specific order, starting with the lowest energy levels, before moving to higher energy levels.

Overall, the arrangement of electrons in an atom is governed by these fundamental principles of quantum mechanics, which lead to the filling of the lowest energy levels first to achieve a more stable and energetically favorable configuration.

Example :

Following the pattern across a period from B (Z=5) to Ne (Z=10), the number of electrons increases and the subshells are filled. This example focuses on the p subshell, which fills from boron to neon.

B (Z=5) configuration : $1s^2\ 2s^2\ 2p^1$

C (Z=6) configuration :$1s^2\ 2s^2\ 2p^2$

N (Z=7) configuration :$1s^2\ 2s^2\ 2p^3$

O (Z=8) configuration :$1s^2\ 2s^2\ 2p^4$

F (Z=9) configuration :$1s^2\ 2s^2\ 2p^5$

Ne (Z=10) configuration :$1s^2\ 2s^2\ 2p^6$

4. Periodic table

The periodic table is a tabular arrangement of the chemical elements, organized by their atomic number, electron configuration, and recurring chemical properties. The elements are arranged in order of increasing atomic number, which is the number of protons in the nucleus of an atom. Each element is represented by its chemical symbol, typically one or two letters derived from its name. The rows of the periodic table are called periods, and the columns are called groups or families. Elements within the same group tend to have similar chemical properties due to their similar electron configurations. The periodic table allows scientists to predict the properties of elements and how they may react with other elements based on their position in the table.

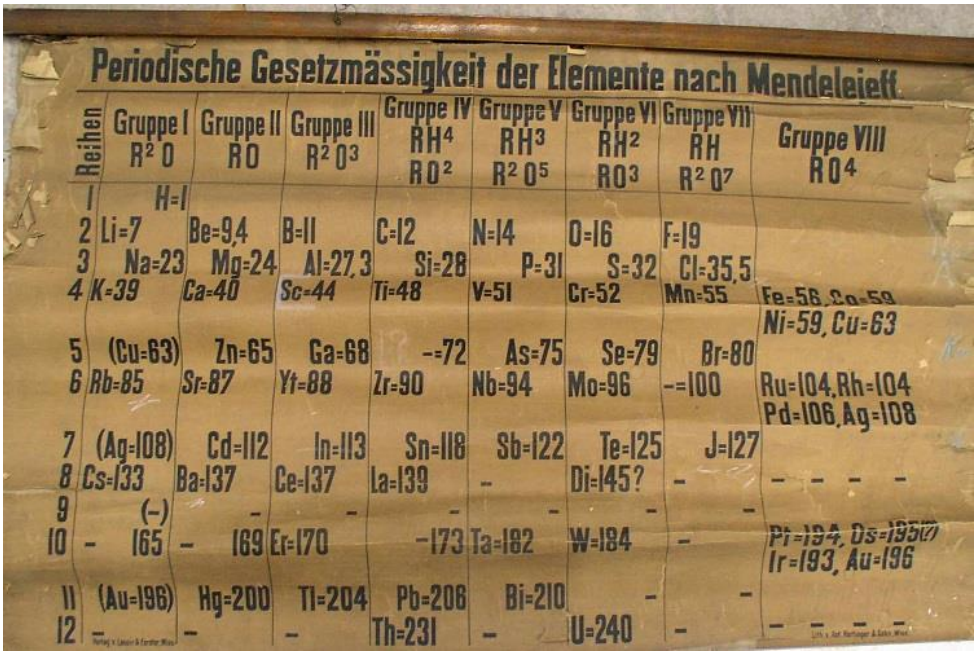
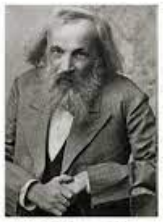


Figure.5. Periodic table chart discovered at the University of St Andrews is thought to be the oldest in the world, dating from 1885.

4.1. Modern Periodic Table


Dmitri Mendeleev
1834 – 1907

Lothar Meyer
1830 - 1895

The modern periodic table is based on the work of Dmitri Mendeleev and Julius Lothar Meyer, who independently developed similar tables in the late 19th century (1869). Mendeleev is often credited with the creation of the first widely recognized periodic table, which he organized according to atomic weight and predicted the properties of missing elements. Over time, the table has evolved as new elements have been discovered and our understanding of atomic structure has advanced.

The present form of a periodic table (Figure.6) that is widely used across the globe is the long form of the periodic table. In this form of a periodic table, the horizontal rows are called periods and the vertical columns are known as the groups.

Groups consist of elements that have similar outer shell electronic configuration in their atoms. Previously the groups were named as IA,…VIIIA, VIII, IB…VIIB and 0. But now they are named as 1, 2, 3…18. In the modern periodic table, periods are the seven horizontal rows. Principle quantum number ‘n’ decides the period of the element. Principle quantum number (n) is one of the four quantum numbers $(n, l, m_l, and\ m_s)$. It

tells us about the principle electron shell. For example, if $n = 3$, then it indicates the principle shell as 3.

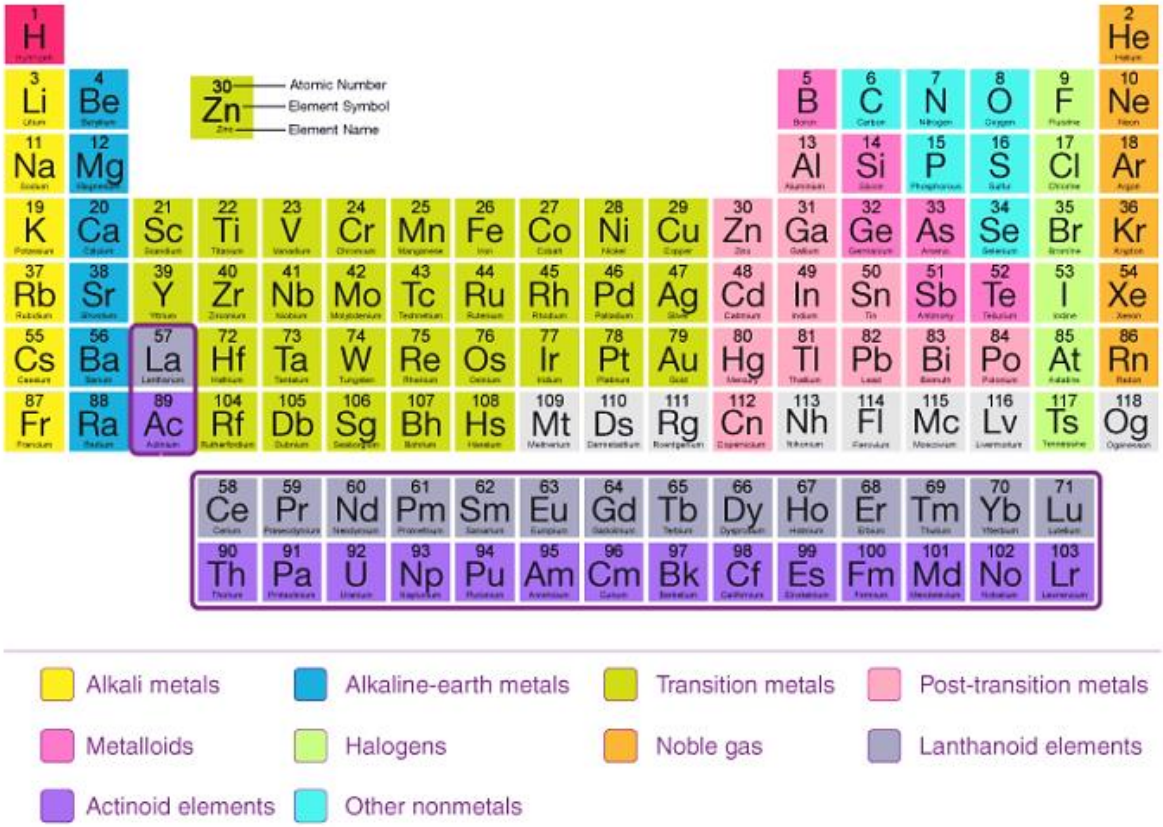


Figure.6. Modern periodic table with detailed periodic classification of elements.

4.2. Classification of the elements in the periodic table

Classification of the elements in the periodic table can be done in four ways on the basis of their electronic configurations:

4.2.1. Noble gas elements

Elements of group 18 of the modern periodic table are considered a noble gas. The electronic configuration of the first element (helium) of this group is $1s^2$. Rest all the elements (neon, argon, krypton, xenon, and radon) have their outer shell electronic configuration is ns^2np^6. As the octet of these elements is complete, hence they are highly stable elements.

4.2.2. Representative elements

S-lock and P-block elements come under the category of representative elements. Elements in groups 1 and 2 are known as the s – block elements (elements with $1s^2$ and $2s^2$ outermost configuration). Group 13-17 are known as the p-block elements (outermost configuration varies from ns2np1 to ns^2np^5).

4.2.3. Transition elements

Elements which belong to group 3 to 12 and have their outer shell electronic configuration as $(n-1)d^{1-10}ns^{1-2}$ are referred to as transition elements. These elements are also known as the d-block elements.

4.2.4. Inner transition elements

Lanthanides and actinides series which fall at the bottom of the periodic table comes under the category of inner transition elements. In these elements the 4f and 5f orbitals are partially filled, rendering them special properties.

4.3. Trends or Periodicity

The periodic table is organized according to trends in element properties:

Moving Left to Right Across the Row

- Atomic Radius Decreases
- Ionization Energy Increases
- Electron Affinity Generally Increases (except Noble Gases)
- Electronegativity Increases

Moving Top to Bottom Down a Column

- Atomic Radius Increases
- Ionization Energy Decreases
- Electron Affinity Usually Decreases Moving Down a Group
- Electronegativity Decreases

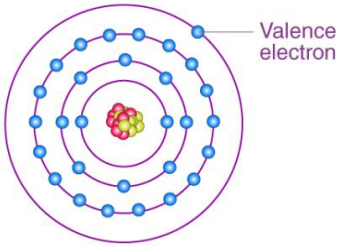
5. Valence electrons

Valence electrons are the electrons located in the outermost shell, or energy level, of an atom. These electrons are involved in the formation of chemical bonds between atoms and are responsible for the chemical properties of the element. Understanding the concept of valence electrons is important in chemistry as it helps predict how atoms will combine with each other to form molecules and compounds. The number of valence electrons an atom has can determine its reactivity and how it will bond with other atoms.

5.1. Number of valence electrons

The valence electrons are part of the chemical reactions because they contain more energy compared to the electrons present in inner orbits. Meanwhile, the number of valence electrons present also helps us determine a specific element’s chemical

properties, such as its valence or valency, the formation of bonds with other elements. It also gives us an idea of how readily the atoms can form bonds, the number of unpaired electrons and how many atoms can take part.



5.2. Characteristics of valence Electrons

Electrons are involved in the chemical bonding and reactions of the atom. It is said to occupy orbitals in an atom. The number of valence electrons of an atom can be obtained from the periodic table because it is equal to the group number of the atom. Atoms are most stable if they have a filled valence shell of electrons. Atoms transfer or share electrons in such a way that they can attain a filled shell of electrons.

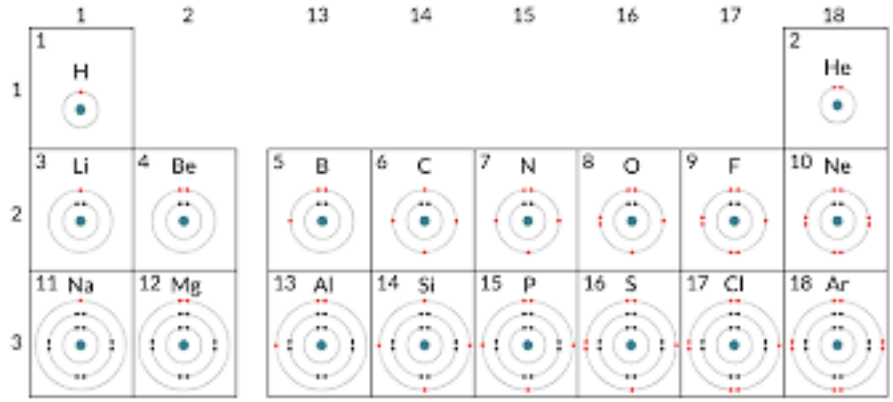
Some key characteristics of a valence electron are :

- For the main group elements, the valence electron exists only in the outermost electron shell.
- A valence electron can exist in the inner shell of a transition metal.
- An atom consisting of a closed shell of valence electrons will usually be chemically inert.
- A valence electron can either absorb or release energy in the form of a photon.
- Valence electrons also determine the electrical conductivity of an element. Depending on the nature of elements can be metal, non-metal, or metalloid.

5.3. Determination of valence electrons

5.3.1. Using periodic table

One of the easiest ways to find valence electrons is by checking out the elements' place in the periodic table. The valence electrons of an element can be found by closely examining the vertical column in which the elements are grouped. By looking at the group number that is given we can identify the number of valence electrons that an element which is listed under that specific column has. The number of valence electrons increases going left to right across a period. But, with the exception of He, the number of valence electrons remains the same going down a group.



For example, H, Li and Na are in group 1 and all have one valence electron. Both N and P in group 15 and have five valence electrons. This is why elements in the same group have similar chemical properties—they have the same number of valence electrons. This pattern allows us to quickly identify the number of valence electrons for main group elements on the periodic table, even if we don't have Bohr models to reference. The diagram below shows the number of valence electrons (VE) for the main group elements.

5.3.2. Using electronic configuration

Another way to find or determine valence electrons is by knowing the electronic configuration. However, if we take the transition metals (groups 3-12), finding the valence electron is quite complicated. These elements' atomic structure is rigid and the d subshell is incomplete and sits lower than the outer shell. Here is a list of the number of valence electrons present in the different groups.

Periodic Table Group	Valence Electrons
Alkali metals – Group 1 (I)	1
Alkaline earth metals – Group 2 (II)	2
Boron group – Group 13 (III)	3
Carbon group – Group 14 (IV)	4
Nitrogen group – Group 15 (V)	5
Oxygen group – Group 16 (VI)	6
Halogens – Group 17 (VII)	7
Noble gases – Group 18 (VIII or 0)	8

Table.1. determination of valence electrons number by using electronic configuration of elements present in periodic table.

CHAPTER. V. X-RAYS

Introduction

In the previous chapter, we were interested in the energy levels of valence electrons. Transitions between these levels give photons having energies vary between~10 eV up to 10^{-6} eV. These energies correspond to wavelengths of the order of 10^{-7} m to 1 m (ultraviolet, visible, infrared, microwave and radio waves). When the energy of the photon is much greater than 10 eV (~KeV) then the interaction can disrupt the core electrons. The transition of a core electron from one layer to another will involve the emission or absorption of a high energy, short wavelength photon; X-rays. X-rays are commonly used in the medical field for diagnostic imaging to visualize the internal structures of the body, such as bones, organs, and tissues. They are also used in other fields such as security screening, industrial testing, and material analysis.

1. X-rays

An X-ray is a form of electromagnetic radiation of extremely short wavelength and high frequency. It can pass through solid objects and produce images of the internal structures of those objects on a photographic film or a digital detector. X-ray wavelengths are approximately between 10^{-3} nm and 10 nm corresponding to frequencies from 31016 Hz to 31020 Hz and energies from 100 eV, to about 100 keV.

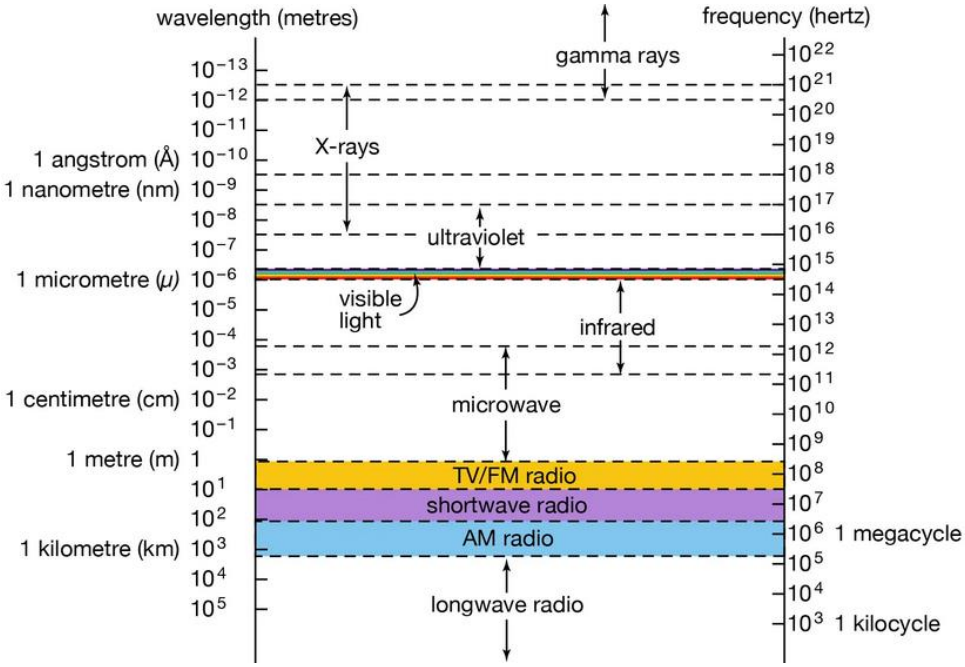


Figure.1. X-ray wavelengths and frequencies ranges in electromagnetic spectrum.

X-rays are ionizing radiations. When interacting with matter, they are energetic enough to cause neutral atoms to eject electrons. Through this ionization process the energy of the X-rays is deposited in the matter. When passing through living tissue, X-rays can cause harmful biochemical changes in genes, chromosomes, and other cell components. The biological effects of ionizing radiation, which are complex and highly dependent on the length and intensity of exposure, are still under active study (see radiation injury). X-ray radiation therapies take advantage of these effects to combat the growth of malignant tumours.

1.1. History of X-rays

X-ray were discovered, in 1895 by the German physicist Wilhelm Röntgen, while investigating the effects of electron beams (then called cathode rays) in electrical discharges through low-pressure gases. Röntgen uncovered a startling effect—namely, that a screen coated with a fluorescent material placed outside a discharge tube would glow even when it was shielded from the direct visible and ultraviolet light of the gaseous discharge. He deduced that an invisible radiation from the tube passed through the air and caused the screen to fluoresce. Since he could not identify the type of this radiation, he named it X (The usual name for the unknown in mathematics, X). Röntgen was able to show that the radiation responsible for the fluorescence originated from the point where the electron beam struck the glass wall of the discharge tube. Opaque objects placed between the tube and the screen proved to be transparent to the new form of radiation; Röntgen dramatically demonstrated this by producing a photographic image of the bones of the human hand. His discovery of so-called Röntgen rays was met with worldwide scientific and popular excitement, and, along with the discoveries of radioactivity (1896) and the electron (1897), it ushered in the study of the atomic world and the era of modern physics.

1.2. Production of X-rays

X ray is produced inside the x ray tube when high energy electrons from cathode filament interact with the atoms of the anode. In fact only 1% of electron energy is converted to x ray while the remaining energy goes in form of heat.

1.2.1 Equipment

a). Cathode

Filament

• Made of thin (0.2 mm) tungsten wire because tungsten:

- has a high atomic number (A 184, Z 74)
- is a good thermionic emitter (good at emitting electrons)
- can be manufactured into a thin wire
- has a very high melting temperature (3422°C)

• The size of the filament relates to the size of the focal spot. Some cathodes have two filaments for broad and fine focusing

Focusing cup

• Made of molybdenum as:

- high melting point
- poor thermionic emitter so electrons aren't released to interfere with electron beam from filament

• Negatively charged to focus the electrons towards the anode and stop spatial spreading

b). Anode

• Target made of tungsten for same reasons as for filament

• Rhenium added to tungsten to prevent cracking of anode at high temperatures and usage

• Set into an anode disk of molybdenum with stem

• Positively charged to attract electrons

• Set at angle to direct x-ray photon beam down towards patient. Usual angle is 5º-15º .

Definitions

• **Target, focus, focal point, focal spot**: where electrons hit the anode.

• Actual focal spot: physical area of the focal track that is impacted

• Focal track: portion of the anode the electrons bombard. On a rotating anode this is a circular path

• Effective focal spot: the area of the focal spot that is projected out of a tub

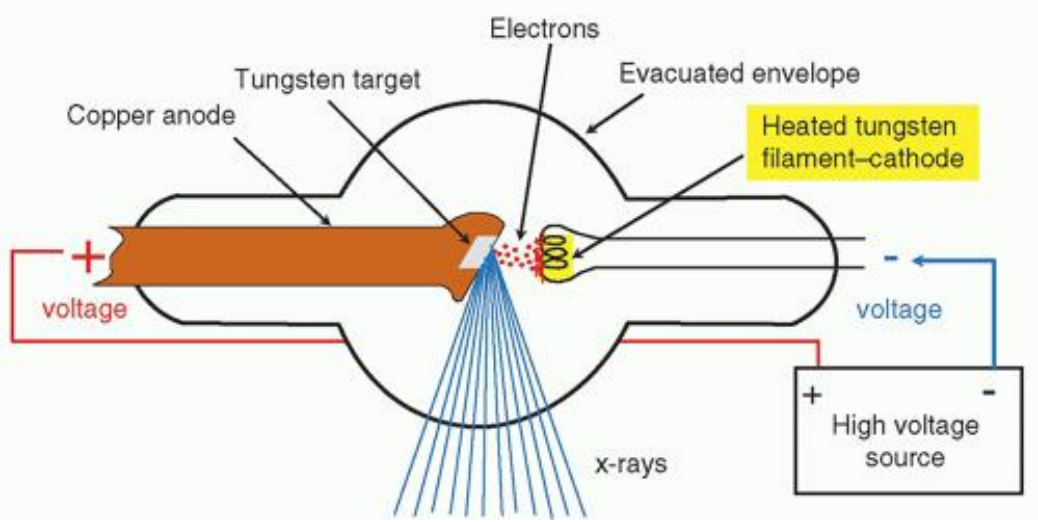


Figure. 2. X-ray production experiment setup.

1.2.2 Experimental process

There are two electrical circuits operating during an x ray exposure. The first of these is the low voltage circuit (step down transformer) which controls the heating of the filament. When the exposure button is depressed, this low voltage circuit operates for ½ second or less to heat up the filament. There are no x ray produced during this time. As we continue to depress the exposure button, the high voltage circuit (step up transformer) is activated. This circuit controls the flow of electrons across the x ray tube; the negative electrons are pulled across the x ray tube to the positive target. X rays are produced until the exposure time ends. The length of the time that the high voltage circuit is operating represents the exposure time. X ray results from conversion of kinetic energy of cathode electrons into X-ray photons energy.

The power P of the generator has the expression:

$$P = U.i \quad \text{.....(Eq.1)}$$

U: is the value of the accelerating voltage expressed in kV

i: is the intensity of the electronic current expressed in mA.

Only a fraction of 1% of this power consumed at the anode is useful for the production of X-rays.

If ϕ represents the flux radiated by the tube (energy transported per second), the energy efficiency$(R)$of the tube is equal to :

$$R = \frac{\phi}{P} = \frac{k.i.U^2Z}{U.i} = k.U.Z \quad \text{.....(Eq.2)}$$

k is the coefficient of proportionality equal to 10^{-10}

U :is the accelerating voltage expressed in volts.

Z :is the atomic number of the target.

1.3. Mechanisms of X-rays production

The study of an emitted X-ray spectrum (Figure.3) shows that it is formed from the superposition of a continuous spectrum and a characteristic spectrum composed of spectral lines.

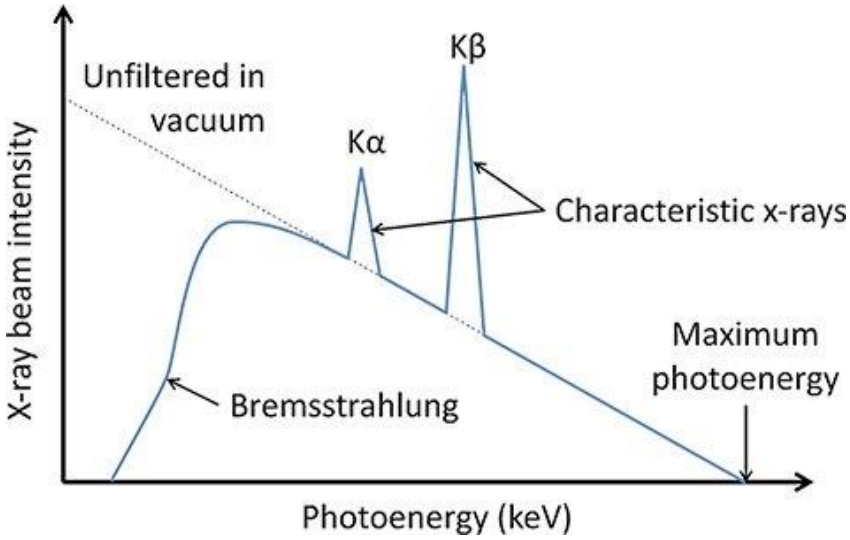


Figure. 3. X-rays emission spectrum.

These two components are due to:

i. The interaction of accelerated electrons with the nuclei of the target (continuous spectrum or Bremsstrahlung spectrum).

ii. The ionization of the deep layers of the target's atoms (line spectrum).

1.3.1. Continuous X-rays (Bremsstrahlung)

Continuous X-rays are produced when high-energy electrons interact with the target material and decelerate, leading to the emission of X-rays over a continuous range of energies. Indeed, the first type of interaction consists of the deceleration of the electron by the positively charged nuclei of the target atoms. When a particle is decelerated, it emits radiation whose energy is equal to the loss in kinetic energy of the particle:

$$h\nu = E_{c,i} - E_{c,f} \text{…..……..……..……...….(Eq.3)}$$

The radiation produced by this mechanism are called “Bremsstrahlung”, German term for “deceleration” of the radiation. An electron as part of the incident electron flow can

produce several Bremsstrahlung type photons before losing all its kinetic energy. When the electron loses all its energy in a single interaction then it will produce a photon of maximum energy or minimum wavelength.

$$h\nu_{max} = \frac{hc}{\lambda_{min}} \text{.....(Eq.4)}$$

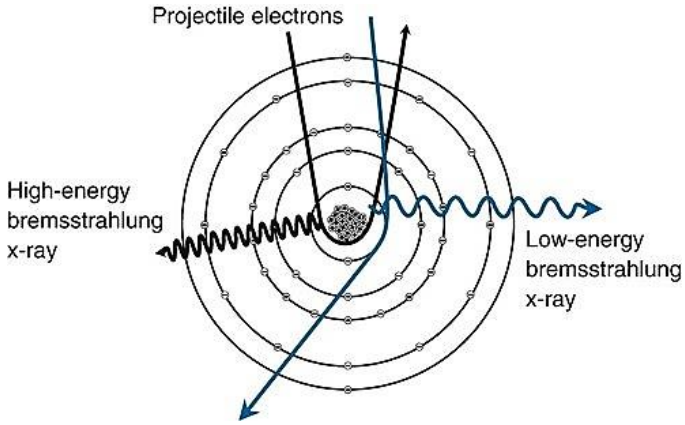


Figure.4. Bremsstrahlung radiation emission mechanisms in the atom.

We must note that :

- The theoretical energy spectrum of the Bremsstrahlung radiation is a continuous spectrum defined by the function $\frac{d\phi}{dE}$(Figure.5).

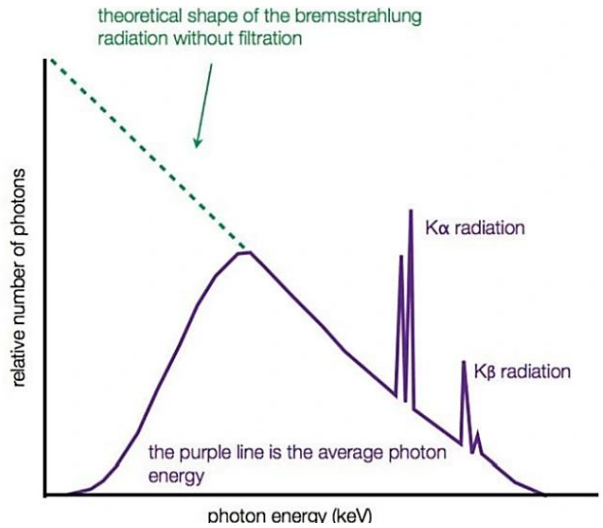


Figure.5. Theoretical spectrum of Bremsstrahlung radiation.

1.3.2. Characteristic X-rays

Characteristic X-rays are emitted when an electron from the inner shell (K) of an atom is ejected by the incoming high-energy electron and an electron from a higher energy level (L) fills the vacancy During this transition, the atom quickly and spontaneously emits an X-ray photon called “X-fluorescence” (Figure.6).

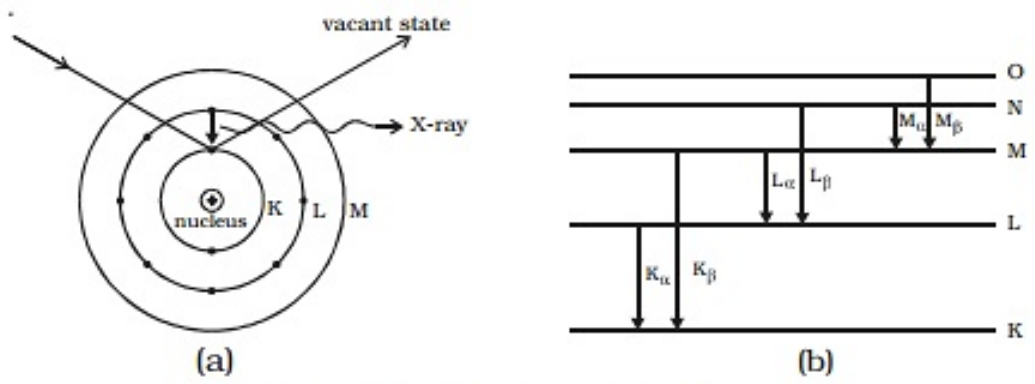


Figure.6. X-ray fluorescence mechanisms emission.

The energy of the characteristic X-rays is specific to the element from which they are emitted, allowing for elemental identification in X-ray spectroscopy. Characteristic X-rays are sharp peaks in the X-ray spectrum, corresponding to the energy difference between the electron energy levels involved in the transition.

The letters K, L, M… correspond to the name of the shell from which the electron was expelled. Greek letters $\alpha, \beta, \gamma \ldots$ indicate whether the transition electron arrives from an immediately higher sub-shell (α) or successively distant (,, ..).

- If the displaced electron was in the K shell, the produced series of X-ray spectral lines are noted $K_\alpha, K_\beta, K_\gamma, \ldots \ldots$
- If an electron from the L layer is displaced, another spectral series called the L series is produced noted noted $L_\alpha, L_\beta, L_\gamma, \ldots \ldots$

<u>We note that:</u>

• Only electrons in the K shell with a high atomic number are capable to produce an energetic photons participated in the X-ray spectrum.

• The energy of a characteristic X-ray increases with the number atomic (Z) of the atom.

• Fluorescence radiation accounts for more than 90% of the total radiation. These Radiation is lower and therefore quickly absorbed by matter. Consequently, electron-matter interactions produce much more heat than X-rays.

• As the accelerating potential increases, as the number of X-rays lines complete each other (Figure.7).

• The amplitude of characteristic peaks depends on the number of electrons that interacted with the electrons of the target atom and the occurred transitions.

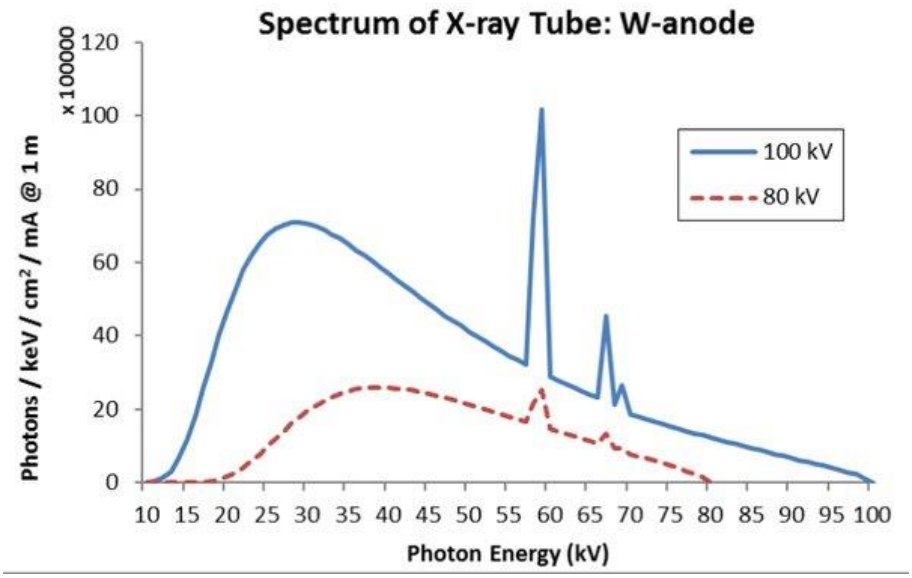


Figure.7. Relationship between the accelerating potential and the number of X-rays lines.

1.4. Moseley's law

Soon after Rutherford's scattering theory had been confirmed by experiment (about 1913), the one-to-one association of an atomic number Z with each element was solidified by the work of Henry Moseley (1887- 1915). He used Bohr's model of atomic structure to determine the energy emitted when low-level electrons change orbitals. This energy has a strong dependence on an atomic number so that by measuring the energy of the x-rays characteristic of an element, its atomic number Z can be unambiguously determined. In today's lab, you will measure the x-ray spectra of a number of elements and also identify several unknown elements by looking at their characteristic x-ray spectra. Moseley's law is an empirical law concerning the characteristic x-rays that are emitted by atoms. The law was discovered and published by the English physicist Henry Moseley in 1913. The law states that the frequency of the x-ray (ν) is related to the atomic number (Z) :

$$\sqrt{\nu} = Z.\sigma \ldots\ldots\ldots\

potential due to a charge. This comes down to the fact that the positive charge of the Ze nucleus is masked by the core electrons forming a cloud of negative charges. The ionization energy of these atoms is thus of the same order of magnitude as the ionization energy of the Hydrogen atom (a few eV). On the other hand, the electrons of the interior shells (n = 1, 2, 3,…) are subjected to a potential field dominated by the charge of the nucleus. The latter is partially masked by the other electrons (screening effect discussed in chapter 4). Considering that the core electrons move in an effective potential due to an effective charge, where:

$$Z^* = (Z - \sigma_n) \quad \text{…..……..……..……...….(Eq.6)}$$

σ is called constant or screening factor ($\sigma_n \ll Z$).

1.4.2. Law's formulation

When one of the two electrons in the K shell($n = 1$) is ejected, the remaining electron reduces the effective charge of the nucleus to (Z −1). The other electrons in higher levels also contribute to the screening effect. The total screening factor of the K shell is estimated at $\sigma_K \cong 2$. Screen factor values are often obtained through experiment because it is difficult to calculate them.

In general, the wavelengths of transitions from one shell (n_j) to a lower shell (n_i) are given by the following formula:

$$\frac{1}{\lambda} = R_H \left[\frac{(Z-\sigma_i)^2}{{n_i}^2} - \frac{(Z-\sigma_j)^2}{{n_j}^2}\right] \text{…...……..……..……..….(Eq.7)}$$

with $n_i < n_j$

where is the Rydberg constant.R_H : $R_H = 1.097 \cdot 10^7\ m^{-1}$

Thus, the wavelengths of the K series are given by:

$$\frac{1}{\lambda_K} = R_H \left[\frac{(Z-\sigma_K)^2}{1^2} - \frac{(Z-\sigma_j)^2}{{n_j}^2}\right] \text{…...……..……...……..….(Eq.8)}$$

giving the X-ray line K_α for $j = 2$, for and K_β for $j = 3$ and so on

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EXERCISES

Exercise 1:

An electron is moving with a velocity of $5 \times 10^6\ m/s$. Calculate its De Broglie wavelength.

We give:

- Mass of electron,$m_e = 9.11 \times 10^{31}\ kg$
- Planck's constant, $h = 6.63 \times 10^{-34}\ J \cdot s$

Exercise 2:

Electrons are accelerated through a potential difference of 150V. Calculate the de Broglie wavelength.

- Mass of electron,$m_e = 9.11 \times 10^{31}\ kg$
- Planck's constant, $h = 6.63 \times 10^{-34}\ J \cdot s$

Exercise 3:

The de-Broglie wavelength of a particle accelerated with a potential difference of 150 V is 10^{-10} m. If it is accelerated with a potential difference of 600 V, calculate its wavelength.

Exercise 4:

A proton when accelerated through a potential V, has a de Broglie wavelength λ associated with it. If an alpha particle is to have the same de Broglie wavelength λ, it must be accelerated through a potential difference of: $\frac{V}{8}$, $\frac{V}{4}$, $4V$ or $8V$.

Exercise 5:

An electron is accelerated through a potential difference of V volt. It has a wavelength λ associated with it. Through what potential an electron must be accelerated so that its de Broglie wavelengths is the same as that of a proton?

Take mass of proton to be 1837 times larger than the mass of electron.

Exercise 6:

An electron of mass m has de Broglie wavelength λ when accelerated through potential V.

Calculate the de Broglie wavelength associated to a proton of mass M, accelerated through a potential difference of 9V, (Assume that wavelength is determined at low voltage).

Exercise 7:

In one experimental setup for studying interference patterns of electron waves, two slits are created in a gold-coated silicon membrane. Each slit is 62nm wide and 4μm long, and the separation between the slits is 272 nm. The electron beam is created in an electron gun by heating a tungsten element and by accelerating the electrons across a 600V potential. The beam is subsequently collimated using electromagnetic lenses, and the collimated beam of electrons is sent through the slits.

1. Find the angular position of the first-order bright fringe on the viewing screen.
2. Find the angular position of the fifth-order bright fringe on the viewing screen.

Strategy

Recall that the angular position θ of the nth order bright fringe that is formed in Young's two-slit interference pattern (discussed in a previous chapter) is related to the separation, d, between the slits and to the wavelength, λ, of the incident light by the equation $dsin\,\theta = n\lambda$, where n = 0, ±1, ±2,.... The separation is given and is equal to d = 272 nm. For the first-order fringe, we take $n = 1$. The only thing we now need is the wavelength of the incident electron wave.

Since the electron has been accelerated from rest across a potential difference of ΔV = 600 V, its kinetic energy is K = e ΔV = 600 eV. The rest-mass energy of the electron is E_0 = 511 keV.

We calculate its de Broglie wavelength as that of a nonrelativistic electron because its kinetic energy K is much smaller than its rest energy E_0, $K \ll E_0$.

Exercise 8:

In an experiment performed by Jönsson in 1961, electrons were accelerated through a 50 kV potential towards two slits separated by a distance, $d = 2 \times 10^{-4}\,cm$, then detected on a screen $L = 35cm$ beyond the slits.

- Calculate the electron's de Broglie (λ) wavelength, and the fringe spacing (Δy).

Exercise 9:

The Davisson-Germer experiment that first demonstrated the wave nature of matter used electrons accelerated to 54 V.

1. Determine the energy of the electrons in electronvolts
2. How fast were the electrons moving in this experiment?
3. What momentum did these electrons have?
4. Determine the wavelength of these electrons.
5. What form of electromagnetic radiation has the same wavelength as the value you calculated in part 4?

Exercise 10:

Davisson-Germer experiment is performed first with X−rays of wavelength λ and then with electrons of same wavelength λ.

- Determine the ratio of energy of X− rays to that of the electrons.

Exercise 11:

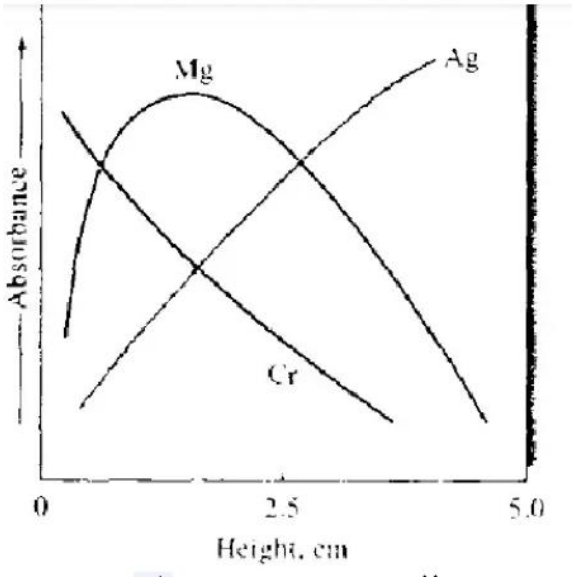
The Davisson-Germer experiment that first demonstrated the wave nature of matter used electrons accelerated to 54 V. Determine the wavelength (in A∘) of the electrons in the Davisson-Germer experiment.

Exercise 12:

1. Explain why a continuous light source is not used in an atomic absorption spectrophotometer.
2. Describe how a hollow cathode lamp works. Why is a different lamp generally needed for each element being measured?
3. Identify two assumptions usually made when making quantitative AAS measurements.
4. Indicate two advantages and one disadvantage of AAS.

Exercise 13:

Describe the effects that are responsible for the three different absorbance profiles in the figure below and select three additional dements you would expect to have similar profiles.



2. Why is an electrothermal atomizer more sensitive than a flame atomizer?

3. Describe how a deuterium lamp can be used to provide background correction for an atomic absorption spectrum.

4. Why is source modulation used in atomic absorption spectroscopy?

5. The emission spectrum of a hollow-cathode lamp for molybdenum has a sharp line at 313.3 nm as long as the lap current is less than 50 mA. At higher currents, however, the emission line develops a cuplike crater at its maximum;

- Explain.

6. Why is atomic emission more sensitive to flame instability than atomic absorption or fluorescence?

Exercise 14:

Assume the mass of an electron is 9.11×10^{-31} kg.

1. Calculate the wavelength of an electron traveling with a speed of 2.65×10^{6} m/s.

2. What would the wavelength of the helium atom be if it were traveling at the same speed as the electron in part a ($1\ amu = 1.6606 \times 10^{-24}\ g$)?

Exercise 15:

RGB color television and computer displays use cathode ray tubes that produce colors by mixing red, green, and blue light. If we look at the screen with a magnifying glass, we can see individual dots turn on and off as the colors change. Using a spectrum of visible light, determine the approximate wavelength of each of these colors. What is the frequency and energy of a photon of each of these colors.

Exercise 16:

A bright violet line occurs at 435.8 nm in the emission spectrum of mercury vapor. What amount of energy, in joules, must be released by an electron in a mercury atom to produce a photon of this light?

Exercise 17:

When rubidium ions are heated to a high temperature, two lines are observed in its line spectrum at wavelengths (a) 7.9×10^{-7} m and (b) 4.2×10^{-7} m. What are the frequencies of the two lines? What color do we see when we heat a rubidium compound?

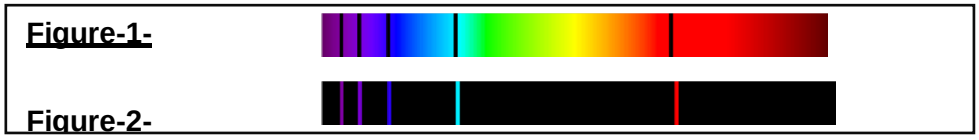
Exercise 18:

The emission spectrum of cesium contains two lines whose frequencies are (a) 3.45×10^{14} Hz and (b) 6.53×10^{14} Hz. What are the wavelengths and energies per photon of the two lines? What color are the lines?

Exercise 19:

From theoretical considerations, Bohr arrives at the conclusion that the energies E_n of the different possible levels of a hydrogen atom verify a relation of the type: $E_n = \frac{E_0}{n^2}$, $E_0 = -13.6\ eV$, $n \in \mathbb{N}^*$.

The following figures represent optical transition spectra of the hydrogen atom.



1. For each figure, specify the optical transition mechanism that gives these spectra.
2. Explain the difference between the two optical spectra.
3. Explain why these spectra have lines.
4. Represent on an energy diagram, the energy levels of the hydrogen atom for n between 1 and 6.
5. What is the corresponding energy:

a- At the fundamental level of the hydrogen atom?

b- At the highest energy level of the hydrogen atom?

6. Define the ionization energy of the hydrogen atom? What is its value?

7. Specify the optical mechanism that can take place during the transition:

a- From the energy level corresponding to n = 1 to the level n = 2

b- From the energy level corresponding to n = 3 to the level n = 2

- The hydrogen atom passes from the energy level corresponding to n = 4 to the level n = 2.

8. Calculate the wavelength of the emitted radiation.

9. To which radiation domain does this wavelength belong?

- The first four lines of the Balmer series corresponding to the return to the level n = 2 have the following wavelengths: λ1 = 410 nm (violet), λ2 = 434.1 nm (indigo), λ3 = 486.1 nm (blue), λ4 = 656.3 nm (red).

10. Associate each wavelength with the corresponding energy transition.

Exercise 20:

The quantized levels in Hydrogen atom are given through the following relation :

$E_n = \frac{E_0}{n^2}$ avec $E_0 = -13.6\ eV$ et $n \in \mathbb{N}^*$.

1. 1. Represent on an energy diagram, the first six energy levels of the hydrogen atom.

2. Identify what the energy levels corresponded to $E_1 = -13.6\ eV$ and $E_\infty = 0\ eV$.

3. Consider the optical transition from level 3 to level 2.

3.a. Is this radiation emitted or absorbed?

3.b. Represent this transition on the diagram.

3.c. Calculate the corresponding transition energy ΔE_{32}.

3.d. Calculate the wavelength corresponding to this transition.

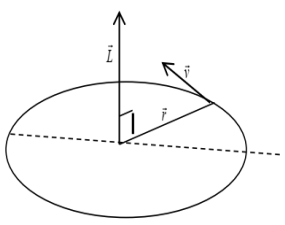
3.e. To which domain of light does this radiation belong?

4. From its first energy state, the hydrogen atom absorbs a photon of wavelength λ = 121.7 nm.

4.a. Identify the energy level E_n that causes this absorption?

Exercise 21:

The orbits of an atom, according to the Bohr model, are quantized and determined from the condition of quantization of the kinetic momentum$\vec{L}$, given by



$$\left|\vec{L}\right| = |\vec{r} \wedge \vec{p}| = mvr = \frac{n\,h}{2\pi} = n\hbar.$$

1. Show that the radius (r) of the permitted orbit is quantized and is denoted r_n.
2. Determine the energy of the allowed orbit $E(r_n)$ corresponding to the radius r_n
3. Calculate r_n.and E_n for the case of the hydrogen atom
4. Determine the expression for the angular velocity (ω) of the electron.

Numerical data:

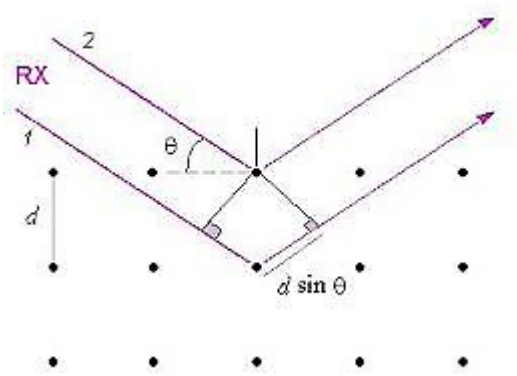
$h = 6{,}62 \times 10^{-34}\, J\,s,\ m_e = 9.1 \times 10^{-31}\, kg\ , e = 1.6 \times 10^{-19}\, C\ ,\ \varepsilon_0 = 8.85 \times 10^{-12}\, SI$.

Exercise 22:

A monokinetic electron beam is reflected from a single crystal. The smallest angle of reflection is 54º. If the atomic lattice planes are spaced 0.215 nm apart, what is the wavelength associated with the electron beam?

An X-ray tube with a copper anticathode operating at a voltage U of 50 kV is passed through by a current of intensity 40 mA.

1. What is the minimum wavelength λ_0 (in nm) of the X-ray photons of the bremsstrahlung radiation? - Knowing that the wavelength of the maximum intensity of the bremsstrahlung radiation is equal to $3\lambda_0/2$.
2. What is the most probable loss of kinetic energy during the bremsstrahlung process for the electrons having penetrated the anticathode? Express the result in keV.
3. What is the value of λ_0 (in nm) when the intensity of the electric current flowing through the tube increases by 20 mA

Exercise 23:

In an X-ray diffraction experiment, at what angles θ will first and second order diffractions be observed for planes separated by 0.315 nm? The wavelength (λ) of the X-rays used is 0.1537 nm. Recall the Bragg relation: $n\lambda = 2d\ sin\theta$ with: n expresses the diffraction order.