Lectures
In
Atomic Physics and Spectra
For
Third Year Students

Physics Department

Faculties of Science and Education

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Chapter (1)

History of Atomic Structures

Chapter (1)
The History of The Atom

Atomic Theory Timeline

Most people know that the atom is the basic building block of all matter, but it is so much more than that. So, what exactly is an atom? Who first came up with the idea of an atom? What is the atomic theory? What is the current model of the atom? Over the past 2000 years our concept of the atom has changed many times. Why does it keep changing? Is there anything smaller than an atom?

The following key scientists have pondered these questions and have contributed greatly to the new Modern Atomic Theory with their individual and collaborative discoveries. Those are the scientists that will be the focus of the activities that follow.

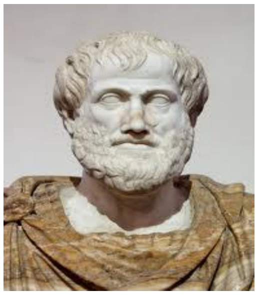
- **Democritus –** All things are "composed of minute, invisible, indestructible particles of pure matter which move about eternally in infinite empty space."
- **John Dalton -** Developed five theories that he believed were true of atoms.
- **J.J. Thomson –** "Plum Pudding" model of the atom; discovered electrons.
- **Ernest Rutherford -** discovered the nucleus of the atom and developed the planetary model of the first structure of the atom.
- **Niels Bohr -** perceived the problem with Rutherford's planetary model of the atom, and used Planck's quantum theory to describe the phenomenon of electron movement. He used Heisenberg's uncertainty principle to redefine further electron motion in the atom.
- **Erwin Schrödinger -** developed the equations that define the wave-like traits of atomic behavior as deduced from spectral analysis.

Democritus (Greek~400B.C.):

More on Democritus

- ž • He came up with the term "atom"
- ž •He thought atoms had different shapes and sizes
- ž •He thought they were indivisible and indestructible "atomists" – people who followed his beliefs

Aristotle (greek~350 B.C.) :



Atoms? Give me a break! I could speak for hours against their existence.

- ž **• His beliefs were more like the early Greeks .**
- ž **• Philosopher**
- ž

John Dalton (England~1800 :

Dalton's Atomic Theory

I. Dalton returns to Democritus' ideas in 1803 with four arguments
II. A tiny solid ball that *could not be broken up into parts*.

aka billiard ball model

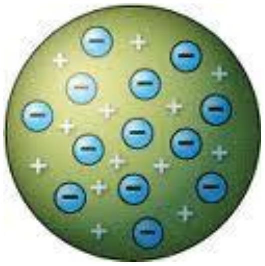
III. All matter is composed of tiny particles called atoms
IV. Atoms of different elements have different masses.
V. Atoms of two or more different elements combine to form compounds.
VI. A chemical reaction involves the rearrangement, separation, or combination of atoms.
VII. *Atoms are never created nor destroyed during a chemical reaction.*

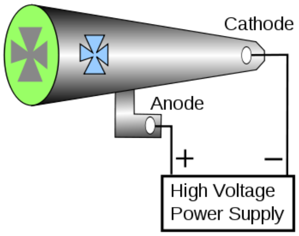
Advantages of Dalton's atomic theory

- **The atomic theory explains the laws of chemical combination (the Law of Constant Composition and the Law of Multiple Proportions).**
- **Dalton was the first person to recognize a workable distinction between the fundamental particle of an element (atom) and that of a compound (molecule).**

JJ Thomson (England – 1897) :

Thomson's ATOMIC MODEL known as the Plum Pudding Model





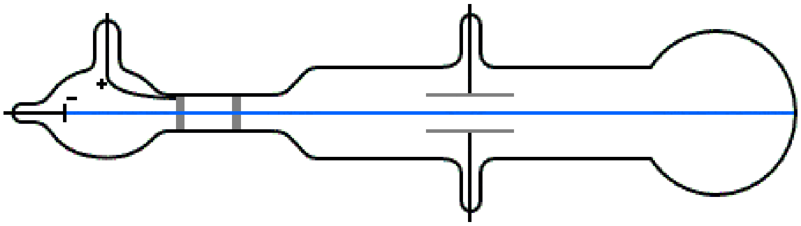
ž • Discovered the electron

ž • Proved the atom can be divided

ž • Plum pudding model

ž • 1906 Nobel Prize Winner-conduction of electricity through gases.

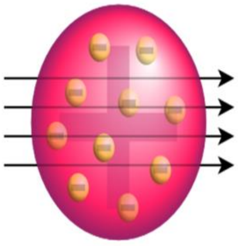
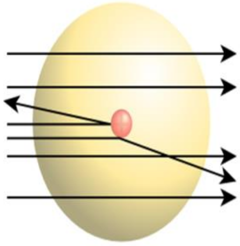
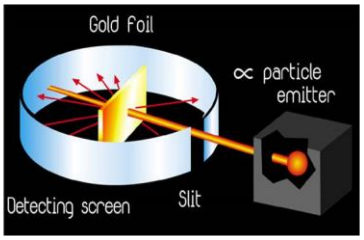
ž • The Cathode Ray Tube : Thompson created a tube that had a positively charged anode on one side and a negatively charged cathode on the other side.

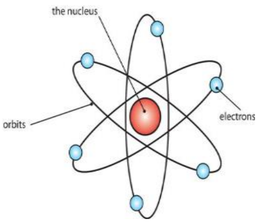


ž

Thompson then applied a magnet to the middle of the tube, equal distance from the cathode and anode, and discovered that negatively charged particles were emanating towards the positive magnetic field. From this, Thompson concluded that negatively charged particles, called electrons, were present in atoms. Thompson then created the Plum Pudding model, which suggested that electrons and protons were randomly placed throughout the atom. This theory wasn't correct, but led to the discovery of the nucleus, made by Ernest Rutherford.

Ernest Rutherford (1871-1937) (England – 1909) :



ž • **Atoms have a dense "nucleus"**

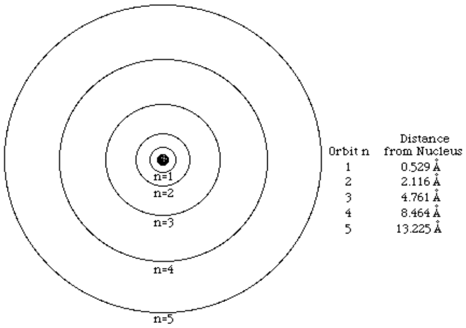
ž • **Discovered the proton**

ž • **Rutherford worked with radiation and had heard of Thompson's plumb pudding model.**

• **He wanted to use radiation to prove Thompson's model.**

• **With the help from Marie Curie, he shot alpha particles (+) at an ultra-thin piece of gold foil, with a Geiger counter on the other side.**

Niels Bohr (1885-1962) :

Orbit n	Distance from Nucleus
1	0.529 Å
2	2.116 Å
3	4.761 Å
4	8.464 Å
5	13.225 Å

Planetary Model of the Atom :

- **integrated all known information into a new, math based, model of the atom**
- **He kept electrons in energy levels or fixed orbits around the nucleus**

"Bohr Theory of the Atom" was the closest to the currently accepted atomic model, re-emphasized the idea of electrons around the nucleus. Bohr suggested that electrons orbited around the nucleus in seven different quantum levels, or shells. The evidence that Bohr used to imply this theory was the measurement of the line spectrum given off by each of the electrons. Bohr determined that different energy levels could be found by using mathematical formulas, which measured the wavelengths of the different energy levels. Bohr went on to suggest that electrons would only occupy the lowest possible energy level on the respective level they were on. Furthermore, electrons would only move up a level if the lower levels were full. Bohr's model was very accurate, and would lead to Schrodinger's idea of the current Atomic Model.

James Chadwick (English – 1932)

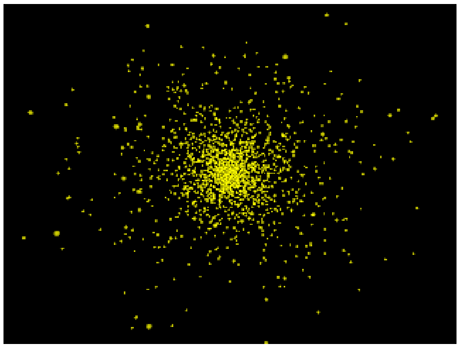
The Third Subatomic Particle (Discovered the neutron) :

- **Missing mass** in the nucleus
- James Chadwick – determined that a another subatomic particle must be in the nucleus with the protons.
- Called this subatomic particle: **neutron** because it has **NO** charge.

Erwin Schrödinger's 1930's :

Most important contribution to the current Atomic Model was his development of the mathematical description that described the paths electrons would most likely follow in their orbits around the nucleus. The formulas that Schrödinger developed in 1926 would be later called the basis of quantum mechanics, and awarded him a Nobel Prize. Eventually, Schrödinger determined that instead of Bohr's suggested orbits, there were actually orbitals. Instead of the idea of the electrons following a pre-determined path, the electrons would be moving around in an area. These ideas, including the quantum mechanical formulas, were presented in his "Wave Mechanical Formula." This model eventually became the new Modern Atomic Theory.

Here is a quantum mechanical picture of a Hydrogen atom. The nucleus is not shown, but is located at the center of the picture.



Some things to notice:

- You can see where the electron is most likely to be: near the nucleus.
- You can't tell exactly where the electron is, just where it is most likely to be.

- The individual dots are not electrons. They are meant to be used in the context of how dense or heavy an area of dots appears.
- The more crowded (or heavier packed) the dots are in a particular region, the better chance you have of finding the electron there.

Wave Mechanical Model: Power Boat Analogy

When a power boat is cruising on a lake, the wave which it produces has its greatest amplitude right at the boat, and the amplitude decreases as the distance from the boat increases. Thus you could locate the most probable location of the boat by analyzing the amplitude and energy of its associated water wave.

This is analogous to the wave mechanical model which visualizes the atom as a positive nucleus surrounded by vibrating electron waves. The Schrödinger Wave Equation describes the amplitude and other characteristics of the waves which are associated with the moving electrons, and thus it also is able to describe the energy and location of the orbiting electrons.

Problems

In the Beginning

- Who came up with the term ‘atom’?

Democritus

- Who was Democritus? Include full name, time, profession, other interesting personal information.
- What was the main difference between Democritus and “the others” that came after him?

Dalton

- Who was Dalton? Include full name, time, profession, other interesting personal information.
- What was Dalton’s atomic theory?
- What was his atomic model?
- What did he say about compounds and chemical reactions?
- What was the problem or issues with this model?

Thomson

- Who was Thomson? Include full name, time, profession, other interesting personal information.
- What was Thomson’s model?
- What is the special name of his model?
- Which subatomic particles does his model have?
- What was the problem or issues with this model?

Rutherford

- Who was Rutherford? Include full name, time, profession, other interesting personal information.
- What was his model?
- What led him to make his theory?
- What experiment did he do and why was he so astonished?
- What was significant about his discovery?
- Which subatomic particles does his model have?

- Who discovered the proton?
- What was the problem or issues with this model?

Bohr

- Who was Bohr? Include full name, time, profession, other interesting personal information.
- What was his model?
- How did he explain the main problem with the Rutherford model?
- How were the energy levels described?
- What does quantized mean?
- What is an orbit?
- Can electrons move from energy level to energy level?
- What was the problem or issues with this model?

Schrödinger

- Who was Schrödinger? Include full name, time, profession, other interesting personal information.
- What was his model?
- How does this model describe the atom?
- Why is it better than the Bohr model?
- What is an orbital and how is it different than an orbit?

Included at the end are links to websites that you will help you complete this project.

Sample Presentation Rubric:

	Levels of Performance			
Scientist	**1**	**2**	**3**	**4**
Democritus	Explains some of the information but not all of it, or the information is incorrect.	Explains who he was or his concept of the atom but is missing information.	Explains who he was and his concept of the atom, but is missing some information.	Fully explains who he was and his concept of the atom.
Dalton	Explains some of the information but	Explains who he was, his Atomic Theory, or his	Explains who he was, his Atomic Theory,	Fully explains who he was, his Atomic Theory and his Atomic Model,

	not all of it, or the information is incorrect.	Atomic Model, but is missing information.	and his Atomic Model, but is missing some information.	and includes a description of his experiments.
Thomson	Explains some of the information but not all of it, or the information is incorrect.	Explains who he was or his concept of the atom, but is missing information.	Explains who he was and his concept of the atom, but is missing some information.	Fully explains who he was and his concept of the atom; includes a description of his experiments and how it built on the previous atom.
Rutherford	Explains some of the information but not all of it or the information is incorrect.	Explains who he was or his concept of the atom, but is missing information.	Explains who he was and his concept of the atom, but is missing some information.	Fully explains who he was and his concept of the atom; includes description of his experiments and how it built on the previous atom.
Bohr	Explains some of the information but not all of it or the information is incorrect.	Explains who he was or his concept of the atom, but is missing information.	Explains who he was and his concept of the atom, but is missing some information.	Fully explains who he was and his concept of the atom; includes a description of his experiments and how it built on the previous atom.
Schrödinger (Quantum Theory)	Explains some of the information but not all of it or the information is incorrect.	Explains who he was or his concept of the atom, but is missing information.	Explains who he was and his concept of the atom, but is missing some information.	Fully explains who he was and his concept of the atom; includes a description of his experiments and how it built on the previous atom.

Match the person to the model

1. Dalton
2. Democritus
3. Thomson
4. Rutherford
5. Schrodinger and DeBroglie
6. Bohr

a. Atomic theory of matter: atoms are like marbles. Different for each element. Cannot be broken down. Combine in whole numbers.

b. Matter is made up of indivisible particles called *atomos*

c. Electrons orbit the nucleus in energy shells or *orbitals*

d. Electrons can be seen as waves surrounding the nucleus like a cloud. You cannot exactly say where the electron is at any time, only the probability.

e. The mass of an atom is concentrated in a positively charged nucleus. Most of the atom is empty space.

f. The atom is like a plum pudding: a positively charged "dough" contained negatively charged particles called electrons.

Who discovered:

7. The electron
8. The neutron
9. The nucleus

a. Thomson
b. Rutherford
c. Democritus
d. Chadwick

10. Science changes over time. Scientists discover new concepts and change their ideas. They think of new "models" of how the world works.

Place the models in the correct order (oldest to most recent):

a. Wave F. Greek
b. Dalton
c. Plum pudding
d. Rutherford e. Bohr

Summary Questions:

1. How were the atomic models developed when no one had seen the atom?
2. What flaws exist in Dalton's, Thomson's, Rutherford's and Bohr's model of the atom? Do any flaws exist in the modern quantum model of the atom? Explain.
3. Which of Dalton's principles were contradicted by the work of J.J.Thomson? Do any of Dalton's principles still hold true completely today? If so, which ones hold true?
4. Describe Rutherford's model of the atom. Why was he so amazed by the results of his experiment? What flaws exist in his model?

It turns out that this quantum mechanical view of the atom is our best theory to date on how atoms work. The quantum mechanical model does a much better job in describing and predicting how atoms behave than the planetary/orbit model does.

Chapter (2)

Classical models of Atomic Structure

Chapter (2)
Classical Models Of Atomic Structure

2 - Discovery of Electrons

At atmospheric pressure, air and other gases are poor conductors of electricity. This is because, they do not have free charged particles. However, electric current may be passed through a gas if by some mechanism, charged particles are produced in the gas. This can be done in many ways, such as (i) by applying a large potential difference across a gas column at very low pressure and (ii) by allowing X-rays to pass through the gases.

The study of electric discharge through gases gives valuable information regarding the structure of atoms. This has led to the discovery of electrons by J. J. Thomson and later on, to the discovery of X-rays by Roentgen.

2.1 Discharge of electricity through gases at low pressure - Discovery of electrons

A discharge tube is an arrangement to study the conduction of electricity through gases. It is a closed, strong glass tube of length 50 cm and diameter 4 cm, filled with a gas. Two metal electrodes C and A are fitted inside the tube at the ends as shown in Fig 6.1. The side tube P is connected to a high vacuum pump and a low pressure gauge. The electrodes C and A are connected to the secondary of a powerful induction coil, which maintains a potential difference of 50,000 V. The electrode C connected to the negative terminal of the induction coil is called the cathode and the electrode A connected to the positive terminal is called the anode.

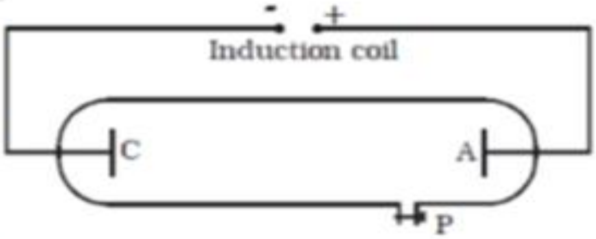


Fig (1)Discharge tube

When the pressure of the gas inside the discharge tube is reduced by working the vacuum pump, to about 110 mm of Hg, no discharge occurs through the tube. At a pressure of about 100 mm of Hg, the discharge of electricity through the gas begins and irregular streaks of light appear, accompanied by a crackling sound. As the pressure is reduced to the order of 10 mm of Hg, the irregular streaks broaden out into a luminous column extending from the anode, almost upto the cathode. This column is known as the positive column. With further reduction in pressure to around 0.01 mm of Hg, the positive column disappears and Crooke's dark space fills the whole tube. At this stage, the walls of the glass tube fluoresce with green colour. This greenish glow in the final stage of the gaseous discharge is found to be a fluorescence of the glass produced by some invisible rays emanating from the cathode (shown in the wrapper). These rays are called cathode rays and are found to be electrons.

6.1.1 Properties of Cathode rays

Cathode rays have the following properties:

(i) They travel in straight lines.

(ii) Cathode rays possess momentum and kinetic energy.

(iii) Cathode rays produce heat, when allowed to fall on matter.

(iv) Cathode rays produce fluorescence when they strike a number of crystals, minerals and salts.

(v) When cathode rays strike a solid substance of large atomic weight, X-rays are produced.

(vi) Cathode rays ionize the gas through which they pass.

(vii) Cathode rays affect the photographic plates.

(viii) The cathode rays are deflected from their straight line path by both electric and magnetic fields. The direction of deflection shows that they are negatively charged particles.

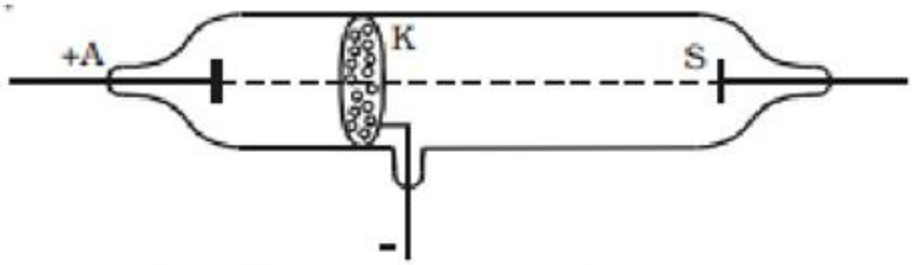
(ix) Cathode rays travel with a velocity upto $(1/10)^{th}$ of the velocity of light.

(x) Cathode rays comprises of electrons which are fundamental constituents of all atoms.

6.1.2 : Positive rays (or) Canal rays

Positive rays are sometimes known as the canal rays. These were discovered in 1896 by Goldstein. If the cathode of a discharge tube has holes in it and the pressure of the gas is around 1 mm of mercury than faint luminous glow come out from each hole on the backside of the cathode. This shows that something is coming out of the holes. These are called canal rays or positive rays.

Origin of positive rays :



Fig(**B**) : *Production of canal rays.*

When potential difference is applied across the electrodes, electrons (cathode rays) are emitted from the cathode. As they move towards anode, they gain energy.

These energetic electrons which collide with the atoms of the gas in the discharge tube, they ionize the atoms. The positive ions formed at various places between cathode and anode, travel towards the cathode.

Since during their motion, the positive ions when reach the cathode, some pass through the holes in the cathode. These stream of positive ions are the positive rays or canal rays.

If the discharge tube is totally evacuated then no positive rays are produced. Thus positive rays are positive ions of the gas in the tube. Properties of positive rays were studied by Thomson. The q/m of the hydrogen was found to be ~10^8 C/kg much less then the e/m of electron ~10^{11} C/kg indicating that mass of positive rays is much greater than that of electrons.

Properties of Positive Rays :

(i) These are positive ions having same mass if the experimental gas does not have isotopes. However if the gas has isotopes then positive rays are group of positive ions having different masses.

(ii) They travel in straight lines and cast shadows of objects placed in their path. But the speed of the positive rays is much smaller than that of cathode rays.

(iii) They are deflected by electric and magnetic fields but the deflections are small as compared to that of cathode rays.

(iv) They show a spectrum of velocities. Different positive ions move with different velocities.

(v) q/m ratio of these rays depends on the nature of the gas in the tube (while in case of the cathode rays q/m is constant and does not depend on the gas in the tube).

(vi) They carry energy and momentum.

(vii) They cause ionization (which is much more than that produced by cathode rays).

(viii) They cause fluorescence (in ZnS or CdS screen) and affect photographic plates.

(ix) They have a little penetration power (but much less in comparison to cathode rays)

6.1.3 Determination of specific charge (e/m) of an electron – Thomson's method.

In 1887, J.J. Thomson, measured the specific charge (e/m) of the cathode ray particles. The specific charge is defined as the charge per unit mass of the particle. Thomson discovered that the value of (e/m) was independent of the gas used and also independent of the nature of the electrodes.

Principle

The fact that the cathode rays (electrons) are deflected by electric and magnetic fields is made use of in this method.

Experimental arrangement

A highly evacuated discharge tube used in this experiment is as shown in Fig. 6.3. Cathode rays are produced by the discharge between the cathode and the anodes D_1 and D_2. A thin pencil of cathode ray comes out through fine pin holes in the anode discs. The cathode rays then pass between two parallel metal plates P_1 and P_2 and strike the flat face of the tube. This face is coated with suitable fluorescent material. A spot of light is produced at Q But when a potential difference V is applied between P_1 and P_2, the beam is deflected to point Q_1. By the use of a pair of coils, uniform magnetic field is produced perpendicular to the plane of the paper and outwards through out the region between P_1 P_2.

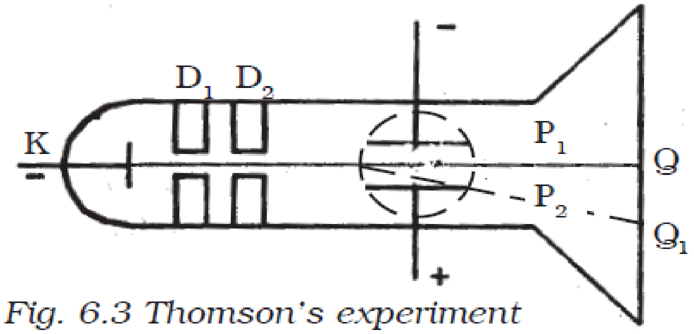


Fig. 6.3 Thomson's experiment

Theory

1. Determination of V

With a given electric intensity between the plates P_1 and P_2 the magnetic induction B is adjusted until the beam strikes the screen at the original position Q. Then the downward force Ee due to the electric field is balanced by the force Bev due to magnetic induction where e is the charge of the cathode ray particle and v is the velocity of the cathode rays.

$$Ee = Bev$$

$$v = \frac{E}{B} \qquad \ldots(1)$$

2. Determination of e/m

Now the magnetic induction is switched off. The deflection Q Q_1 = y caused by the electric field alone is measured. At the instant when the cathode rays enter the region between the plates P_1 and P_2, initial velocity in the downward direction u = 0

Acceleration along the downward direction $a = \frac{Ee}{m}$, where m is the mass of each cathode ray particle.

Time for which the electron moves in the electric field $t = \frac{l}{v}$ where l is the length of either of the plates and v is the velocity of the electron.

The deflection produced on the cathode rays along the downward direction in the electric field is given by

$$y_1 = \frac{1}{2}\left(\frac{Ee}{m}\right)\left(\frac{l}{v}\right)^2 \ldots.\ (2)$$

Substituting for v from equation (1) in equation (2) we get

$$y_1 = \frac{1}{2}\left(\frac{Ee}{m}\right)\left(\frac{l^2}{E^2}\right)B^2 = \frac{1}{2}\frac{e}{m}\frac{l^2B^2}{E}$$

The displacement of the spot of light on the screen is given by (Fig 6.4)

$y = K\,y_1$, where K is a constant determined by the geometry of the discharge tube. Substituting for y_1 we get,

$$y = K\,\frac{1}{2}\frac{e}{m}\frac{l^2B^2}{E} \quad \ldots(3)$$

$$\frac{e}{m} = \frac{2yE}{Kl^2B^2} \qquad \ldots(4)$$

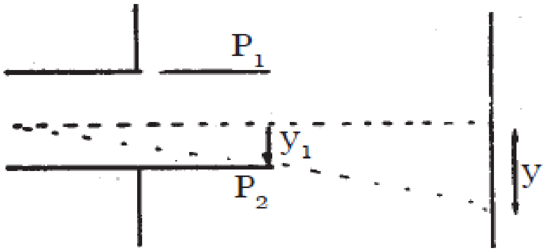


Fig. 6.4 Path of an electron in the electric filed

By substituting the known values in the above relation e/m of an electron can be calculated. The value of e/m calculated using this experiment was found to be 1.7592 × 10^{11} C kg^{-1}

Note: The value of e/m of an electron can also be calculated, by applying uniform magnetic field perpendicular to the path of the electron.

6.1.4 Determination of charge of an electron – Millikan's oil drop experiment

Millikan's experiment is used for the measurement of charge of an electron.

Principle

This method is based on the study of the motion of uncharged oil drop under free fall due to gravity and charged oil drop in a uniform electric field. By adjusting uniform electric field suitably, a charged oil drop can be made to move up or down or even kept balanced in the field of view for sufficiently long time and a series of observations can be made.

Experimental arrangement

The apparatus consists of two horizontal circular metal plates A and B, about 22 cm in diameter and separated by a distance of about 16 mm as shown in Fig 6.5. The upper plate has a hole (H) in the middle. These plates are held together by insulating rods of glass or ebonite, so that they are perfectly parallel to each other.

The plates are surrounded by a constant temperature bath D and the chamber C containing dry air. The plates are connected to a battery which can provide a potential difference of the order of 10000 V.

Theory

A spray of fine droplets of a highly viscous liquid (such as glycerine) is produced by means of an atomiser (AT) near the hole H and enter the space between A and B. The droplets are illuminated by an arc lamp L and are seen through a microscope whose eyepiece is provided with a micrometer scale. One such droplet is viewed through the microscope as it descends under gravity. The viscous force due to air increases and soon it attains a constant terminal velocity and let it be v. The terminal velocity v of the droplet is measured using the microscope.

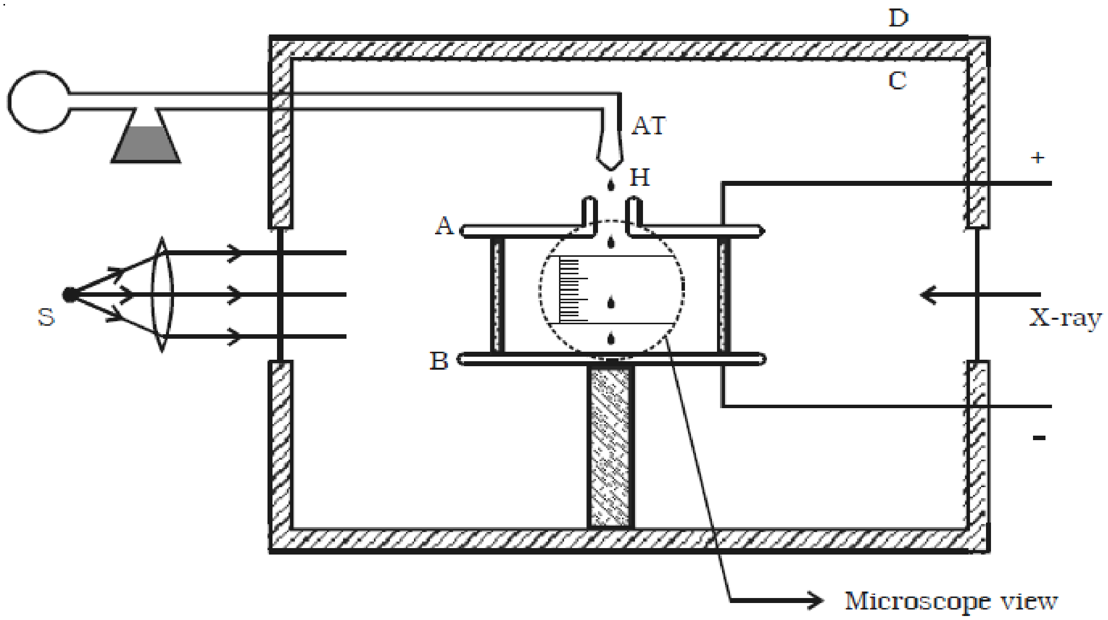


Fig 6.5 Millikan's oil drop experiment

(i) Motion under gravity

The gravitational force acting on the oil drop downwards is equal to $mg = \frac{4}{3}\pi a^3 \rho g$, where a is the radius of the oil drop, ρ is the density of the oil and g, the acceleration due to gravity.

The upthrust experienced by the oil drop due to the displaced air is $\frac{4}{3}\pi a^3 \sigma g$, where σ is the density of air.

$\therefore$ The net downward force acting on the oil drop = weight of the oil drop – upthrust experienced by the oil drop.

$$= \frac{4}{3}\pi a^3 \rho g - \frac{4}{3}\pi a^3 \sigma g$$

$$= \frac{4}{3}\pi a^3 (\rho - \sigma) g \qquad \ldots(1)$$

Since the oil drop attains a terminal velocity υ, the net downward force acting on the oil drop is equal to the viscous force acting opposite to the direction of motion of the oil drop.

By Stoke's law, the viscous force on the oil drop is $6\pi a\eta v$, where η is the co-efficient of viscosity of air.

$$\frac{4}{3}\pi a^3(\rho - \sigma)g = 6\pi a\eta v \qquad \ldots(2)$$

The radius of the oil drop is,

$$a = \left[\frac{9\eta v}{2(\rho-\sigma)g}\right]^{\frac{1}{2}} \qquad \ldots(3)$$

(ii) Motion under electric field

The air inside the parallel plates is ionized by sending a beam of X-rays. The droplets pickup one or more electrons from the ionized air.

Let q be the charge carried by the droplet under observation. Let E be the electric field applied between the plates A and B, so that the drop moves upwards with a terminal velocity v_1, which can be determined using the microscope.

The force on the droplet due to electric field is Eq. Since the velocity of the droplet is uniform, we have

$$Eq = \frac{4}{3}\pi a^3 (\rho - \sigma)g + 6\pi a\eta v_1$$

$$\therefore \quad Eq - \frac{4}{3}\pi a^3 (\rho - \sigma)g = 6\pi a\eta v_1 \qquad \ldots(4)$$

Adding equations (2) and (4),

$$Eq = 6\pi a\eta(v + v_1) \qquad \ldots(5)$$

Substituting the value of a in equation (5) from equation (3),

$$Eq = 6\pi\eta^{3/2}(v + v_1)\left[\frac{9v}{2(\rho-\sigma)g}\right]^{\frac{1}{2}} \qquad \ldots(6)$$

If V is the potential difference between A and B, d is the distance between them, then $E = \frac{V}{d}$

Millikan determined the value q for a large number of oil drops using equation (6) and found that they are an integral multiple of a least value. The greatest common factor gives the charge e of the electron.

The charge of an electron was found to be 1.602×10^{-19} coulomb.

6.2 Atom models

As far back as 1803, Dalton, an English teacher, showed that the matter is made up of extremely small particles called atoms. Prout (1815), suggested that all elements are made up of atoms of hydrogen. Since many of the elements were found to have atomic weights that were not exact multiples of that of hydrogen, the suggestion was not accepted. After the discovery of radioactivity and electron, interest in the study of atomic structure increased and many models of atom were suggested at different times.

6.2.1 Thomson atom model

From the study of discharge of electricity through gases, it became clear that an atom consists of positive and negative charges. J.J. Thomson tried to explain the arrangement of positive charge and the electrons inside the atom. According to him, an atom is a sphere of positive charge having a radius of the order of 10^{-10}m. The positive charge is uniformly distributed over the entire sphere and the electrons are embedded in the sphere of positive charge as shown in Fig 6.6. The total positive charge inside the atom is equal to the total negative charge carried by the electrons, so that every atom is electrically neutral.

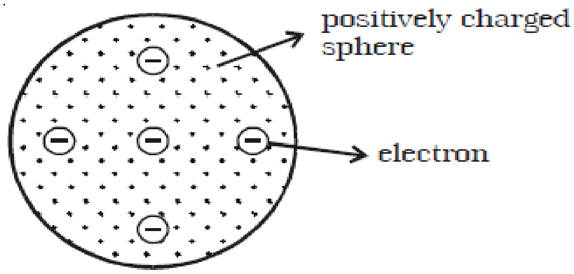


Fig 6.6 Thomson atom model

According to Thomson, if there is a single electron in the atom (like a hydrogen atom), the electron must be situated at the centre of the positive sphere. For an atom with two electrons (helium atom), the electrons should be situated symmetrically with respect to the centre of the sphere i.e., opposite sides of the centre at a distance of $\frac{r}{2}$, where r is the radius of the positive sphere. In a three electron system of the atom, the electrons should be at the corners of a symmetrically placed equilateral triangle, the side of which was equal to the radius of the sphere. In general, the electrons of an atom are located in a symmetrical pattern with respect to the centre of the sphere.

It was suggested that spectral radiations are due to the simple harmonic motion of these electrons on both sides of their mean positions. Moreover, the stability of the atom was very well explained on the basis of this model.

Drawbacks

(i) According to electromagnetic theory, the vibrating electron should radiate energy and the frequency of the emitted spectral line should be the same as the electron. In the case of hydrogen atom, Thomson's model gives only one spectral line of about 1300 Å. But the experimental observations reveal that hydrogen spectrum consists of five different series with several lines in each series.

(ii) It could not account for the scattering of α-particles through large angles.

6.2.2 Rutherford's α - particle scattering experiment

Rutherford and his associates studied the scattering of the α - particles by a thin gold foil in order to investigate the structure of the atom. An α-particle is a positively charged particle having a mass equal to that of helium atom and positive charge in magnitude equal to twice the charge of an electron. They are emitted by many radioactive elements. The scattering of α-particles provide useful information about the structure of the atom.

Experimental arrangement

A fine pencil of α–particles was obtained from a radioactive material like radium or radon by placing it in a lead box with narrow opening as shown in Fig 6.7.

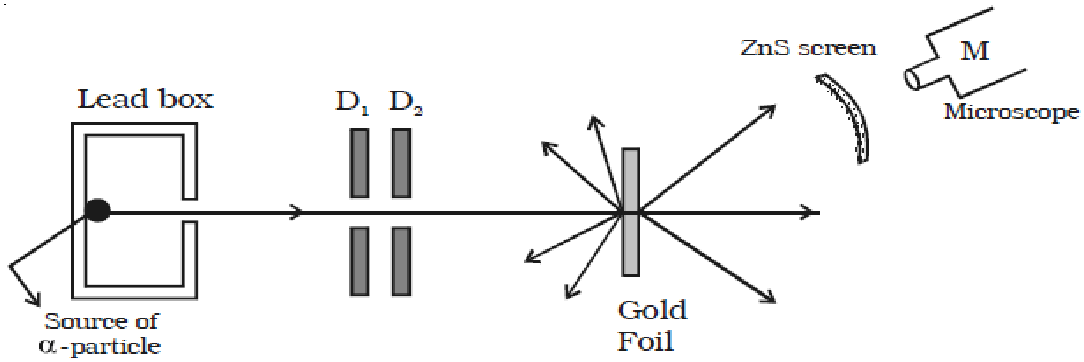


Fig 6.7 Rutherford's α - particle scattering experiment

The α-particles are emitted from the source in all possible directions, but only a narrow beam emerges from the lead box. The remaining α-particles are absorbed in the lead box itself. After passing through the diaphragms D_1 and D_2, a narrow beam of α-particles incident on a thin gold foil, are scattered through different angles. The scattered α-particles strike a fluorescent screen coated with zinc sulphide. When the α-particles strike the screen, tiny flashes of light are produced. The observations can be made with the help of a low power microscope.

Observations and conclusions

(i) Most of the α particles either passed straight through the gold foil or were scattered by only small angles of the order of a few degrees. This observation led to the conclusion that an atom has a lot of empty space as shown in Fig 6.8.

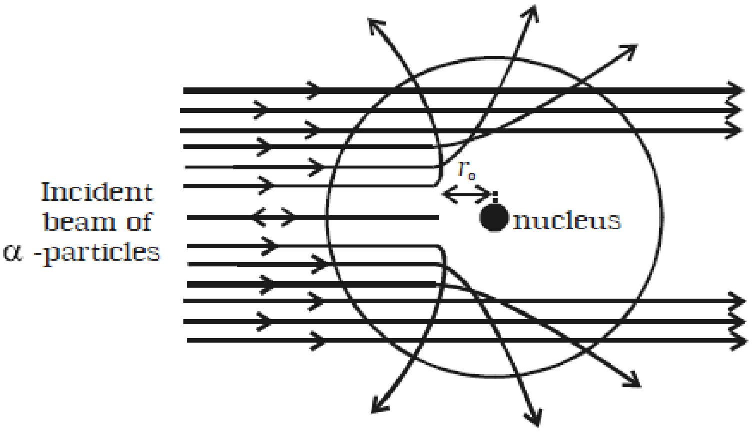


Fig 6.8 Scattering of α – rays

(ii) A few α particles were scattered in the backward direction, which led Rutherford to conclude that the whole of the positive charge was concentrated in a tiny space of about 10^{-14}m. This region of the atom was named as nucleus. Only a small number of particles approaches the nucleus of the atom and they were deflected at large angles.

Distance of closest approach

An α particle directed towards the centre of the nucleus will move close upto a distance r_0 as shown in Fig 6.8, where its kinetic energy will appear as electrostatic potential energy. After this, the α particle begins to retrace its path. This distance r_0 is known as the distance of the closest approach.

Let m and v be the mass and velocity of the α particle directed towards the centre of the nucleus. Then, the kinetic energy of the particle,

$$E_k = \frac{1}{2}mv^2 \qquad \ldots(1)$$

Since, charge of an α-particle is 2e and that of the nucleus of the atom is Ze, the electrostatic potential energy of the α particle, when at a distance r_o from the centre of the nucleus is given by,

$$E_p = \frac{1}{4\pi\varepsilon_o}\cdot\frac{(2e)(Ze)}{r_o} \qquad \ldots(2)$$

where Z is the atomic number of the atom and ε_o, the permittivity of free space.

On reaching the distance of the closest approach r_o, the kinetic energy of the α particle appears as its potential energy.

$$\therefore \quad E_p = E_k$$

$$\frac{1}{4\pi\varepsilon_o}\cdot\frac{(2e)(Ze)}{r_o} = \frac{1}{2}mv^2$$

(or)

$$r_o = \frac{1}{4\pi\varepsilon_o}\cdot\frac{4Ze^2}{mv^2} \qquad \ldots(3)$$

6.2.3 Rutherford atom model

Based on the results of α-particle scattering experiment, Rutherford suggested the following picture of the atom.

(i) Atom may be regarded as a sphere of diameter 10^{-10}m, but whole of the positive charge and almost the entire mass of the atom is concentrated in a small central core called nucleus having diameter of about 10^{-14}m as shown in Fig 6.9a.

(ii) The electrons in the atom were considered to be distributed around the nucleus in the empty space of the atom. If the electrons were at rest, they would be attracted and neutralized by the nucleus. To overcome this, Rutherford suggested that the electrons are revolving around the nucleus in circular orbits, so that the centripetal force is provided by the electrostatic force of attraction between the electron and the nucleus.

(iii) As the atom is electrically neutral, the total positive charge of the nucleus is equal to the total negative charge of the electrons in it.

Drawbacks

Rutherford atom model offered serious difficulties as regards the stability of the atom. Following are the two drawbacks of Rutherford's model: (i) The electron in the circular orbit experiences a centripetal acceleration. According to electromagnetic theory, an accelerated electric charge must radiate energy in the form of electromagnetic waves. Therefore, if the accelerated electron lose energy by radiation, the energy of the electron continuously decreases and it must spiral down into the nucleus, as shown in Fig 6.9b. Thus, the atom cannot be stable. But, it is well known that most of the atoms are stable. (ii) According to classical electromagnetic theory, the accelerating electron must radiate energy at a frequency proportional to the angular velocity of the electron. Therefore, as the electron spiral towards the nucleus, the angular velocity tends to become infinity and hence the frequency of the emitted energy will tend to infinity. This will result in a continuous spectrum with all possible wavelengths. But experiments reveal only line spectra of fixed wavelength from atoms.

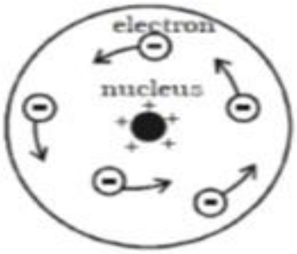


Fig 6.9a Ruterford atom model

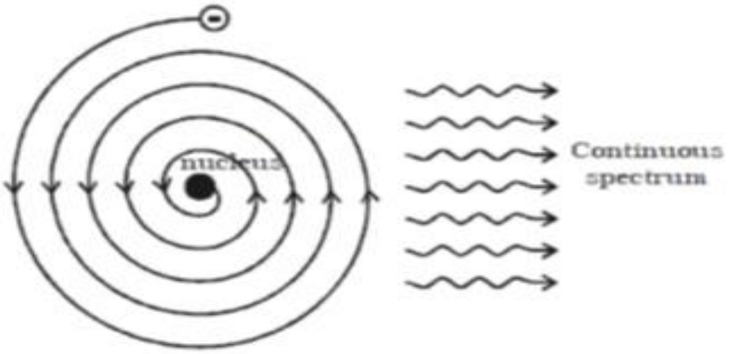


Fig 6.9b Motion of electrons in spiral path into the nucleus.

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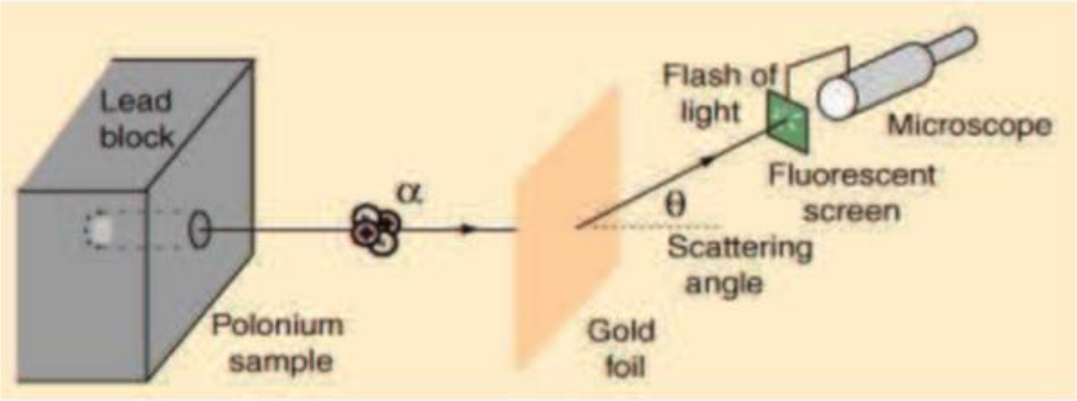
Rutherford Scattering Theory



- A beam of α particles were aimed at a thin gold foil.
- Most of the particles passed through without deflection.
- Others were deflected by various angles
- Some were backscattered .

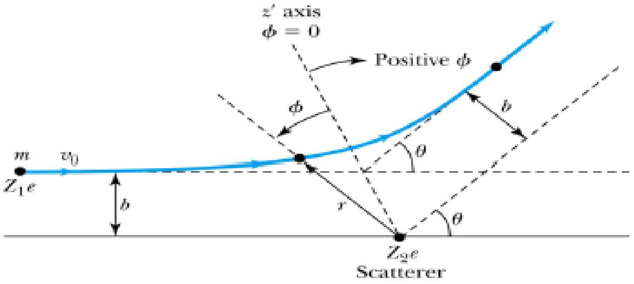
From these results Rutherford concluded that the majority of the mass was concentrated in a minute, positively charged region (the nucleus) surrounded by electrons. When a (positive) alpha particle approached sufficiently close to the nucleus, it was repelled strongly enough to rebound at high angles. The small size of the nucleus explained the small number of alpha particles that were repelled in this way. Rutherford showed, using the method below, that the size of the nucleus was less than about 10–14 m .

Main assumptions

- Collision between a point charge but heavy nucleus with charge Q=Ze and
a light projectile with charge q = ze is considered to be elastic,
- Momentum and energy are conserved,
- The particles interact by the Coulomb force;
- The vertical distance the projectile is from the center of the target, the impact parameter b, determines the scattering angle θ.

Rutherford Scattering

- Scattering experiments help us study matter too small to be observed directly.
- There is a relationship between the impact parameter *b* and the scattering angle θ.



When *b* is small,

→ *r* gets small.

→ Coulomb force gets large.

→ θ can be large and the particle can be repelled backward.

$$b = \frac{Z_1 Z_2 e^2}{8\pi\varepsilon_0 K}\cot\frac{\theta}{2} \qquad \text{where } K = m{v_0}^2/2$$

The Relationship Between the Impact Parameter b and the Scattering Angle α

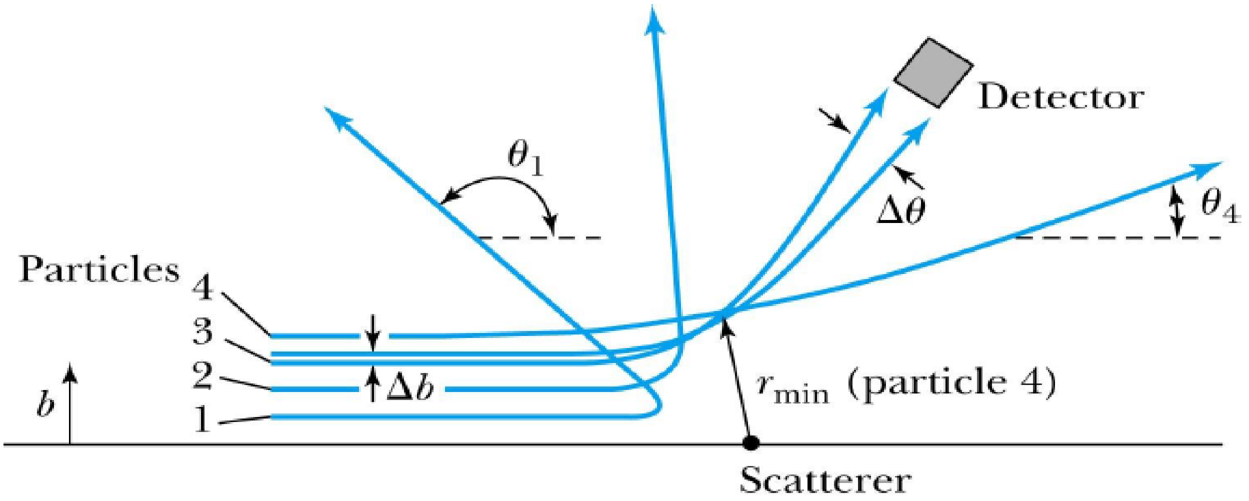
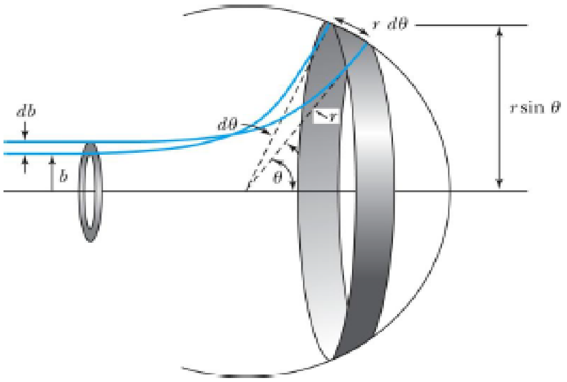
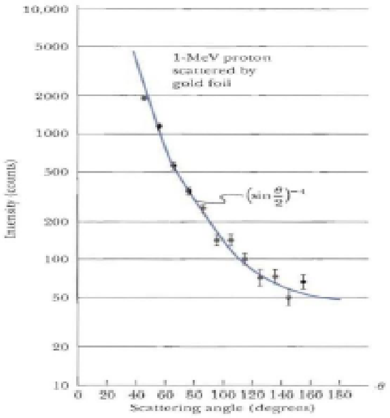


Figure 4.7 The relationship between the impact parameter b and scattering angle u. Particles with small impact parameters approach the nucleus most closely (rmin) and scatter to the largest angles. Particles within the range of impact parameters b will be scattered within u.

Rutherford Scattering Equation

- In actual experiment a detector is positioned from θ to $\theta + d\theta$ that corresponds to incident particles between b and $b + db$.





- The number of particles scattered per unit area is

$$\boxed{N(\theta) = \frac{N_i n t}{16}\left(\frac{e^2}{4\pi\varepsilon_0}\right)^2 \frac{Z_1^{\,2} Z_2^{\,2}}{r^2 K^2 \sin^4(\theta/2)}}$$

The Important Points

1. The scattering is proportional to the square of the atomic number of *both* the incident particle (Z_1) and the target scatterer (Z_2).
2. The number of scattered particles is inversely proportional to the square of the kinetic energy of the incident particle.
3. For the scattering angle θ, the scattering is proportional to 4th power of sin($\theta/2$).
4. The Scattering is proportional to the target thickness for thin targets.

Problems

1. **Match the Scientist with the discovery that they made.**
    a. Neils Bohr
    b. Ernest Rutherford
    c. Erwin Schrödinger
    d. J.J Thomson
    e. John Dalton

    i. Atoms of a particular element were identical
    ii. Electrons could behave like waves as well as particles
    iii. That the atom was mostly empty space
    iv. The arrangement of electron orbitals
    v. The electron

2. **What can conclusion can be drawn from the fact the atomic model continues to be updated?**
    a. Scientists are still discovering new information about atoms.
    b. Old information about atoms is has no use.
    c. Scientists did not have any information about atoms until very recently.
    d. Scientists like to confuse everyone.

3. **Why did Rutherford's gold foil experiment show that the atom is mostly empty space?**
    a. All of the alpha particles passed directly through the foil.
    b. All of the alpha particles were deflected at large angles.
    c. Some of the alpha particles were deflected at large angles.
    d. Most of the alpha particles passed straight through the foil.

4. **Place the following scientists in order, from earliest to latest:**

    1. Ernest Rutherford; 2. J.J. Thomson; 3. John Dalton

    a. 1, 3, 2 b. 2, 3, 1 c. 3, 2, 1 d. 3, 1, 2

b. Who proposed the plum pudding model?
J.J Thomson

c. In the plum pudding model of the atom, what do the plums represent?
Electrons

d. In this model, what does the dough represent?
The sea of positive charge surrounding the electrons

e. What major step does the plum pudding model represent in terms of atomic research?
It suggested that atoms were in fact divisible and provided the first evidence of subatomic particles, namely the electron.

f. How is this model different from modern modes of the atom?

Electrons are distributed throughout the atom, while in later models they are in orbitals. Thomsons atom contains no nucleus and instead has a sea of positive charge, rather than a central positive charge.

g. Briefly describe the apparatus Thomson used in his experiments.

The cathode ray tube is a sealed glass container with two electrodes that are separated by a vacuum. When voltage is applied across the electrodes, cathode rays are generated.

h. Describe what Thomson observed during his experiments.

The cathode rays were deflected by electric and magnetic fields.

i. Thomson named the particles he discovered during his experimentation 'corpuscles'. What do we now know these particles as?

Electrons

j. What awards did Thomson receive for his work on the atom?

Nobel prize

k. Which model replaced Thomson's?

The Rutherford model

l. What is the 'Thomson Problem'?

The Thomson problem was that the was unable to prove that the atom possessed a "the sea" of positive background charge.

m. How did Geiger and Marsden contribute to the model of the atom?

By measuring the scattering patterns of alpha particles with a fluorescent screen, they were able observe the variety of angles the particles were deflected at.

n. What are alpha particles?

Helium nuclei

o. What role did Rutherford play in the modelling of the atom?

Rutherford was responsible for interpreting Geiger and Marsden's experiments, establishing proof for a positive nucleus and the rest of the atom being empty space.

p. Why are models useful in Science?

Models allow us to represent ideas which we cannot experience firsthand. They help scientists to communicate their ideas and support explanations of scientific phenomena.

Chapter (3)

Quantum models of Atomic Structure

Chapter (3) : Quantum Models Of Atomic Structure

6.2.4 Bohr atom model

Neils Bohr in 1913, modified Rutherford's atom model in order to explain the stability of the atom and the emission of sharp spectral lines. He proposed the following postulates :

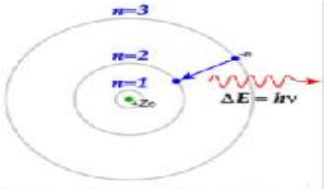


Fig.1. 6 A Bohr Picture of the Hydrogen Atom

(i) An electron cannot revolve round the nucleus in all possible orbits. The electrons can revolve round the nucleus only in those allowed or permissible orbits for which the angular momentum of the electron is an integral multiple of $\frac{h}{2\pi}$ (where h is Planck's constant = 6.626×10^{-34} Js). These orbits are called stationary orbits or non-radiating orbits and an electron revolving in these orbits does not radiate any energy.

If m and v are the mass and velocity of the electron in a permitted orbit of radius r then angular momentum of electron = $mvr = \frac{nh}{2\pi}$, where n is called principal quantum number and has the integral values 1,2,3 ... This is called Bohr's quantization condition.

(ii) An atom radiates energy, only when an electron jumps from a stationary orbit of higher energy to an orbit of lower energy. If the electron jumps from an orbit of energy E_2 to an orbit of energy E_1, a photon of energy $h\nu = E_2 - E_1$ is emitted. This condition is called Bohr's frequency condition.

Radius of the nth orbit (r_n)

Consider an atom whose nucleus has a positive charge Ze, where Z is the atomic number that gives the number of protons in the nucleus and e, the charge of the electron which is numerically equal to that of proton. Let an electron revolve around the nucleus in the nth orbit of radius r_n.

By Coulomb's law, the electrostatic force of attraction between the nucleus and the electron = $\frac{1}{4\pi\varepsilon_o}\cdot\frac{(Ze)(e)}{r_n{}^2}$ ...(1)

where ε_o is the permittivity of the free space.

Since, the electron revolves in a circular orbit, it experiences a centripetal force, $\frac{mv_n{}^2}{r_n} = mr_n\omega_n{}^2$ ...(2)

where m is the mass of the electron, v_n and ω_n are the linear velocity and angular velocity of the electron in the nth orbit respectively.

(or) $$r_n = \frac{n^2h^2\varepsilon_o}{\pi m Z e^2} \qquad \ldots(9)$$

From equation (9), it is seen that the radius of the nth orbit is proportional to the square of the principal quantum number. Therefore, the radii of the orbits are in the ratio 1 : 4 : 9....

For hydrogen atom, Z = 1

$\therefore$ From equation (9)

$$r_n = \frac{n^2h^2\varepsilon_o}{\pi m e^2} \qquad \ldots(10)$$

Substituting the known values in the above equation we get,

$r_n = n^2 \times 0.53$ Å

If $n = 1$, $r_1 = 0.53$Å

This is called Bohr radius.

Energy of an electron in the n^{th} orbit (E_n)

The total energy of the electron is the sum of its potential energy and kinetic energy in its orbit (Fig 6.10).

The potential energy of the electron in the nth orbit is given by,

$$E_p = \frac{(Ze)(-e)}{4\pi\varepsilon_o r_n} = \frac{-Ze^2}{4\pi\varepsilon_o r_n} \qquad \ldots(11)$$

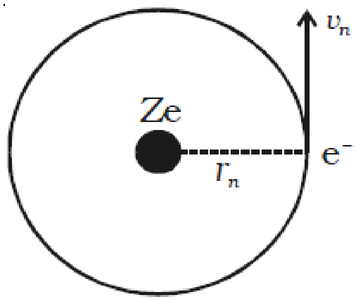


Fig 6.10 Energy of the electron

The kinetic energy of the electron in the nth orbit is,

$$E_k = \frac{1}{2}mv_n^{\,2} \qquad \ldots(12)$$

From equation (3),

$$\frac{1}{4\pi\varepsilon_o}\cdot\frac{Ze^2}{r_n} = mv_n^{\,2} \qquad \ldots(13)$$

Substituting equation (13) in (12)

$$E_k = \frac{1}{2}\left[\frac{1}{4\pi\varepsilon_o}\ \frac{Ze^2}{r_n}\right] = \frac{Ze^2}{8\pi\varepsilon_o r_n} \qquad \ldots(14)$$

The total energy of an electron in its nth orbit is,

$$E_n = E_p + E_k = \frac{-Ze^2}{4\pi\varepsilon_o r_n} + \frac{Ze^2}{8\pi\varepsilon_o r_n}$$

$$E_n = \frac{-Ze^2}{8\pi\varepsilon_o r_n} \qquad \ldots(15)$$

Substituting the value of r_n, from equation (10) in equation (15),

$$E_n = \frac{-Z^2 me^4}{8\varepsilon_o{}^2 n^2 h^2} \qquad \ldots(16)$$

For hydrogen atom, $Z = 1$

$$\therefore \quad E_n = \frac{-me^4}{8\varepsilon_o{}^2 n^2 h^2}$$

Substituting the known values and calculating in electron-volt,

$$E_n = \frac{-13.6}{n^2} eV \qquad \ldots(17) \qquad [\because 1eV = 1.602 \times 10^{-19} J]$$

As there is a negative sign in equation (17), it is seen that the energy of the electron in its orbit increases as n increases.

Frequency of spectral line

According to Bohr's second postulate, when an electron jumps from an outer orbit of quantum number n_2 to an inner orbit of quantum number n_1, the frequency of the photon emitted is given by,

$$\nu = \frac{E_{n_2} - E_{n_1}}{h}$$

Using equation (16)

$$\nu = \frac{Z^2 me^4}{8\varepsilon_o{}^2 h^3}\left(\frac{1}{n_1{}^2} - \frac{1}{n_2{}^2}\right) \qquad \ldots(18)$$

The wave number $\bar{\nu}$ of a radiation is defined as number of waves per unit length. It is equal to reciprocal of the wavelength

$$\bar{\nu} = \frac{1}{\lambda} = \frac{\nu}{c} \qquad [\text{since } c = \nu\lambda]$$

where c is the velocity of light

∴ From equation (18),

$$\bar{\nu} = \frac{Z^2 m e^4}{8\varepsilon_o^2 c h^3}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \qquad \ldots(19)$$

For hydrogen atom, Z=1

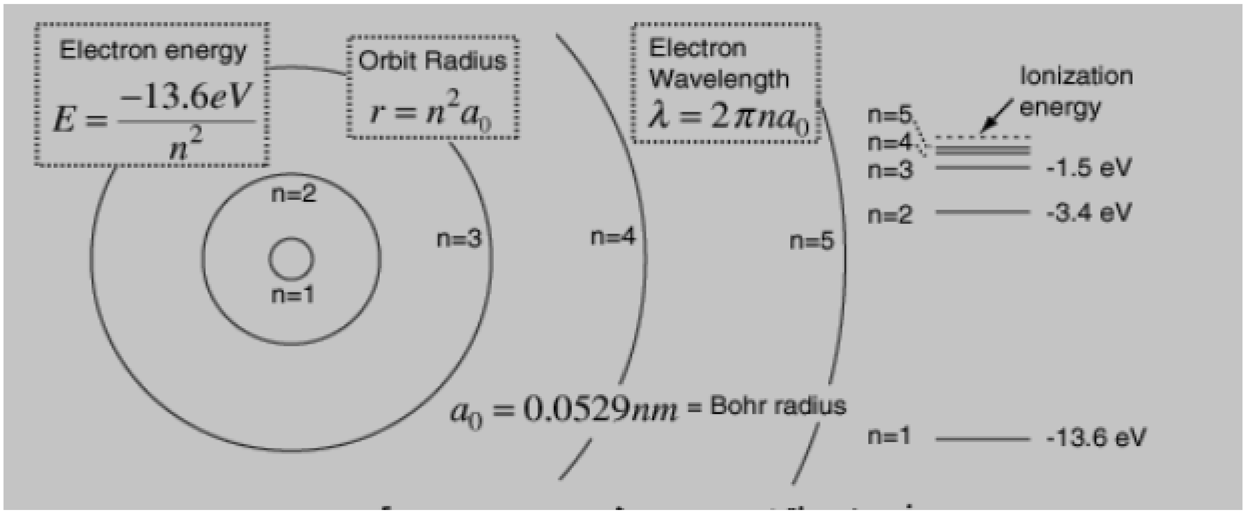
$$\bar{\nu} = \frac{m e^4}{8\varepsilon_o^2 c h^3}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) = R\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \qquad \ldots(20)$$

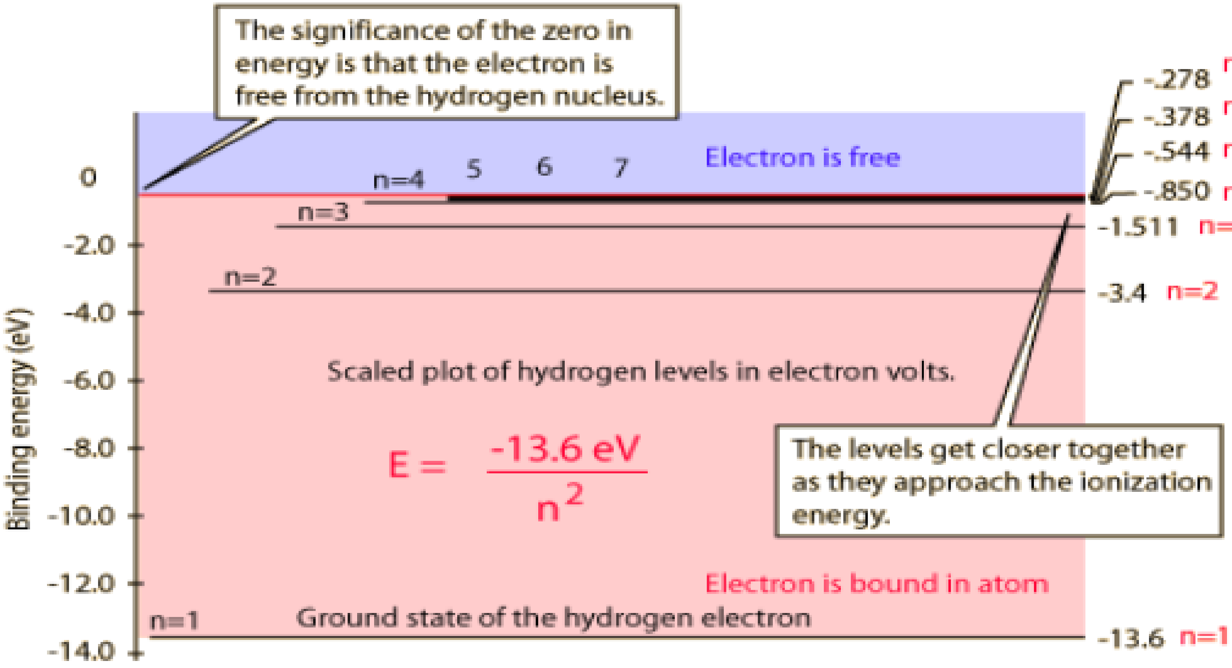
where R is a constant called Rydberg's constant

$$\therefore \quad R = \frac{m e^4}{8\varepsilon_o^2 c h^3} \qquad \ldots(21)$$

Substituting the known values, we get

$R = 1.094 \times 10^7 \text{m}^{-1}$





6.2.8 Excitation and ionization potential of an atom

According to Bohr's theory, there are certain discrete orbits permitted for the motion of the electron. Electron can revolve in these orbits without radiating energy. An atom is said to be in the ground state, when its energy is least. Before an atom can emit spectral radiation, the electron in it has to be raised to a higher orbit. This process is known as the excitation of the atom. The energy required to raise an atom from its normal state into an excited state is called *excitation potential energy* of the atom. For example, the energy required to transfer the electron in hydrogen atom from the ground state to the first excited state = (13.6-3.4) = 10.2eV. The energy required to raise it to the second excited state = (13.6 – 1.51) = 12.09 eV. The potentials corresponding to these energies are called as the excitation potentials.

The ionisation potential is that accelerating potential which makes the impinging electron acquire sufficient energy to knock out an electron from the atom and thereby ionise the atom. For hydrogen atom, the energy required to remove an electron from first orbit to its outermost orbit(n=∞) 13.6-0=13.6eV. This energy is known as the ionization potential energy for hydrogen atom. 13.6 V is the ionisation potential of hydrogen atom.

The excitation potential and ionization potential are called as the critical potentials of the atom. The *critical potential* of an atom, is defined as the minimum potential required to excite a free neutral atom from its ground state to higher state.

6.2.9 Shortcomings of Bohr's theory

Bohr's theory was able to explain successfully a number of experimental observations and has correctly predicted the spectral lines of hydrogen atom. However, the theory fails in the following aspects.

(i) The theory could not account for the spectra of atoms more complex than hydrogen.

(ii) The theory does not give any information regarding the distribution and arrangement of electrons in an atom.

(iii) It does not explain, the experimentally observed variations in intensity of the spectral lines of the element.

(iv) When the spectral line of hydrogen atom is examined by spectrometers having high resolving power, it is found that a single line is composed of two or more close components. This is known as the fine structure of spectral lines. Bohr's theory could not account for the fine structure of spectral lines.

(v) It is found that when electric or magnetic field is applied to the atom, each of the spectral line split into several lines. The former effect is called as Stark effect, while the latter is known as Zeeman effect. Bohr's theory could not explain the Stark effect and Zeeman effect.

6.2.10 Sommerfeld atom model

In order to explain the observed fine structure of spectral lines, Sommerfeld introduced two main modifications in Bohr's theory.

(i) According to Sommerfeld, the path of an electron around the nucleus, in general, is an ellipse with the nucleus at one of its foci.

(ii) The velocity of the electron moving in an elliptical orbit varies at different parts of the orbit. This causes the relativistic variation in the mass of the moving electron.

Now, when elliptical orbits are permitted, one has to deal with two variable quantities.

(i) The varying distance of the electron from the nucleus (r).

(ii) The varying angular position of the electron with respect to the nucleus i.e the azimuthal angle ϕ (Fig 6.13).

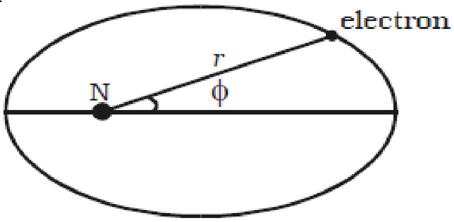


Fig 6.13 Sommerfeld atom model

To deal with these two variables, two quantum numbers are introduced

(i) The principal quantum number n of Bohr's theory, which determines the energy of the electrons, and (ii) a new quantum number called orbital (or azimuthal) quantum number (l) which has been introduced to characterize the angular momentum in an orbit i.e., it determines the orbital angular momentum of the electron. Its values vary from zero to (n-1) in steps of unity.

This orbital quantum number (l) is useful in finding the possible elliptical orbits. The possible elliptical orbits are such that

$$\frac{b}{a} = \frac{l+1}{n}$$

where a and b are semi-major and semi-minor axes respectively of the ellipse.

According to Sommerfeld's model, for any principal quantum number n, there are n possible orbits of varying eccentricities called sub-orbits or sub-shells. Out of n subshells, one is circular and the remaining (i.e., n-1) are elliptical in shape.

These possible sub-orbits possess slightly different energies because of the relativistic variation of the electron mass.

Consider the first energy level (n=1). When n = 1, l = 0 i.e., in this energy level, there is only one orbit or sub-shell for the electron. Also, when a = b, the two axes of the ellipse are equal. As a result of this, the orbit corresponding to n=1 is circular. This subshell is designated as s sub-shell. Since, this sub-shell belongs to n=1, it is designated as 1s (Fig 6.14a).

Similarly, for the second energy level n=2, there are two permissible sub-shells for the electrons. For n=2, l can take two values, 0 and 1.

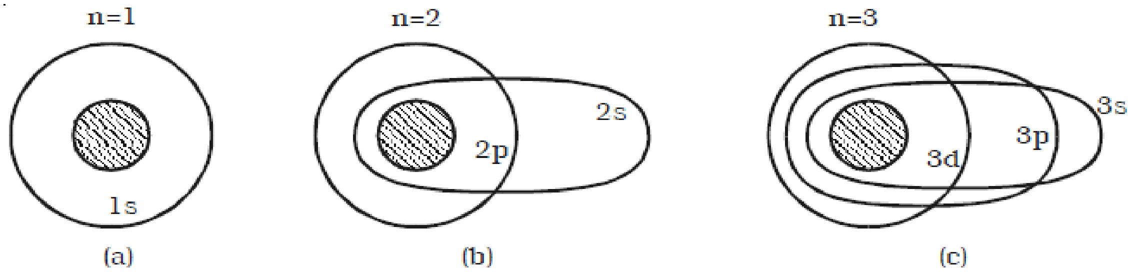


Fig 6.14 Various sub-shells for the electrons

When $n = 2$, $l = 0$.

$$\frac{b}{a} = \frac{0+1}{2} = \frac{1}{2} \quad \text{(or)} \quad b = \frac{a}{2}$$

This subshell corresponding to $l = 0$ is elliptical in shape and is designated as 2s.

when $n = 2$, $l = 1$.

$$\frac{b}{a} = \frac{1+1}{2} = \frac{2}{2} = 1 \qquad \text{(or)} \qquad b = a$$

This sub-shell corresponding to $l = 1$ is circular in shape and is designated as 2*p* (Fig 6.14b).

For n = 3, l has three values 0, 1 and 2, i.e. there are three permissible sub-shells for the electrons.

when n = 3, $l = 0$.

$$\frac{b}{a} = \frac{0+1}{3} = \frac{1}{3} \quad \text{(or)} \quad b = \frac{a}{3}$$

when n = 3, $l = 1$.

$$\frac{b}{a} = \frac{1+1}{3} = \frac{2}{3} \quad \text{(or)} \quad b = \frac{2a}{3}$$

and when n = 3, $l = 2$.

$$\frac{b}{a} = \frac{2+1}{3} = \frac{3}{3} \quad \text{(or)} \quad b = a$$

The sub-shells corresponding to $l = 0$, 1 and 2 are designated as 3s, 3*p* and 3*d* respectively. The circular shell is designated as 3*d* and the other two are elliptical in shape (Fig 6.14c).

It is common practice to assign letters to l-values as given below:

Orbital quantum number l	:	0	1	2	3	4
electron state	:	*s*	*p*	*d*	*f*	*g*

Hence, electrons in the $l = 0, 1, 2, 3$ ... states are said to be in the *s, p, d, f* ... states.

Fine structure of spectral line

Based on Sommerfeld atom model, the total energy of an electron in the elliptical orbit can be shown as,

$$E_n = \frac{-me^4Z^2}{8\varepsilon_o{}^2h^2n^2}$$

This expression is the same as that obtained by Bohr. Thus the introduction of elliptical orbits gives no new energy levels and hence no new transition. In this way, the attempt of Sommerfeld to explain the fine structure of spectral lines failed. But soon, on the basis of variation of mass of electron with velocity, Sommerfeld could find the solution for the problem of the fine structure of the spectral lines.

According to Sommerfeld, the velocity of the electron is maximum when the electron is nearest to the nucleus and minimum when it is farthest from the nucleus, since the orbit of the electron is elliptical. This implies that the effective mass of the electron will be different at different parts of its orbit. Taking into account the relativistic variation of the mass of the electron, Sommerfeld modified his theory and showed that the path of electron is not a simple ellipse but a precessing ellipse called a rosette (Fig 6.15).

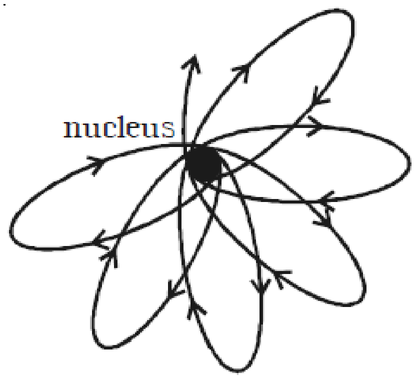


Fig 6.15 Rosette path of an electron

Based on this idea, Sommerfeld successfully explained the fine structure of spectral lines of hydrogen atom.

Drawbacks

(i) Though Sommerfeld's modification gave a theoretical background of the fine structure of spectral lines of hydrogen, it could not predict the correct number of observed fine structure of these lines.

(ii) It could not explain the distribution and arrangement of electrons in atoms.

(iii) Sommerfeld's model was unable to explain the spectra of alkali metals such as sodium, potassium etc.

(iv) It could not explain Zeeman and Stark effect.

(v) This model does not give any explanation for the intensities of the spectral lines.

7: Franck-Hertz experiment

7-1: Objectives

To verify the existence of discrete atomic energy levels of Argon atom and determine the minimum excitation energy of argon.

Planck (1900) put forward the idea of quantization while solving a long standing problem of the black body radiation. He proposed that the exchange of the energy between the radiation and the matter is discrete rather than continuous. This hypothesis fueled to look for a modification in the understandings of classical physics which only deals with the continuous exchange of energy.

In 1905, Einstein solved the photoelectric effect problem assuming the quantization of the light. Inspired from the success of Planck's hypothesis and Einstein's theory, Bohr proposed the quantization theory in describing the spectrum of hydrogen atom. According to Bohr's assumptions, the electron in an atom revolves around the nucleus in a circular orbit under the influence of the electrostatic attraction of the nucleus placed at the centre of the orbit. Also, the electron is allowed to move in a certain set of orbits called as stationary states with discrete energy values. While moving in these orbits the electron does not radiate its energy. In these orbits the angular momentum of the electron is quantized and can take values equal to the integral multiple of $h/2\pi$, where h is the Planck constant. Each of such states of atom having a fixed energy value are called as atomic energy level. The transitions from one energy level to another can happen only if a photon of the energy equal to the difference of energies between the two energy levels is absorbed or emitted. For instance a transition between two discrete atomic energy levels E_a and E_b is associated with emission or absorption of a photon of frequency

$$\nu=(E_a - E_b)/h.$$

Bohr's theory successfully explained the observed spectrum of the hydrogen atom and established the belief that the transfer of energy to the electrons in an atom by any mechanism should always be in discrete amounts. However, this theory required endorsements from the experiments other than the spectroscopy of Hydrogen.

One such mechanism of energy transfer is through the inelastic scattering of low-energy electrons which was explored through series of experiments on the mercury vapor by James Franck and Gustav Hertz in 1914. The results of this experiment are indictment that the atoms can absorb energy only in discrete amount, no matter how the energy is supplied to the atoms.

In 1914, James Franck and Gustav Hertz published the results of an experiment which provided strong evidence that Bohr's model of atoms with quantized energy levels was correct. But, in the haphazard manner of real research, the authors weren't trying to test Bohr's model; in fact, they **weren't even aware of Bohr's theory!**. As Franck admitted later "It might interest you to know that when we made the experiments that we did not know Bohr's theory. We had neither read nor heard about it. We had not read it because we were negligent to read the literature well enough -- and you know how that happens. On the other hand, one would think that other people would have told us about it. For instance, we had a colloquium at that time in Berlin at which all the important papers were discussed. Nobody discussed Bohr's theory. Why not? The reasons is that fifty years ago, one was so convinced that nobody would, with the state of knowledge we had at that time, understand spectral line emission, so that if somebody published a paper about it, one assumed, "Probably it is not right." So we did not know it. But we made that experiment (and got the result that confirmed Bohr's theory) because we hoped that if we found out where the borderline between elastic and inelastic impact lies ... only one line might appear. But we did not know whether that would be so, and we did not know whether at all an emission of an atom is of such a type that one line alone can be emitted and all the energy can be used for that purpose. The experiment gave it to us, and we were surprised about it. But we were not surprised after we read Bohr's paper later, after our publication."

A nice accident, to win a Nobel Prize (1925) for an experiment that you didn't really understand at the time.

In addition, Franck and Hertz interpreted their experimental results incorrectly in the paper below: they believed that the collisions between electrons and mercury atoms were ionizing the mercury atoms; but actually the collisions were exciting the mercury atoms from their ground n=1 state to the first excited n=2 state.

Fortunately, other scientists quickly realized how this experiment did confirm Bohr's hypothesis that atoms make only certain transitions between discrete energy states.

As per James Franck confessions (Gerald Holton, Americal Journal of Physics, vol. 29 p.805 (1961)) Franck and Hertz were not aware of Bohr’s theory while performing their experiment. The early days of spectroscopy and the close observation of spectral lines was motivation for the setup of this peculiar experiment. Their aim was to find the borderline between the elastic collision and inelastic collision with an expectation of only one emission line in the spectrum and to their surprise, they could reach to their expectation, and the emission line 4.89 eV for mercury which corresponds to the 2536 A ultraviolet line.

Theoretical Understanding

Thermionic emission is a useful technique to get a source of the electrons. The cathode plate while heated emits electrons with the very small kinetic energy. These electrons can be pushed by a grid (G1) kept on a slightly positive potential relative to the cathode plate while passing through the glass tube filled with an inert gas (See Fig. 1). In the original experimental set up by Franck and Hertz mercury vapours were kept inside the glass tube. However, in the present experimental set up the tube is filled with the argon gas. Usually the monoatomic gases like Argon, Mercury, Neon etc., are filled in the chamber in order to prevent complications involving molecular transitions. Few details about argon (Ref.: NIST Basic atomic spectroscopy data) are given below:

☐ Atomic number Z=18
☐ Electron configuration= [Ne]3s2 3p6
☐ 1st Ionization energy=15.75 eV
☐ 2nd Ionization energy=27.62 eV
☐ 3rd Ionization energy=40.74 eV

Accelerating potential is applied by introducing another grid (G2) which is kept positive relative to the cathode and anode plates. This grid G2 acts as a filter for higher energy electrons to pass through it.

During the motion of electrons from the cathode to anode plate there is a possibility of collision with the gas atoms inside the tube. This collision may be elastic or inelastic in nature depending upon the energy of the electrons. If the electron collides with the argon gas elastically the energy loss of the electron will be negligible (me << MAr) and electron would pass through the anode without affecting the Argon atom.

In the case of argon this elastic collision happens for the electrons with energy less than 11.83 eV.

If the electron acquires energy nearly equal to 11.83 eV, the collision is inelastic and a part of the energy of the electron may be available to excite the argon atom. The energy level diagram of argon atom is shown in fig. 2. **The electron after collision slows down and unable to reach at the anode depending**

upon the potential difference between the grid G2 and anode. This results a drop in the current while increasing the potential between the cathode and grid G 2.

Let us consider that the electron is accelerated due to the potential difference V between the cathode and grid G2 and V-ΔV be the potential difference between the grid G2 and the anode. In that case the electron needs minimum eΔV energy to reach at the anode and contribute to the current in the circuit.

The Franck-Hertz experiment demonstrates that the current in the circuit increase as we increase the potential V till a cutoff value Vc1 is reached with a maximum current output. However, above Vc1, the current declines and reaches to minimum at Vc2. This trend follows the pattern of periodic maximum and minimum currents in the circuit (Fig. 4). Classical physics has no explanation of this behavior.

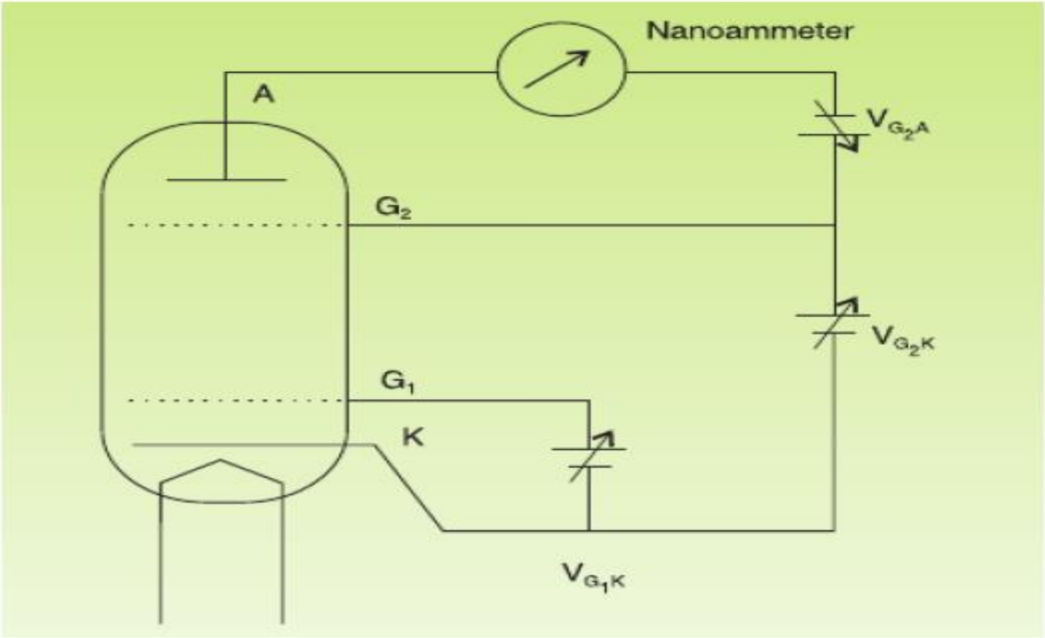


Fig. 1 A circuit diagram for the Franck-Hertz experiment. (Diagram is taken from the user Manual for FH3001)

This maxima and minima of the output current can be explained by the inelastic collision of electrons with the argon atoms. Only those electrons with a critical value Vc1 hitting the argon atoms, transfer their energy and excite the argon atoms. During the process of inelastic collision they loss their kinetic energy, and unable to reach the anode resulting a significant drop in the current output after Vc1.

At Vc2 maximum number of these energetic electrons loase their energy and a minimum in current can be observed. Others electrons still have sufficient energy to pass through the barrier voltage between the anode and grid G2 and contribute to the net current. It is interesting to see that both the minimum and maximum values of the current grow larger with increasing accelerating voltage in a similar fashion of a diode or a tetrode. Further increasing the voltage again raises the energy of the electrons. There is a possibility that those electrons who retarded after exciting the argon atom gain sufficient energy between two collision and excite several argon atoms. Another possibility is that the electrons starting from the cathode gain sufficient energy to excite more than one atom. Therefore, the peak of the next maximum is higher than the preceding one. A sharp downfall of the current after the second peak can be attributed to those electrons that suffered two inelastic collisions with two argon atoms, losing all their kinetic energy and so on.

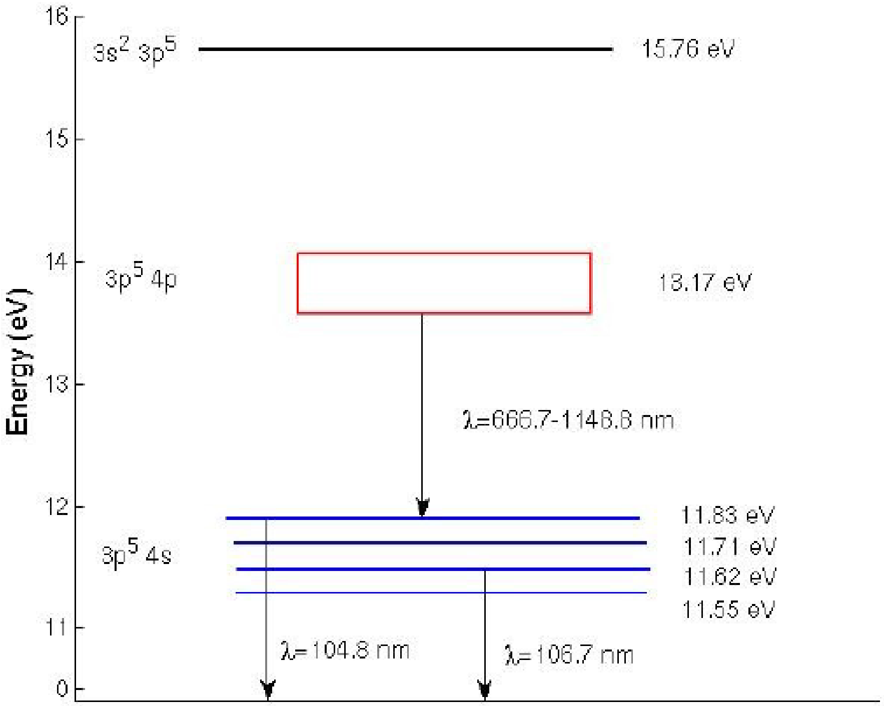


Fig. 2 Energy level diagram for Argon atom.

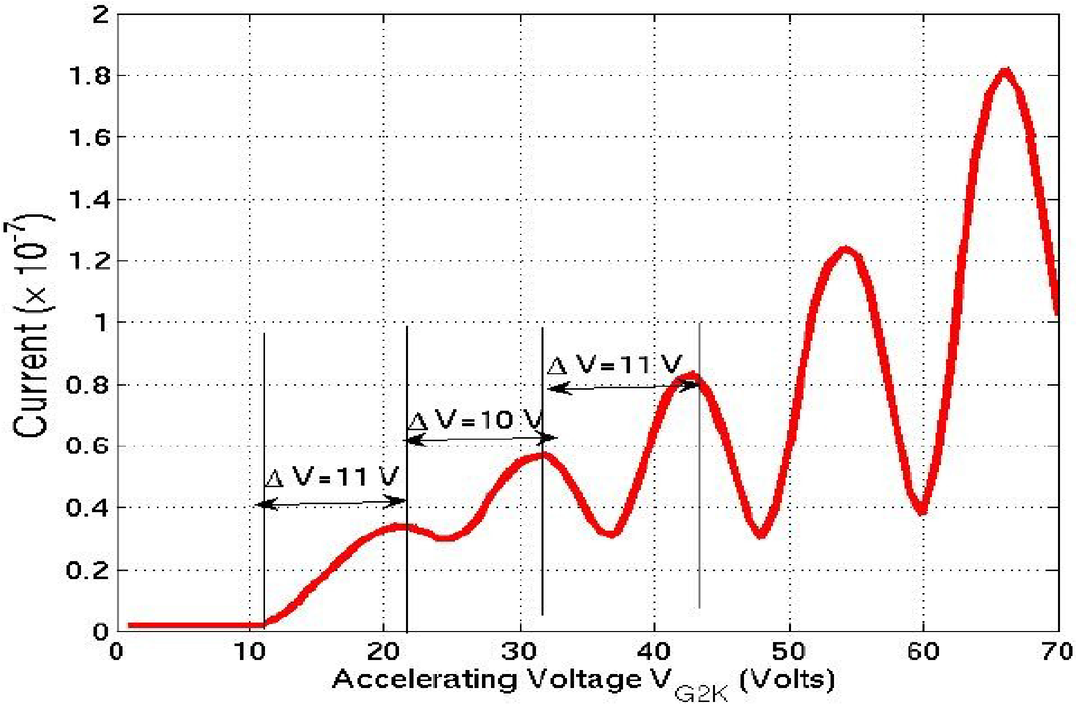


Fig. 4 The current vs accelerating voltage VG2K observed from the Franck-Hertz experiment for the argon atoms.

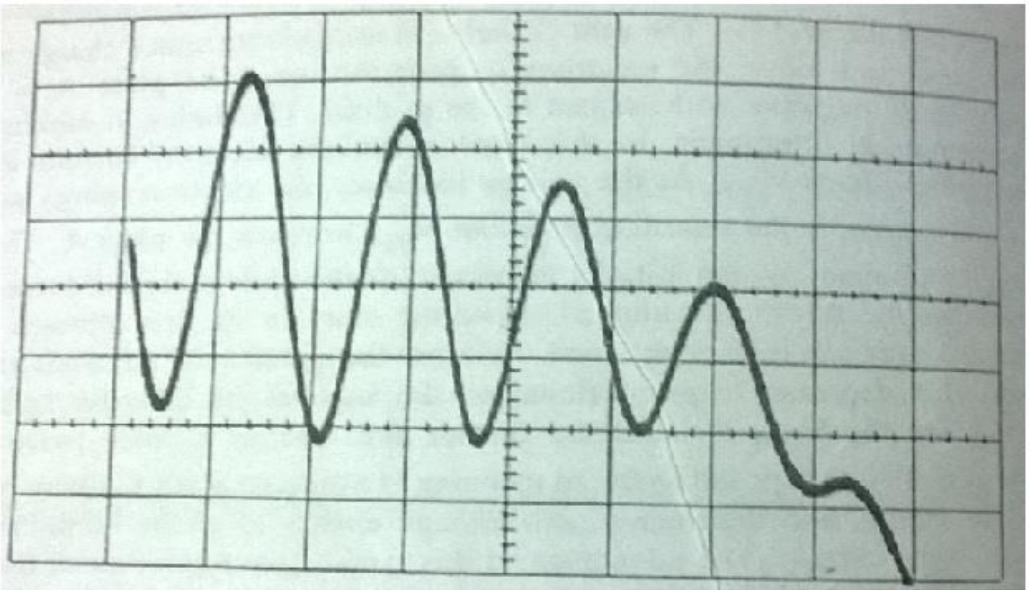
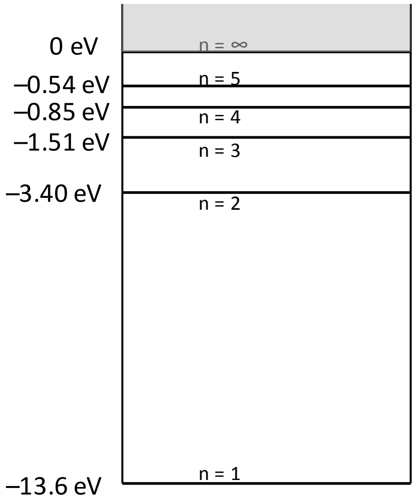


Fig. 5 Display of the CRO screen arranged for the Franck-Hertz experiment.

Problems

1. Describe how the emission and absorption spectra of hydrogen are explained by the Bohr model of the atom.
2. What are the strengths of the Bohr model? What are the weaknesses of the Bohr model?

Use the energy level diagram for hydrogen to answer questions 5 to 11.



3. How much energy must a hydrogen electron in energy level n = 1 absorb in order to jump to energy level n = 2 and n = 3? (10.2 eV, 12.1 eV)
4. How does the total energy of photons emitted by an electron as it jumps back down to its ground state compare with the energy absorbed by the electron when it jumped to the higher level?
5. Why is a blue photon emitted when a hydrogen electron jumps from energy level n = 5 to n = 2, but a red photon is emitted when an electron jumps from level n = 3 to n = 2?
6. What is the ionization energy for the electron in hydrogen from its ground state?
7. What is the wavelength of a photon emitted when an electron in a hydrogen atom falls:
   A. From n = 4 to n = 2. (487 nm)

B. From n = 5 to n = 1. (95.1 nm)

8. Electrons are accelerated through hydrogen gas at room temperature in a Franck-Hertz experiment by a potential difference of 12.3 V. What wavelengths of light can be expected to be emitted by the hydrogen? (122 nm, 103 nm, 657 nm)

9. What energy is needed to ionize hydrogen from the n=2 state? How likely is this to occur? Explain. (3.40 eV)

10. Use the energy level diagram below to answer the following questions.

$n = \infty$	0.000 eV
$n = 9$	-0.450 eV
$n = 8$	-0.570 eV
$n = 7$	-0.744 eV
$n = 6$	-1.013 eV
$n = 5$	-1.458 eV
$n = 4$	-2.278 eV
$n = 3$	-4.050 eV
$n = 2$	-9.113 eV
$n = 1$	-36.450 eV

11. What is the wavelength of the photon emitted when an electron falls from the sixth to second energy level? (153 nm)

12. What is the frequency of the photon emitted when an electron falls from n = 7 to n = 3? (7.987×10^{14} Hz)

13 What is the energy absorbed by an electron to jump from n = 1 to n = 8? (35.880 eV)

14. What is the ionization energy of this element?

15. Hydrogen atoms in states of high quantum number have been created in a lab. (a) Find the quantum number of the Bohr orbit in a hydrogen atom whose radius is 0.01 mm. (b) What is the energy of a hydrogen atom in this state?

Solution:

(a) $$n=\sqrt{\frac{r_n}{a_0}}=\sqrt{\frac{1.0\times 10^{-5}m}{5.29\times 10^{-11}}}=435$$

(b) $$E_n=\frac{E_1}{n^2}=\frac{-13.6eV}{(435)^2}=-7.19\times 10^{-5}eV$$

16. Find the longest wavelength present in the Balmer series of hydrogen, corresponding to the Hα line.

In the Balmer series the quantum number of the final state is $n_f=2$. The longest wavelength corresponds to the smallest energy difference between energy levels. Hence the initial state must be $n_i=3$. Then

Solution:

$$\frac{1}{\lambda}=R(\frac{1}{n_f^2}-\frac{1}{n_i^2})=R(\frac{1}{2^2}-\frac{1}{3^2})=0.139R$$

$$\lambda=\frac{1}{0.139R}=6.56\times 10^{-7}m;$$

This wavelength is near the red end of the visible spectrum.

17. Find the de Broglie wavelength of (a) a 46-g golf ball with a velocity of 30 m/s, and (b) an electron with a velocity of 10^7 m/s.

Solution:

Both speeds are nonrelativistic: $v \ll c$. Hence:

$$\text{(a)}\ \lambda = \frac{h}{mv} = \frac{6.63\times10^{-34}\,J\cdot s}{(0.046\,kg)(30\,m/s)} = 4.8\times10^{-34}\,m$$

The wavelength of the golf ball is so small compared with its dimensions that we would not expect to find any wave aspect in its behavior.

$$\text{(b)}\ \lambda = \frac{h}{mv} = \frac{6.63\times10^{-34}\,J\cdot s}{(9.1\times10^{-31}\,kg)(10^{7}\,m/s)} = 7.3\times10^{-11}\,m$$

The dimensions of atoms are comparable with this figure—the radius of the hydrogen atom, for instance, is 5.3×10^{-11} m. Thus, we need the wave properties of a moving electron to understand atomic structure and behavior.

18. Hydrogen atoms in states of high quantum number have been created in a lab. (a) Find the quantum number of the Bohr orbit in a hydrogen atom whose radius is 0.01 mm. (b) What is the energy of a hydrogen atom in this state?

Solution:

$$\text{(a)}\ n = \sqrt{\frac{r_n}{a_0}} = \sqrt{\frac{1.0\times10^{-5}m}{5.29\times10^{-11}}} = 435$$

$$\text{(b)}\quad E_n = \frac{E_1}{n^2} = \frac{-13.6eV}{(435)^2} = -7.19\times10^{-5}eV$$

20. Find the longest wavelength present in the Balmer series of hydrogen, corresponding to the Hα line.

In the Balmer series the quantum number of the final state is $n_f=2$. The longest wavelength corresponds to the smallest energy difference between energy levels. Hence the initial state must be $n_i=3$. Then

Solution:

$$\frac{1}{\lambda}=R(\frac{1}{n_f^2}-\frac{1}{n_i^2})=R(\frac{1}{2^2}-\frac{1}{3^2})=0.139R$$

$$\lambda=\frac{1}{0.139R}=6.56\times10^{-7}m;$$

This wavelength is near the red end of the visible spectrum.

21. Find the de Broglie wavelength of (a) a 46-g golf ball with a velocity of 30 m/s, and (b) an electron with a velocity of 10^7 m/s.

Solution:

Both speeds are nonrelativistic: $v \ll c$. Hence:

$$\text{(a)}\ \lambda=\frac{h}{mv}=\frac{6.63\times10^{-34}J\cdot s}{(0.046kg)(30m/s)}=4.8\times10^{-34}m$$

The wavelength of the golf ball is so small compared with its dimensions that we would not expect to find any wave aspect in its behavior.

$$\text{(b)}\ \lambda=\frac{h}{mv}=\frac{6.63\times10^{-34}J\cdot s}{(9.1\times10^{-31}kg)(10^7m/s)}=7.3\times10^{-11}m$$

The dimensions of atoms are comparable with this figure—the radius of the hydrogen atom, for instance, is 5.3×10^{-11} m. Thus, we need the wave properties of a moving electron to understand atomic structure and behavior.

22. Using Balmer's formula, calculate the wave lengths of the first few lines of the visible regions of the hydrogen atomic spectrum n=3, n=4

Solution:

The first line is obtained by setting n= 3

$$\bar{\nu}=109.680\left(\frac{1}{2^2}-\frac{1}{3^2}\right)\mathbf{Cm^{-1}}$$

$\bar{\nu}$ **=1.523x10^{4}Cm^{-1}**

$$\bar{\nu}=\frac{1}{\lambda}$$

$\lambda = 6.564\times10^{-5}$Cm = 6564 Å

The next line is obtained by setting n=4

$$\bar{\nu} = 109.680\left(\frac{1}{2^2} - \frac{1}{4^2}\right) \text{ Cm}^{-1}$$

$\bar{\nu} = 2.056\times10^{4}$Cm^{-1}

$\lambda = 4.863\times10^{-5}$Cm=4863 Å

The Balmer series occurs in the visible and near ultraviolet regions. There are lines in the hydrogen atomic spectrum in other regions; in fact there are series of lines similar to the Balmer series in the ultraviolet and in the infrared region.

The Rydberg formula accounts for all the lines in the hydrogen atomic spectrum. Rydberg accounted for all lines in the hydrogen atomic spectrum by generalizing the Balmer formula to

$$\bar{\nu} = 109.680\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) Cm^{-1} \quad (n_2 > n_1) \qquad \textbf{(1-15)}$$

This equation is called Rydberg formula.

The constant in Eq 1-15 is called Rydberg Constant

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

R_H is the Rydberg constant = 109.67 Cm^{-1}

23. Calculate the wavelength of the second line in the Paschen series and show that this line lies in the near infrared, that is, in the infrared region near the visible.

Solution:

In the paschen series, n_1=3 and n_2= 4, 5, 6… According to figure Thus the second line in the Paschen series is given by setting n_1=3 and n_2=5 in Eq. 1-15:

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

$$\bar{\nu} = 109.680\left(\frac{1}{3^2}-\frac{1}{5^2}\right)\ \mathrm{Cm}^{-1}$$

$$\bar{\nu} = 7.799\times10^{3}\,\mathrm{Cm}^{-1}$$

$$\because\quad \lambda=\frac{1}{\bar{\nu}}$$

$$\because\quad \lambda=1.282\times10^{-4}\ \mathrm{Cm}=12.820\ \text{Å}$$

Atomic Structure MCQs

1. Arnold Sommerfeld improved Niels Bohr's atomic model by proposing that electrons had _____ orbitals around the nucleus.

- **a. circular**
- **b. no**
- **c. elliptical**
- **d. triangular**

2. Arnold Sommerfeld’s semi-classical electron theory would become the foundation of which modern field in physics?

- **a. Quantum Theory of Solids**
- **b. General Relativity**
- **c. Quantum Electrodynamics**
- d. **Electromagnetism**

3-Sommerfeld’s modification in Bohr’s model is

A. Orbit is cylindrical
B. Orbit is elliptical
C. Orbit is longitudinal
D. Orbit is asymmetrical

4. Quantum number which tells the energy of an electron is

A. n
B. 1
C. m
D. s

5. Who was measured the size of the nucleus

A. Rutherford
B. Thomson
C. Newton
D. None of these

6. The sum of a number of proton and neutron is called:

A. Atomic number
B. Mass number
C. Isotopes
D. None of these

7.The Atomic number is:

1. Number of electrons
2. Number of neutrons
3. Number of protons
4. All of these

8. Which of the following statements is **NOT** part of Dalton's atomic model?
a) each element has its own type of atom
b) atoms of the same element are identical

c) all matter is made of tiny particles called atoms
d) atoms can be broken down into sub-atomic particles

9. Which atomic model was the **first** one to include electrons?
a) Dalton's billiard ball model
b) Thomson's raisin bun model
c) Rutherford's electron cloud model
d) Bohr's planetary model

10. The cathode ray tube was instrumental in the discovery of:

a) the electron b) the proton c) the neutron
d) the atom, which is mostly empty space

11. Which atomic model was the **first** one to include a nucleus?
a) Dalton’s billiard ball model b) Thomson’s raisin bun model
c) Rutherford’s electron cloud model d) Bohr’s planetary model

12. Which of the following items was used by Bohr to investigate the structure of the atom?
a) x-rays b) cathode ray tube c) spectroscope d) particle accelerator

13. What is the key difference between the models of the atom proposed by Bohr and Rutherford?
a) Bohr’s model includes a nucleus, but Rutherford’s does not
b) Bohr’s model has the atom made up of mostly empty space, but Rutherford’s does not
c) Bohr’s model includes neutrons, but Rutherford’s does not
d) Bohr’s model has the electrons moving in fixed energy levels, while in Rutherford’s they do not
12. The gold foil experiment contributed to the discovery that:
a) atoms contain electrons b) atoms contain a nucleus
c) atoms are mostly empty space d) both “b” and “c”
13. Which of the following is/are part of Bohr’s interpretation of the hydrogen line spectrum?
a) electrons release energy as light as they move to a higher energy level
b) different wavelengths of light correspond to electrons dropping between different quantum levels
c) the potential energy of an electron decreases as it moves further from the nucleus
d) all of the above

14. Which of the statements of Dalton’s atomic model is now known to be incorrect?
a) each element has its own type of atom
b) atoms of the same element are identical

c) all matter is made of tiny particles called atoms
d) atoms can be joined together to form compound

Chapter (4)

Atomic Spectra

Chapter (4)
Atomic Spectra

Electromagnetic Spectrum

The electromagnetic spectrum covers electromagnetic waves with frequencies ranging from below one hertz to above 10^{25} hertz, corresponding to wavelengths from thousands of kilometers down to a fraction of the size of an atomic nucleus. This frequency range is divided into separate bands, and the electromagnetic waves within each frequency band are called by different names; beginning at the low frequency (long wavelength) end of the spectrum these are: radio waves, microwaves, terahertz waves, infrared, visible light, ultraviolet, X-rays, and gamma rays at the high-frequency (short wavelength) end. The electromagnetic waves in each of these bands have different characteristics, such as how they are produced, how they interact with matter, and their practical applications. The limit for long wavelengths is the size of the universe itself, while it is thought that the short wavelength limit is in the vicinity of the Planck length.[4]

Gamma rays, X-rays, and high ultraviolet are classified as *ionizing radiation* as their photons have enough energy to ionize atoms, causing chemical reactions. Exposure to these rays can be a health hazard, causing radiation sickness, DNA damage and cancer. Where as, radiation of visible light wavelengths and lower are called *nonionizing radiation* as they cannot cause these effects. In most of the frequency bands above, a technique called spectroscopy can be used to physically separate waves of different frequencies, producing a spectrum showing the constituent frequencies.

Spectroscopy is used to study the interactions of electromagnetic waves with matter.[5] Other technological uses are described under electromagnetic radiation.

• Electromagnetic radiation and matter

Electromagnetic radiation exhibits properties of both particles and waves, known as the wave–particle duality. In the wave model, electromagnetic radiation is characterized by its frequency, υ , wavelength, λ, and velocity, c. These three values are related by the relationship

$$C = \upsilon \lambda \quad \text{------------------------}(1)$$

The value of c is constant in a given medium (e.g., 2.99 9 10^8 ms-1 in vacuum), while the frequency and wavelength of light are inversely proportional to one another. The SI units for wavelength and frequency are the meter (m) and the hertz (Hz), respectively. Traditionally, spectroscopy also define electromagnetic radiation by the unit wavenumbers, defined as

$$\tilde{\upsilon} = \lambda^{-1} \ \text{cm}^{-1} \quad \text{------------------}(2)$$

where λ denotes the wavelength in centimeters.

The energy of a photon (quantum of electromagnetic radiation) depends solely on its frequency (or wavelength) and is defined as:

$$E = h\upsilon = hc / \lambda = h\,c\,\tilde{\upsilon} \quad \text{----------------------------}(3)$$

where h is Planck’s constant (6.63 9 10^{-34} Js) [1]. Note that energy is directly proportional to frequency and wavenumber, and inversely proportional to wavelength. General ranges for frequency, wavelength, and energy limits for several regions of the electromagnetic spectrum are given in Table 1.1.

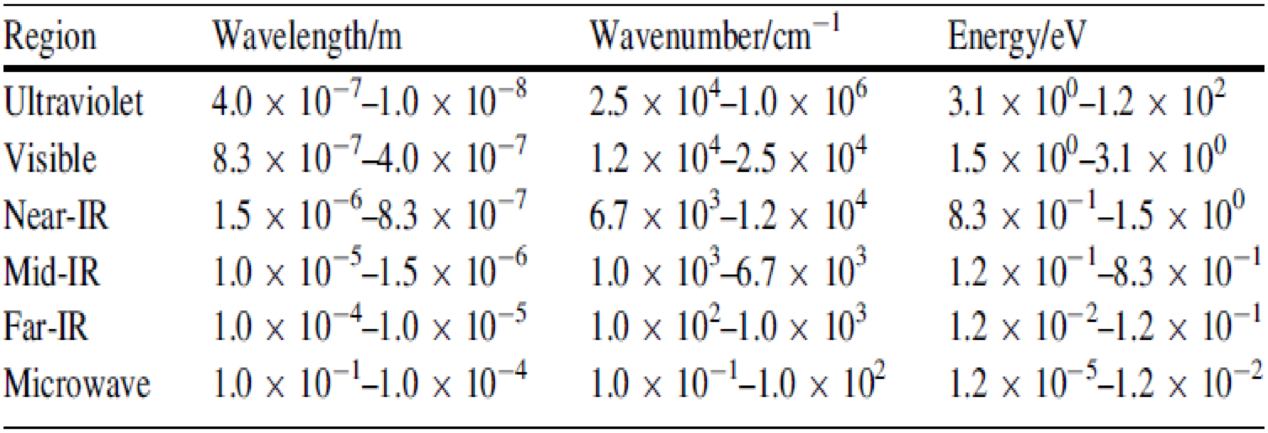


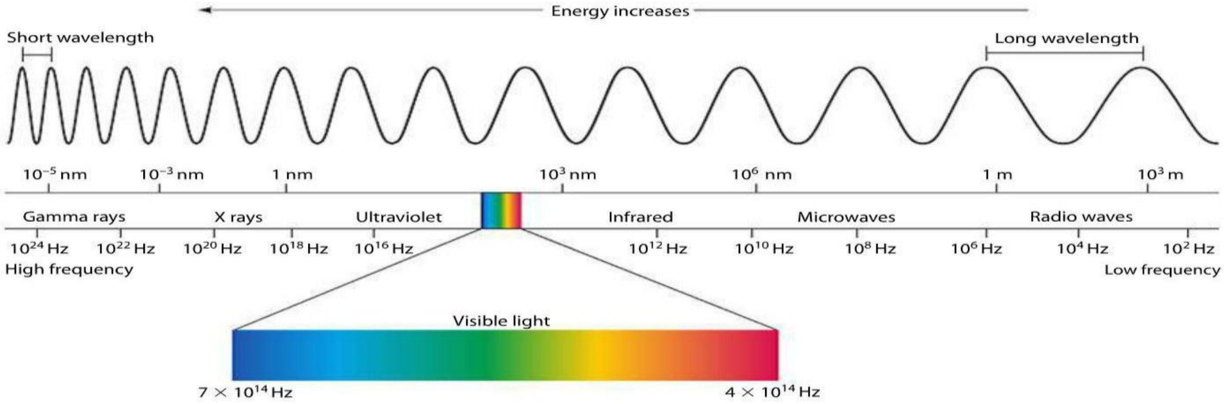
Table 1.1 Summary of the frequency, wavenumber, and energy ranges for several regions of the electromagnetic spectrum

Region	Wavelength/m	Wavenumber/cm^{-1}	Energy/eV
Ultraviolet	4.0×10^{-7}–1.0×10^{-8}	2.5×10^{4}–1.0×10^{6}	3.1×10^{0}–1.2×10^{2}
Visible	8.3×10^{-7}–4.0×10^{-7}	1.2×10^{4}–2.5×10^{4}	1.5×10^{0}–3.1×10^{0}
Near-IR	1.5×10^{-6}–8.3×10^{-7}	6.7×10^{3}–1.2×10^{4}	8.3×10^{-1}–1.5×10^{0}
Mid-IR	1.0×10^{-5}–1.5×10^{-6}	1.0×10^{3}–6.7×10^{3}	1.2×10^{-1}–8.3×10^{-1}
Far-IR	1.0×10^{-4}–1.0×10^{-5}	1.0×10^{2}–1.0×10^{3}	1.2×10^{-2}–1.2×10^{-1}
Microwave	1.0×10^{-1}–1.0×10^{-4}	1.0×10^{-1}–1.0×10^{2}	1.2×10^{-5}–1.2×10^{-2}

●The Nature of Electromagentic Spectrum

Visible (vis) light, microwaves, X-rays, and so forth are all different kinds of electromagnetic radiation. Taken collectively, they make up the electromagnetic spectrum, depicted in Fig. 1.1. The electromagnetic spectrum is arbitrarily divided into regions, and it is clear that the familiar, visible portion of the spectrum (i.e., 390–750 nm) constitutes only a small section of the full spectrum. The visible region is flanked by the higher-energy, ultraviolet (UV) and the lower-energy, infrared (IR) and microwave regions.

These frequency ranges are the most widely used in spectroscopic measurements, as they can each provide key structure



The electromagnetic spectrum, starting with low frequency and low wavelength on the left. (Image source)

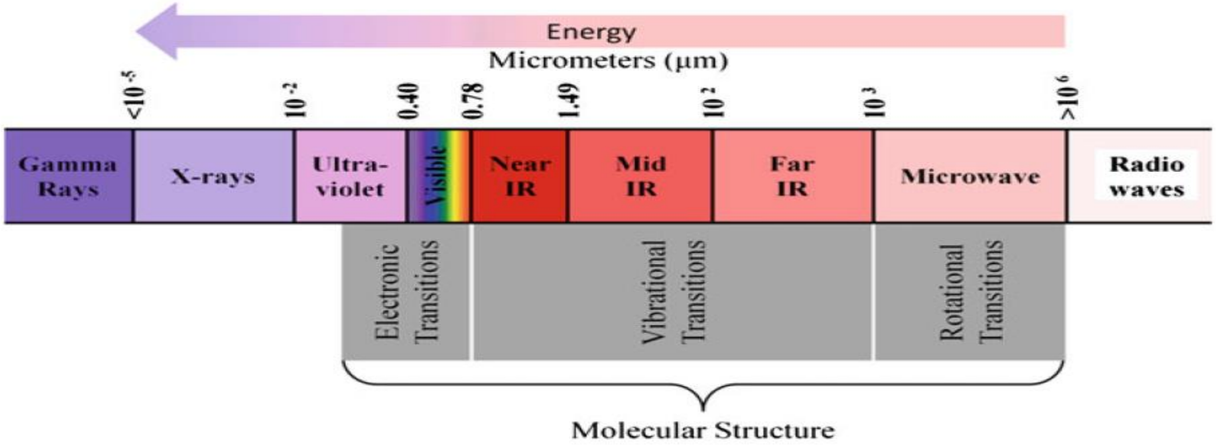
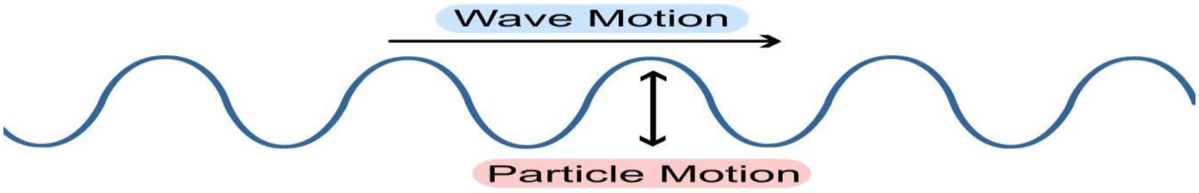


Fig. 1.1 The electromagnetic spectrum covers a continuous range of wavelengths, from low-energy radio waves to gamma (γ) rays at the high-energy end

Table.2 Molecular Energy levels and the Regions of Electromagnetic Radiation

Region of the Spectrum	Frequency Range (Hz)	Wavelength Range	Energy range	Kind of Spectroscopy
X-rays	3×10^{16} to 3×10^{18}	10nm to 100pm	~10^4 kJ/mol	**X-ray photo-electron Spectroscopy (inner electrons)**
Visible and UV	3×10^{14} to 3×10^{16}	1μm to 10nm	~10^2 kJ/mol	**Electronic Spectroscopy**
Infrared	3×10^{12} to 3×10^{14}	100μm to 1μm	~10 kJ/mol	**Vibrational Spectroscopy**
Microwave	3×10^{10} to 3×10^{12}	1cm to 100μm	100J/mol	**Rotational Spectroscopy**
Radio frequency	3×10^{6} to 3×10^{10}	10m to 1 cm	0.001 to 10J/mol	**Magnetic Resonance Spectroscopy**

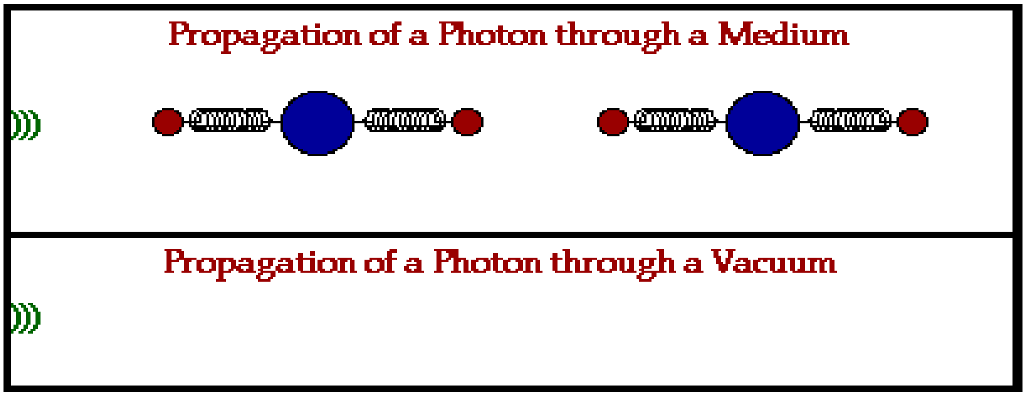
Unlike mechanical waves, electromagnetic waves don't require the presence of physical medium, and you'll find them hurtling through the emptiness of space without a second thought. Electromagnetic waves are unique in their composition, bringing together both electric and magnetic fields, which dance together in a perfect spiral as they go traveling about space as a transverse wave.



Transverse waves have both a vertical wave* motion *and a horizontal particle motion.

Because electromagnetic waves don't need a physical medium to travel through to get from point A to B, they're also the fastest wave known to man and can travel through a vacuum of space at the speed of **3.00×10^8 m/s**! That's not to say that these waves can't travel through a physical medium, it just works a little differently when they do. Let's break it down:

- **Absorption**. First, an electromagnetic wave hits the atoms of a physical material, which absorbs the wave.
- **Vibrations**. The absorption of this electromagnetic energy causes the electrons within this atom to start vibrating.
- **Release**. The atom that absorbed the electromagnetic energy releases yet another electromagnetic wave, passing it on to the next atom in line.



How an electromagnetic wave travels through a physical medium is way different than its journey in a vacuum.

In a physical medium, this process of an electromagnetic wave getting absorbed and ejected from atom to atom will cause the wave to travel slightly slower than it does through a vacuum. The denser the physical material, the more delayed the electromagnetic wave will move.

●Classification of Electromagnetic Spectrum

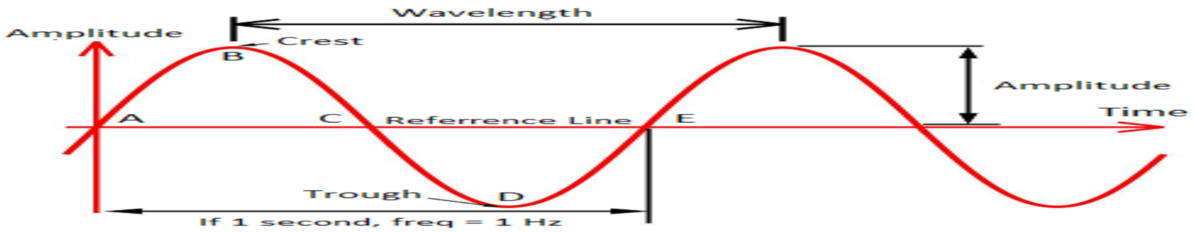
Before diving into all the forms of electromagnetic waves, first, we need to understand how these waves are measured, which also gives you a clue as to how they get organized in the spectrum. While all waves take different shapes, every electromagnetic wave that you'll encounter has the same S-shaped (sine wave) curve as shown below.

These are called **transverse waves**. You can measure these transverse waves in several ways:

- **By Amplitude.** Measuring a transverse wave by its height will get you its amplitude, which measures the wave from the zero point on an x-axis to the top of the highest point of the wave.

- **By Wavelength.** You can also measure an electromagnetic wave by the distance between the two highest points between two waves, called the crests. This gets you the wavelength. Wavelengths can be shorter than the size of an atom, and longer than the diameter of our entire planet!

- **By Frequency.** Lastly, you can measure how many crests pass through a given point every second. How many crests pass a given time is called a wave, or cycle, and is measured in Hertz (Hz). For example, a wave that has four cycles passing through a given point in a second will have a frequency of 4Hz.



Here you can see how we get amplitude, wavelength, and frequency by observing how an electromagnetic wave travels.

All electromagnetic waves are organized in a very detailed hierarchy, all based on our measurements of both frequency and wavelength. Electromagnetic waves on this spectrum progress in order of increasing frequency and decreasing wavelength, like so:

Radio Waves

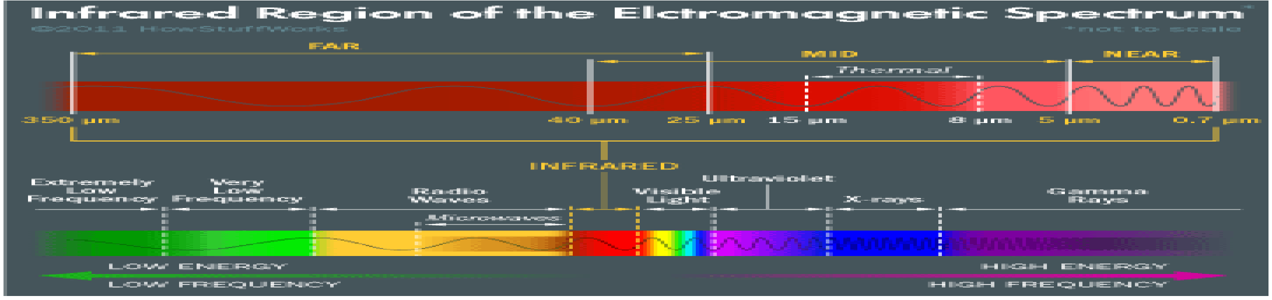
At the minimum end of the electromagnetic spectrum are radio waves, which have frequencies ranging from 30 gigahertz (GHz) to 3 kilohertz (kHz). As the name suggests, radio waves are most famous for their use in radio stations, and if you're listening to AM radio, then you'll be dialing into a specific radio frequency between 520 and 16010. AM radio stations are measured as thousands of hertz per second, called kilohertz (kHz).

You also have FM radio frequencies, which can be dialed in between 87.0 and 107.9 million hertz per second, called megahertz (MHz). Outside of traditional radio, you'll also find radio waves powering nearly all of our wireless electronic systems, like WiFi, Bluetooth, cell phone signals, and even radar. Radio waves can even measure how fast a pitcher throws a baseball using a speed gun or speed camera!.

Microwaves

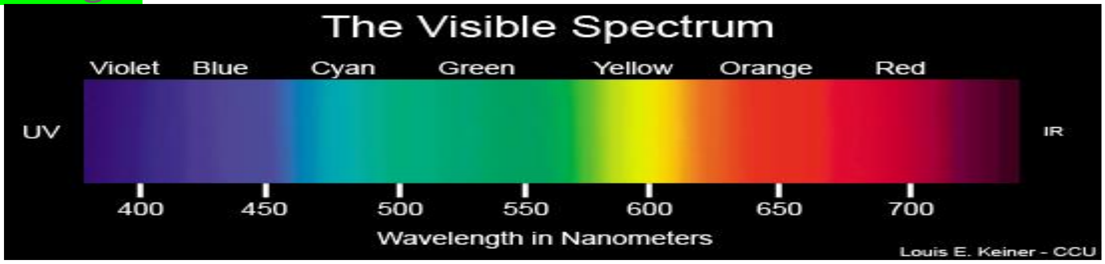
Microwaves rest smack dab in the middle of radio waves and infrared waves and have a frequency between 3 gigahertz (GHz) and 30 terahertz (THz). You won't find microwaves being used just to heat up your leftover for lunch though. Microwaves also have some traditional uses in other high-bandwidth devices, like radar, television, and satellites.

Infrared Waves



Before electromagnetic waves start to become visible, they take on the form of infrared waves. These have a frequency from 30 terahertz (THz) to 400 THz with wavelengths that measure as small as 0.00003 inches! Like all other waves before the visible spectrum, infrared is completely invisible to the human eye although they can be felt as heat. You'll find infrared being used in TV remote controls, and also for thermal imaging for use in night vision goggles in all of your favorite spy movies. Your body also produces infrared waves, just like the sun!

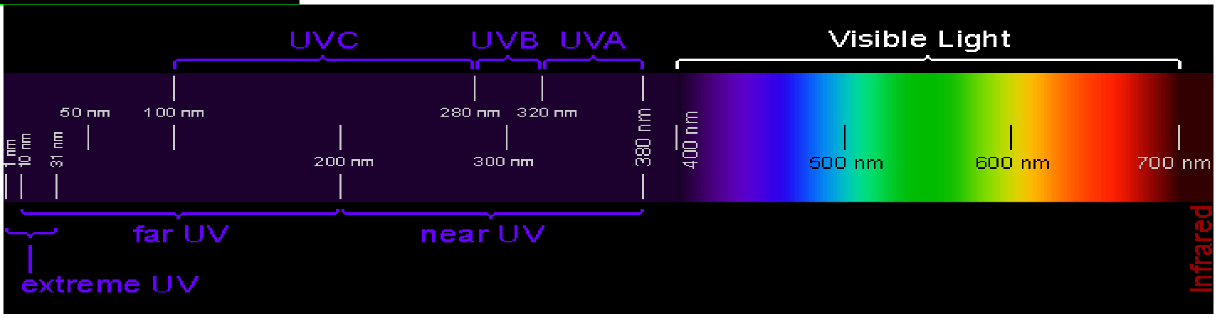
Visible Light



Finally, we come to the one and only visible part of the electromagnetic wave spectrum that our human eyes can behold visible light! This form of electromagnetic energy is visible to all of us as the spectrum of colors found in a rainbow. Colors have a particular wavelength on the electromagnetic spectrum, here's just a few:

- **Red** has the longest wavelength measuring around 700 nanometers.
- **Yellow** comes in second with a wavelength measuring 600 nanometers.
- **Violet** trails in last, with the shortest wavelength measuring at 400 nanometers.

Ultraviolet Waves



Beyond the visible light spectrum, we get into ultraviolet waves, which occur at high frequencies, sending more than 1,000 trillion cycles every second, with a wavelength measuring between 400 and 1 nanometers.

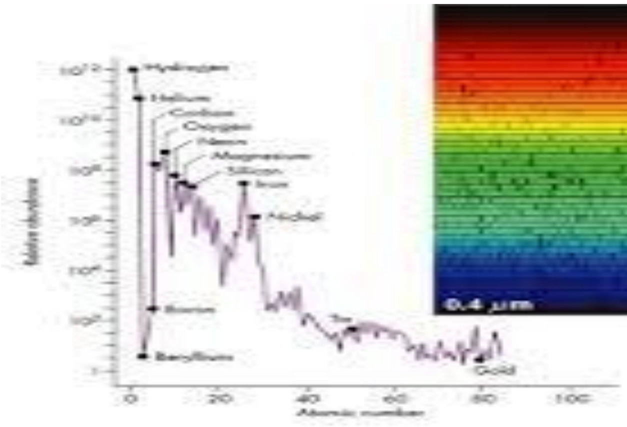
You'll find UV waves being used to sterilize medical equipment and also used to fend off bacteria and viruses. You can also use UV waves to check for counterfeit money, which shows all of the hidden symbols that the US Federal Reserve prints on a legit dollar bill.

X-Ray

Next, we have the x-ray, and if you’ve ever broken a bone or been to the dentist, then you know exactly how this electromagnetic wave is used. The wavelengths in x-rays are so short that they’ll go flying past a given point at one million trillion wavelengths per second. At this point in the electromagnetic spectrum, you need to be careful with how much exposure you get to these waves. X-rays produce such an intense burst of energy that they can kill cells in your body if you contact them unprotected.

Gamma Rays

Gamma rays are the beasts of the electromagnetic spectrum, and wield enough power to break the bonds between molecules! Their frequencies are greater than 108 Hertz, with wavelengths measuring super tiny at only 100 picometers (that’s 4 x 10-9 in inches). As might be expected, gamma rays can cause some unpleasant damage to living tissue, which makes them perfect for attacking cancer cells. However, if you have an uncontrolled gamma ray exposure, like from a nuclear bomb, then you’re likely done-for.



The Sun’ Spectrum

Wave Forms Of EM

1-**Monochromatic light** : This form of EM has the same wavelength , frequency and color in visible spectrum region. It is a type of the same phase of EM

2- Polychromatic light : This form consists of a mixture of wavelength color. As for example exists in visible light, the wavelength in this range is 400-700 nm, which constitute the origenal white light.

3-**Non-polarized light** : when the electric field oscillate in all direction perpendicular to the propagation of ray beam, the light will be non polarized.

4- **Plane-polarized light** : The reflect light for a smooth surfaces by critical angle or which path through a polarized filter, this type of light consider polarized.

5- **Non-coherent light** : Most artificial sources of light or natural light emit light with different phase than other wave length of other beam rays of light, this type of light is called non-coherent light .

6- **Coherent light** **:** When the all wavelenghths which constituent to the light in the same phase is called non-coherent light and are completely different in the properties of light and the interact with mater.

7- **light Collimated** : When the all incident wavelength in space are coaxial and its path relatively non-diverging, then it gives a very narrow light beam, and not necessary its wavelength are very close to each other (narrow band of wavelength) and have the same wavelength.

8-**Non-collimated or divergent of light :** When the all incident wavelength in space are coaxial and its path relatively diverging. To collimated and focused , it should path through a collected lense

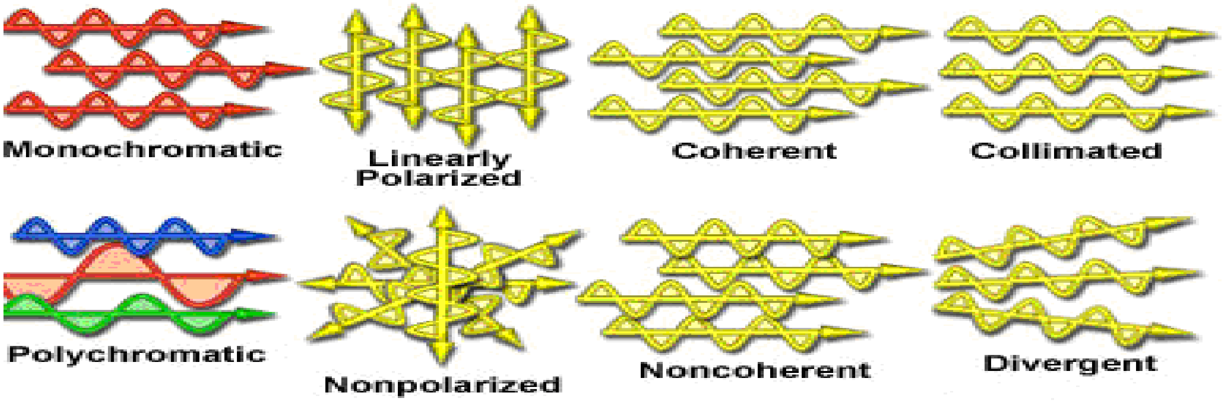


Fig ( ) : Different wave Form of electromagnetic wave

- **Atomic Spectra :**

When light passes through a prism spectroscope or a diffraction-grating spectroscope, an optical spectrum is obtained in which the intensity of the radiation may be analyzed as a function of wavelength. The spectrum may be observed visually in the limited wavelength region to which the eye is sensitive; it may be focused on a photographic plate or upon a thermocouple or thermopile. Our knowledge of the structure of atoms and molecules is largely dependent upon the analyses of optical spectra, for these spectra are characteristic of the emitting atoms or molecules. Even before the spectra of atoms were properly understood in terms of the atomic structure, it was possible to determine the chemical composition of an unknown substance by study of its spectrum.

The spectra obtained from radiating bodies are called *emission spectra* and are classified as *continuous spectra*, *band spectra*, and *line spectra*, according to their appearance in a spectroscope. Continuous spectra are emitted by solids, liquids, and dense opaque gases at high temperatures.

The spectrum of the sun, or of a black body, is a continuous spectrum and, as we have seen in Section 18-6, the shape of the black-body spectrum is characteristic of its temperature. Gases at low pressures emit *band* or *line* spectra. Line spectra have their origin in the energy changes which take place in the atoms of a gas, while band spectra are associated with similar changes in the molecules.

To early investigators the line spectra of atoms and the continuous spectra of black bodies posed seemingly insurmountable problems, for all explanations of the wavelengths of the spectral lines, or of the shape of the continuous spectra, were inadequate. For example, by analogy with the properties of organ pipes and vibrating bodies, a black body was assumed to be capable of sustaining electromagnetic vibrations in much the same manner as an organ pipe is capable of generating a fundamental and its overtones, under appropriate excitation, or as a room is capable of sustaining standing waves. Each harmonic was assumed to be a mode of vibration and to have energy kT, as in the case of the specific heats of gases, but the calculated spectrum was in violent disagreement with the observed spectrum. To explain the shape of this spectrum Max Planck proposed, in 1900, that the energy of a given mode of vibration depended upon its frequency in accordance with the relationship

$$\boxed{\mathscr{E} = hf,} \qquad (1)$$

where $\mathscr{E}$ is the energy, f is the frequency of vibration, and h is a constant now known as *Planck's constant* whose measured value is

$$h = 6.624 \times 10^{-27} \text{ erg sec.}$$

Planck's conception, in contradiction to the well-established principle of *equipartition of energy*, successfully predicted the shape of the black-body radiation spectrum. Planck's formula was subsequently interpreted by Einstein as implying that radiation was emitted or absorbed in discrete units called *quanta*, each of which had an energy given by Equation (1).

This interpretation helped to explain many phenomena observed in the interaction of radiation and matter such as the photoelectric effect and the emission and absorption of radiation. According to the quantum theory of light, the energy in a beam of monochromatic light of frequency f is determined by the number of quanta hf in the beam rather than by the square of the amplitude of vibration.

From our discussion of black-body radiation we have seen that the efficiency of a body as a radiator of energy is equivalent to the efficiency of the body as an absorber of radiation. Thus we should expect that, when white light irradiated a gas, it would absorb precisely those wavelengths which it was capable of emitting. A spectrum produced in this manner is called an *absorption spectrum*. Contrary to classical expectations it was discovered that only a few of the lines in the emission spectrum of a gas were to be found in its absorption spectrum.

- **Atomic spectra**

Even though the spectral nature of light is present in a rainbow, it was not until 1666 that Isaac Newton showed that white light from the sun is composed of a continuum of colors (frequencies). Newton introduced the term \spectrum" to describe this phenomenon. His method to measure the spectrum of light consisted of a small aperture to de_ne a point source of light, a lens to collimate this into a beam of light, a glass spectrum to disperse the colors and a screen on which to observe the resulting spectrum. This is indeed quite close to a modern spectrometer! Newton's analysis was the beginning of the science of spectroscopy (the study of the frequency distribution of light from different sources).

The first observation of the discrete nature of emission and absorption from atomic systems was made by Joseph Fraunhofer in 1814. He noted that when su_ciently dispersed, the spectrum of the sun was not continuous, but was actually missing certain colors as depicted in Fig. 3.2. These appeared as dark lines in the otherwise continuous spectrum, now known as Fraunhofer lines. (These lines were observed earlier (1802) by William H. Wollaston, who did not attach any significance to them.) These were the first spectral lines to be observed. Fraunhofer made use of them to determine standards for comparing the dispersion of different types of glass.

Fraunhofer also developed the diffraction grating to enable not only greater angular dispersion of light, but also standardized measures of wavelength. The latter could not be achieved using glass prisms since the dispersion depended on the type of glass used, which was difficult to make uniform. With this, he was able to directly measure the wavelengths of spectral lines. Fraunhofer's achievements are all the more impressive, considering that he died at the early age of 39.

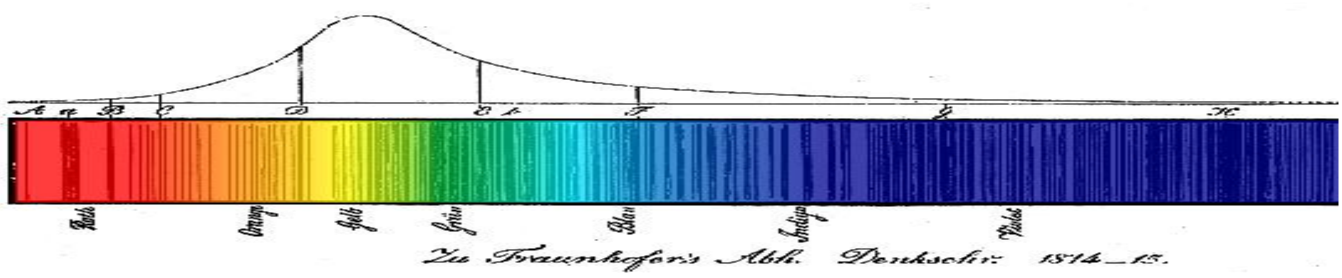


Fig.3.2:Fraunhofer spectrum of the sun.Note the dark lines in the solar spectrum.

The origin of the solar spectral lines were not understood at the time though. It was not until 1859, when Gustav Kircho_ and Robert Bunsen, realized that the solar spectral lines were due to absorption of light by articular atomic species in the solar atmosphere. They noted that several Fraunhofer lines coincided with the characteristic emission lines observed in the spectra of heated elements. By realizing that each atom and molecule has its own characteristic spectrum, Kircho_ and Bunsen established spectroscopy as a tool for probing atomic and molecular structure.

There are two ways in which one can observe spectral lines from an atomic species. The _first is to excite the atoms and examine the light that is emitted. Such emission spectra consist of many bright \lines" in a spectrometer, as depicted in Fig. 3.3. The second approach is to pass white light with a continuous spectrum through a glass cell containing the atomic species (in gas form) that we wish to interrogate and observe the absorbed radiation. This absorption spectrum will contain dark spectral lines where the light has been absorbed by the atoms in our cell, illustrated in Fig. 3.3. Note that the number of spectral lines observed by absorption is less than those found through emission.

The road to understanding the origins of atomic spectral lines began with a Swiss schoolmaster by the name of Johann Balmer in 1885, who was trying to understand the spectral lines observed in emission from hydrogen. He noticed that there were regularities in the wavelengths of the emitted lines and found that he could determine the wavelengths with the following

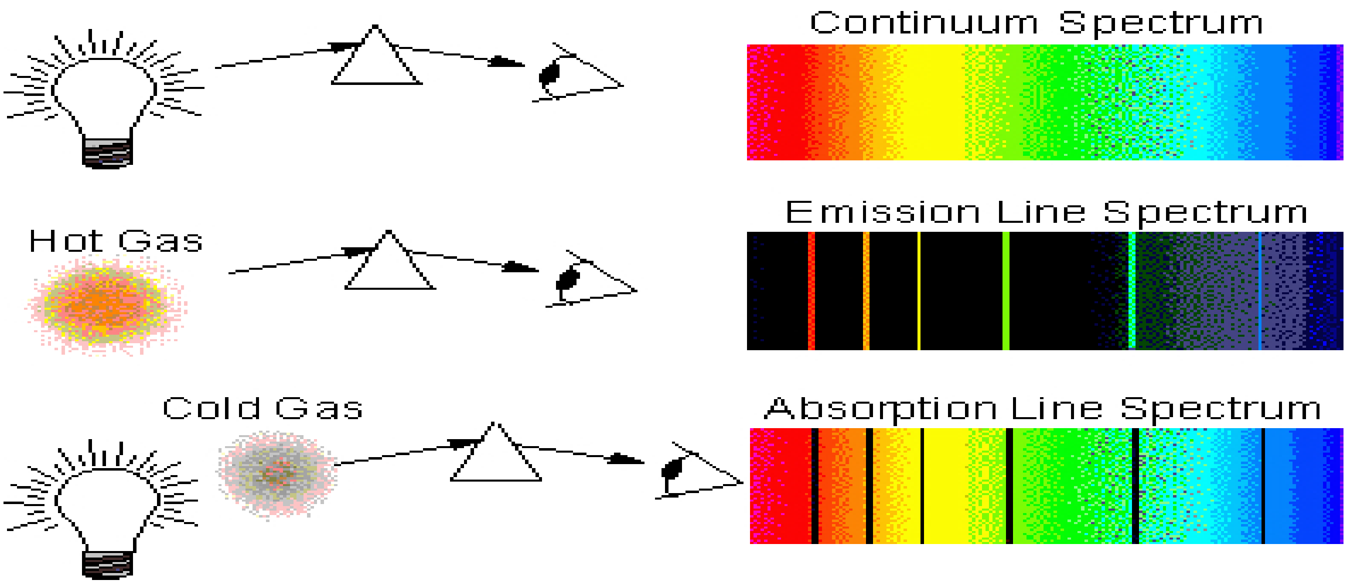


Figure 3.3: Spectra from various experimental setups demonstrating emission and absorption spectra. Spectrum from a white light source (top). Emission spectrum from a hot atomic gas vapor (could also be electrically excited). Absorption spectrum observed when white light is passed through a cold atomic gas. Formula :

$$\lambda = \lambda_0 \left(\frac{1}{4} - \frac{1}{n^2} \right)^{-1}, \qquad (1)$$

where n is an integer greater than two, and _0 is a constant length of 364:56 nm. This empirical result was generalized by Johannes Rydberg in 1900 to describe all of the observed lines in hydrogen by the following formula

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

where m and n are integers (m < n), R is known as the Rydberg constant (R = 13:6 eV), h is Planck's constant (6:626 _ 10□34 Js) and c is the speed of light in vacuum. Although a concise formula for predicting the emission wavelengths for hydrogen were known, there was no physical description or the origin of these discrete lines. The leading theory of the day was that atoms and molecules had certain resonance frequencies at which they would emit, but there was no satisfactory description of the physical origins of these resonances. Furthermore, there were no other closed formulae to predict the emission spectral lines of other, more complex, materials. To take the next steps in understanding these questions required a model of the atom from which the radiation is emitted or absorbed.

•Spectrum of Hydrogen

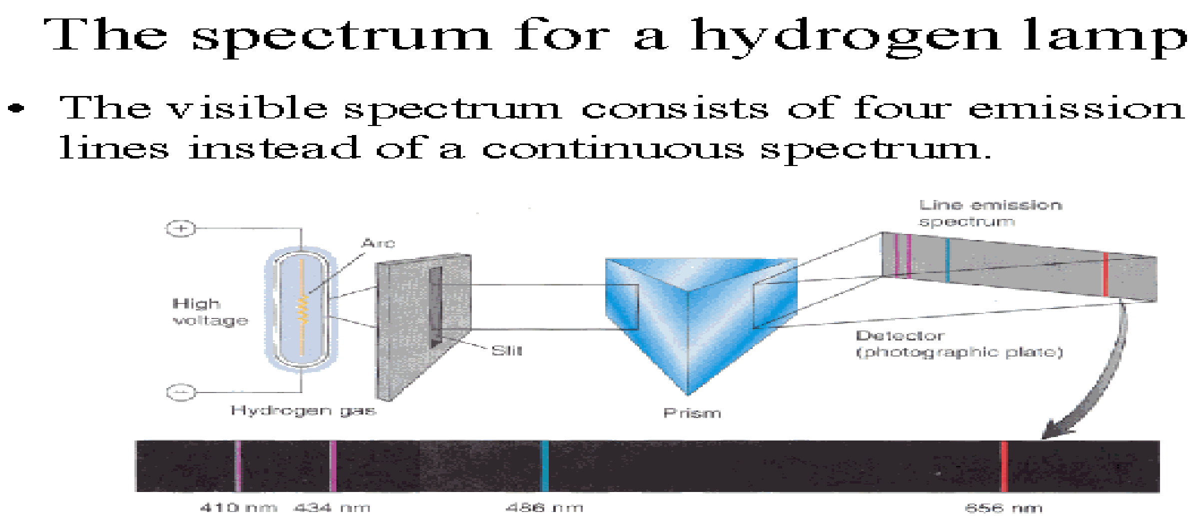
Hydrogen, the simplest of the elements, has been investigated most extensively both theoretically and experimentally. The knowledge gained from this study has acted as a guide to the study of more complex elements.

1: Production of Hydrogen Spectrum

- When hydrogen is heated to a high temperature or an electric discharge is passed through it at low pressure, the hydrogen molecules split into atoms and these absorb energy.

- The hydrogen atom is excited as they contain excess energy. Their electrons are promoted from the ground state (n=1) to high energy level.

- The excited atoms are unstable. When the excited electrons lose energy and fall back to the ground state, they emit light of various wavelengths, producing the emission spectrum of hydrogen.



The spectrum for a hydrogen lamp

- The visible spectrum consists of four emission lines instead of a continuous spectrum.

2: Interpretation of hydrogen spectrum

1-The emission spectrum consists of colored bright lines in dark background.

2-The spectrum of hydrogen consists of several series of discrete lines which converge in different parts of the electromagnetic spectrum.

Lyman series in the ultraviolet region.

Balmer series in the visible region.

Paschen series in the infrared region

3-Within each series, the lines get closer together and converge at shorter wavelengths (or higher frequencies). Finally, these lines merge into a continuum of light (line of higher frequencies). This is the convergence limits.

4-The wavelengths of the special lines are unique to each element.

5-The relation between the wavelengths of the lines in spectrum is as follows:

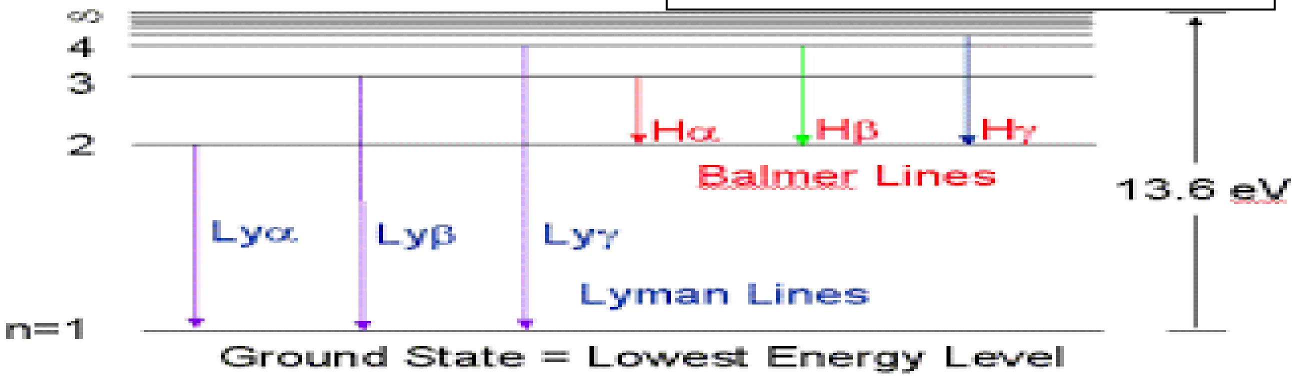
$$1/\lambda = R_H\,(1/n_1^2 - 1/n_2^2)$$

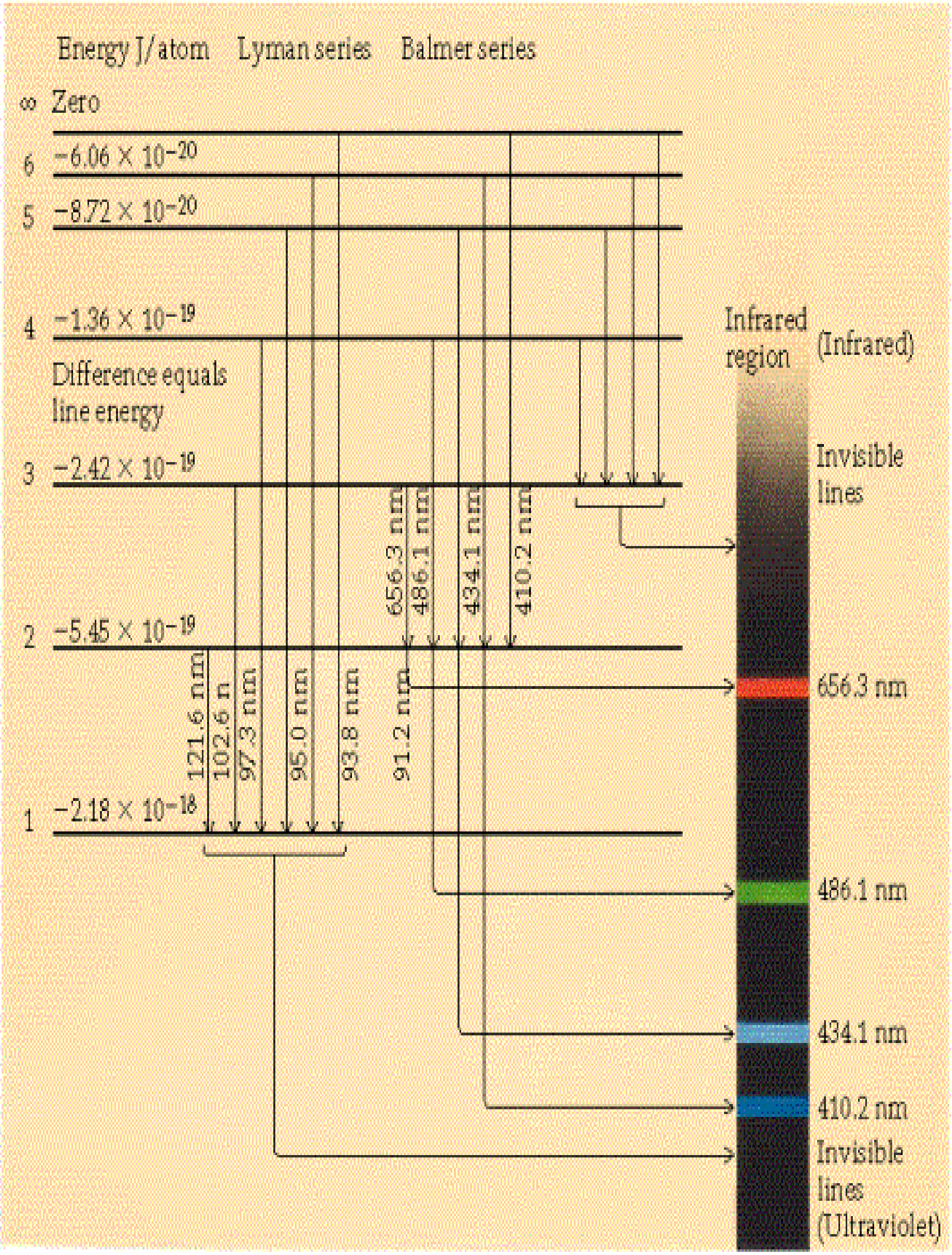
where λ=wavelength of the spectral line and R_H = Ryberg constant, and

n_1 and n_2 are integers which correspond to different series of lines in the spectrum

6-The frequencies of the discrete lines of the various series are found experimentally to obey the line following relationship:

$$\nu = c/\lambda = c\,R_H\,(1/n_1^2 - 1/n_2^2)$$




Energy J/atom
Lyman series
Balmer series
∞ Zero
6 −6.06 × 10−20
5 −8.72 × 10−20
4 −1.36 × 10−19
Difference equals line energy
3 −2.42 × 10−19
2 −5.45 × 10−19
1 −2.18 × 10−18
121.6 nm
102.6 n
97.3 nm
95.0 nm
93.8 nm
91.2 nm
656.3 nm
486.1 nm
434.1 nm
410.2 nm
Infrared region
(Infrared)
Invisible lines
656.3 nm
486.1 nm
434.1 nm
410.2 nm
Invisible lines (Ultraviolet)

The wavelengths for the hydrogen atom are:

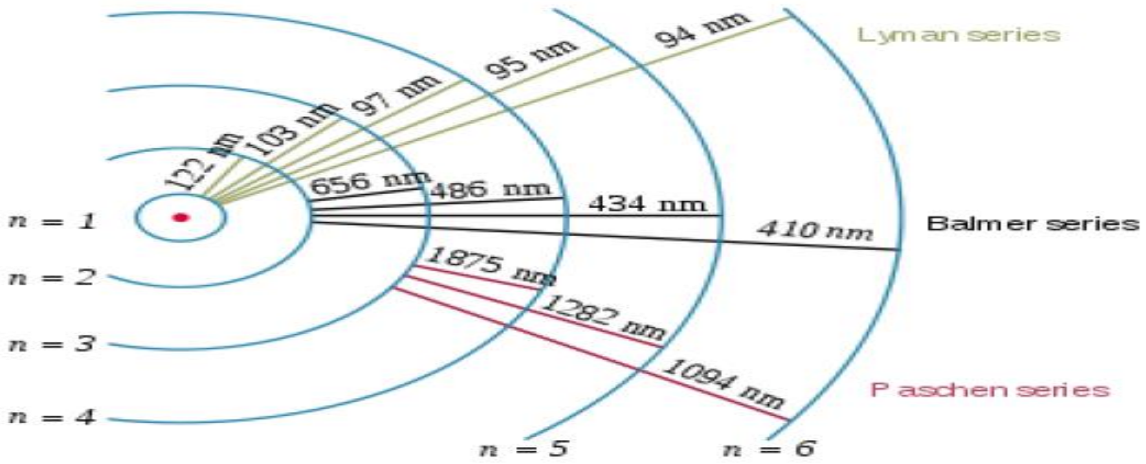
Wavelength (nm)	Relative Intensity	Transition	Color or region of EM spectrum
Lymann Series			
93.782	...	6 -> 1	UV
94.976	...	5 -> 1	UV
97.254	...	4 -> 1	UV
102.583	...	3 -> 1	UV
121.566	...	2 -> 1	UV
Balmer Series			
383.5384	5	9 -> 2	Violet
388.9049	6	8 -> 2	Violet
397.0072	8	7 -> 2	Violet
410.174	15	6 -> 2	Violet
434.047	30	5 -> 2	Violet
486.133	80	4 -> 2	Bluegreen (cyan)
656.272	120	3 -> 2	Red
656.2852	180	3 -> 2	Red
Paschen Series			
954.62	...	8 -> 3	IR
1004.98	...	7 -> 3	IR
1093.8	...	6 -> 3	IR
1281.81	...	5 -> 3	IR
1875.01	...	4 -> 3	IR
Brackett Series			
2630	...	6 -> 4	IR
4050	...	5 -> 4	IR
Pfund Series			
7400	...	6 -> 5	IR

Lyman series (n_2=1)		
Lyα	2 → 1	1216 Å
Lyβ	3 → 1	1026 Å
Lyγ	4 → 1	973 Å
Lyδ	5 → 1	950 Å

Paschen series (n_2=3)		
Paα	4 → 3	1.875 μm
Paβ	5 → 3	1.282 μm
Paγ	6 → 3	1.094 μm
Paδ	7 → 3	1.005 μm

Balmer series (n_2=2)		
Hα	3 → 2	6563 Å
Hβ	4 → 2	4861 Å
Hγ	5 → 2	4340 Å
Hδ	6 → 2	4102 Å

Brackett series (n_2=4)		
Brα	5 → 4	4.05 μm
Brβ	6 → 4	2.63 μm
Brγ	7 → 4	2.17 μm
Brδ	8 → 4	1.95 μm



1-Lyman series (ultraviolet region, highest energy):

$$\text{Ʊ}^{-} = \frac{1}{\lambda} = R_H \left\{ \frac{1}{1^2} - \frac{1}{n^2} \right\}, \quad n = 2, 3, 4, \dots \dots ..$$

Electrons from states with $n_i > 2$ can return, initially, to the first-excited state ($n_f = 2$), emitting one photon and then to the ground state emitting a second photon, with E_{ph} = 10.2 eV, which is part of the **Lyman series.**
α line: 2 —> 1; also known as first line or first member
β line: 3 —> 2; also known as second line or second member
γ line: 4 —> 1; also known as third line or third member

The Lyman series

Initial quantum number	Photon energy (eV)	Wavelength $\lambda = hc/E$
2	$13.6\times(1 - 1/4) = 10.2$	121.6 nm
3	$13.6\times(1 - 1/9) = 12.1$	102.6 nm
4	$13.6\times(1 - 1/16) = 12.75$	97.3 nm
5	$13.6\times(1 - 1/25) = 13.1$	95.0 nm
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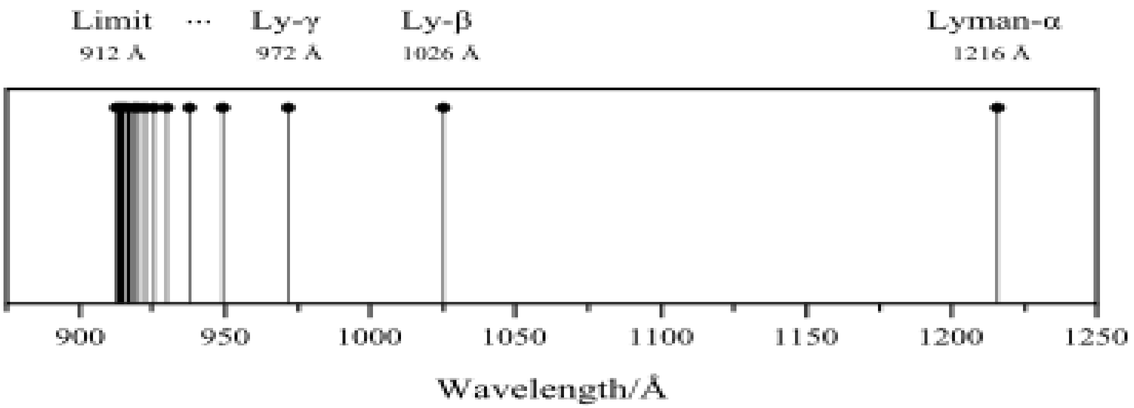
∞	$13.6\times(1 - 1/\infty) = 13.6$	91.2 nm

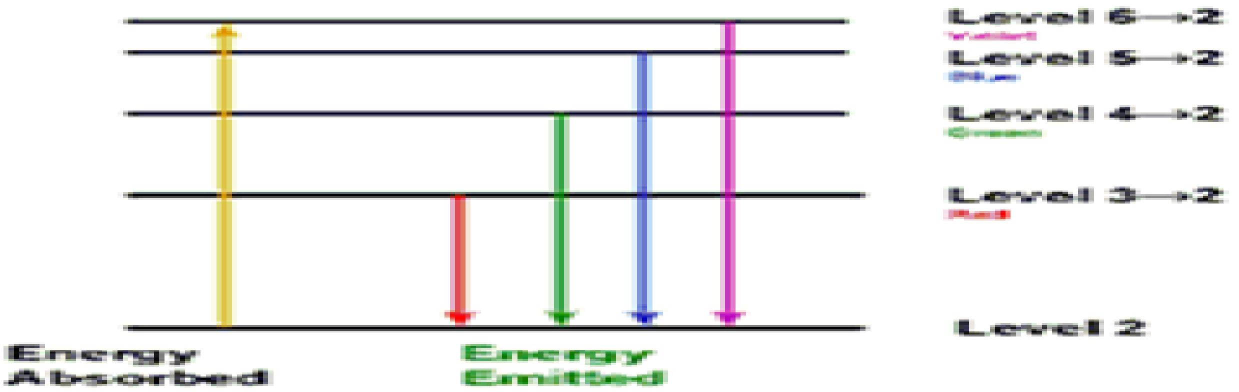


2-Balmer series (visible region) ($n' = 2$)

● Joh Balmer, who discovered the **Balmer formula**, an empirical equation to predict the Balmer series, in 1885 . He is the first scientist who discover a spectral series of hydrogen atom.

●Experimentally, he found that these spectral lines could be expressed mathematically in the form of wavelength as:

$$\text{U}^{-} = \frac{1}{\lambda} = R_H \left\{\frac{1}{2^2} - \frac{1}{n^2}\right\}, \text{where } n_2 = 3,4,5,6 \ldots .\infty.$$



Photons from transitions to the first-excited, (n = 2) state of the hydrogen atom form another series of spectral lines. This series is in the visible part of the spectrum from yellow, for the lowest energy, to violet for the highest energies. It is called the **Balmer Series**.

- Here R= Rhydberg constant = 109677cm^{-1}(found experimentally), n= 3, 4, 5…… (higher discrete energy state from which electron jumps to 2nd energy state thus emitting radiation)

λ = wavelength of emitted radiation in (cm)

- For maximum wavelength(λ_{max}) in the Balmer series, n=3 (has to be minimum):

$$\frac{1}{\lambda_{max}} = R\left(\frac{1}{2^2} - \frac{1}{3^2}\right)$$
$$\lambda_{max} = \frac{36}{5R}$$

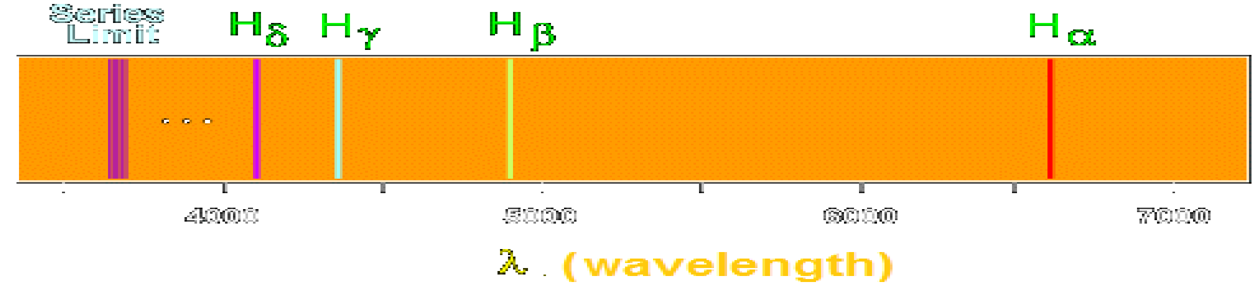
- For minimum wavelength (λ_{min}) in the Balmer series, n=∞(has to be minimum):

$$\frac{1}{\lambda_{min}} = R\left(\frac{1}{2^2} - \frac{1}{\infty^2}\right)$$
$$\lambda_{min} = \frac{4}{R}$$

- α line : 3 –> 2; β line : 4 –> 2; γ line : 5 –> 2

Initial quantum number	Photon energy (eV)	Wavelength $\lambda = hc/E$
3	$13.6\times(1/4 - 1/9) = 1.89$	657 nm
4	$13.6\times(1/4 - 1/16) = 2.55$	487 nm
5	$13.6\times(1/4 - 1/25) = 2.86$	434 nm
6	$13.6\times(1/4 - 1/36) = 3.02$	411 nm
---	---	---
∞	$13.6\times(1/4 - 1/\infty) = 3.4$	365 nm

The Fig 5 Gives possible quantum jumps between stationary orbits giving rise to the different spectral series of hydrogen.



Four visible hydrogen emission spectrum lines in the Balmer series.

Balmer lines are historically referred to as "H-alpha", "H-beta", "H-gamma" and so on, where H is the element hydrogen Four of the Balmer lines are in the technically "visible" part of the spectrum, with wavelengths longer than 400 nm and shorter than 700 nm. Parts of the Balmer series can be seen in the solar spectrum. H-alpha is an important line used in astronomy to detect the presence of hydrogen.. The first four transitions are as follows in Table 1.

Table 1. Balmer Series – Some Wavelengths in the Visible Spectrum.

Name of Line	n_f	n_i	Symbol	Wavelength
Balmer Alpha	2	3	H_α	656.28 nm
Balmer Beta	2	4	H_β	486.13 nm
Balmer Gamma	2	5	H_γ	434.05nm
Balmer Delta	2	6	H_δ	410.17 nm

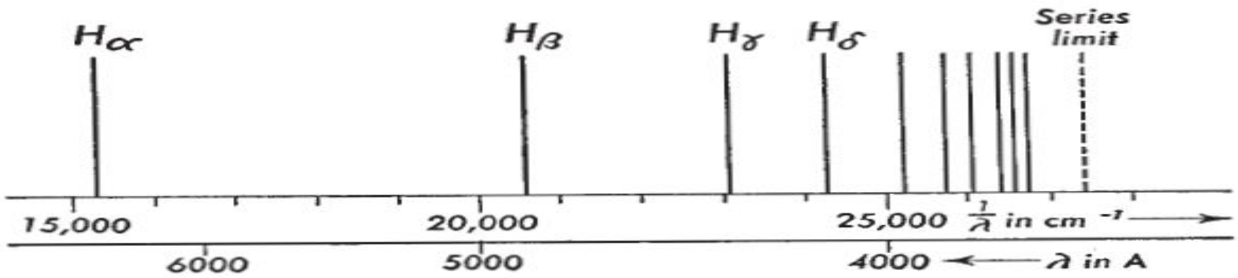
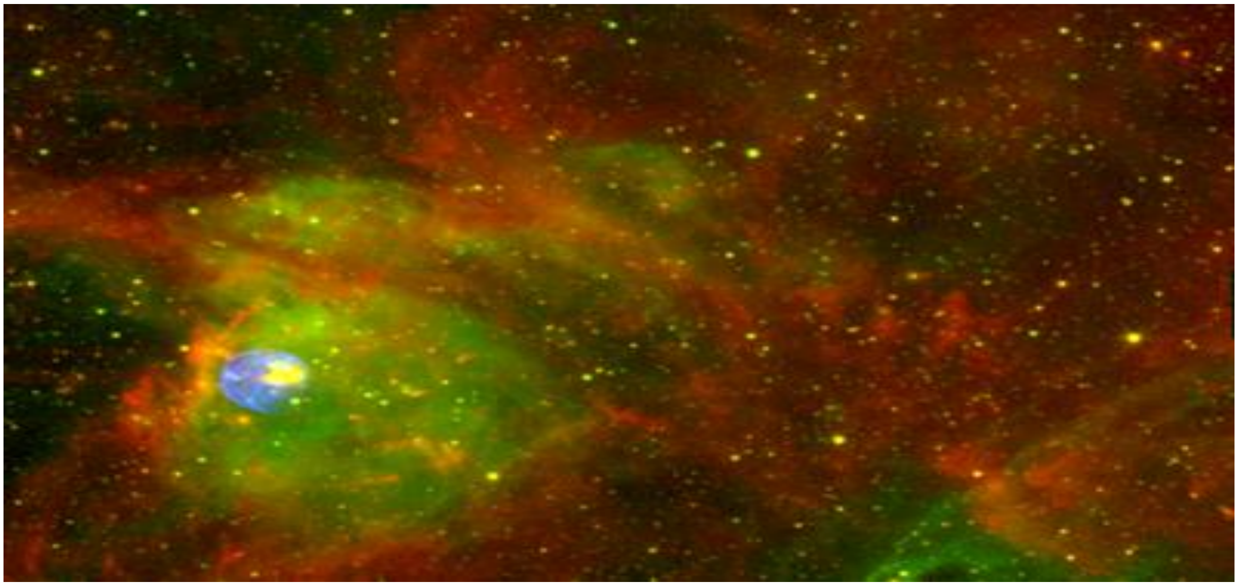


Fig. 2 Graph of the positions of the lines of the Balmer Reries. The upper scale is the reciprocal of the wavelength in centimeters, while the lower scale is the wavelength in angstrom units

Because hydrogen is the most abundant **element** in the **Universe**, the **Balmer lines** are a common feature in optical **astronomy** and the red Hα line corresponding to the electron transition from the n= 3 to the n= 2 energy level gives the characteristic pink/red colour in true-colour images of ionized regions in **planetary nebulae**, **supernova** remnants and **stellar** nurseries.

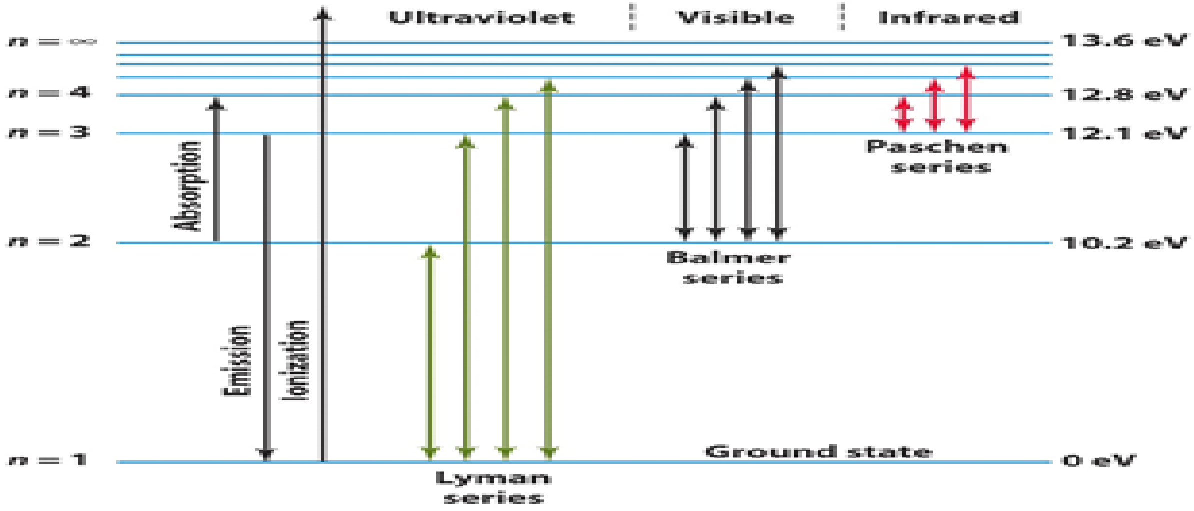


2-Paschen series (Bohr series, n' = 3) (near infrared region)

The German physicist Friedrich Paschen who first observed Paschen lines in 1908. The Paschen lines all lie in the **infrared band**. This series overlaps with the next (Brackett) series, i.e. the shortest line in the Brackett series has a wavelength that falls among the Paschen series. All subsequent series overlap

If electronic transitions are from the higher energy levels to n=3, much less energy is released. The spectral lines in lower energy region (infrared) of the spectrum. The lines form the Paschen series

$$\text{U}^{-} = \frac{1}{\lambda} = R_H\left\{\frac{1}{3^2} - \frac{1}{n^2}\right\}, n = 4, 5, 6, \ldots \ldots \text{where } n_3 = 4,5,6\ldots.\infty$$



4-Brackett series (Bohr series, *n′* = 4) (infrared region)

Named after the American physicist Frederick Sumner Brackett who first observed the spectral lines in 1922.

If electronic transitions are from the higher energy levels to n=4, much less energy is released. The spectral lines in lower energy region (far-infrared) of the spectrum. The lines form the Bracket series

$$\text{U}^{-} = \frac{1}{\lambda} = R_H\left\{\frac{1}{4^2} - \frac{1}{n^2}\right\}, n = 5, 6, \ldots \ldots ..$$

5-Pfund series (Bohr series, *n′* = 5)

Experimentally discovered in 1924 by August Herman Pfund. If electronic transitions are from the higher energy levels to n=5, much less energy is released. The spectral lines in lower energy region (far-infrared) of the spectrum. The lines form the Pfund series

$$\text{U}^{-} = \frac{1}{\lambda} = R_H\left\{\frac{1}{5^2} - \frac{1}{n^2}\right\}, n = 6, 7, 8, \ldots \ldots ..$$

6-Humphreys series (n' = 6)

Discovered in 1953 by American physicist Curtis J. Humphreys

$$\upsilon^{-} = \frac{1}{\lambda} = R_H\left\{\frac{1}{6^2} - \frac{1}{n^2}\right\}, \qquad n = 7, 8, \dots \dots$$

•Absorption spectra

The Bohr model not only helps us to understand the emission spectrum of atoms, but also explain why atoms do not absorb at all the same wavelengths that it emits. Isolated atoms are normally found in the ground state – excited states live for very short time periods before decaying to the ground state. The absorption spectrum therefore contains only transitions from the ground state (n = 1). To observe transitions from the first excited state (n = 2) would require a significant number of atoms to occupy this state initially. Assuming that the atoms are excited by their thermal energies, this implies that to excite an atom to the first excited state from the ground state requires temperature that satis_es

$$k_B T = E_2 - E_1 = 10.2 \text{ eV},$$

which gives a temperature

$$T = \frac{(10.2 \text{ eV})(1.6 \times 10^{-19} \text{ J/eV})}{1.38 \times 10^{-23} \text{ J/K}} \approx 1.2 \times 10^{5} \text{ K},$$

which is much larger than room temperature (the surface of the sun has temperature $T \approx 6 \times 10^3$ K).

•Absorption Lines

- The process of spectral emission can be reversed . Electrons can absorb a photon and jump from a lower energy level to a higher energy level.

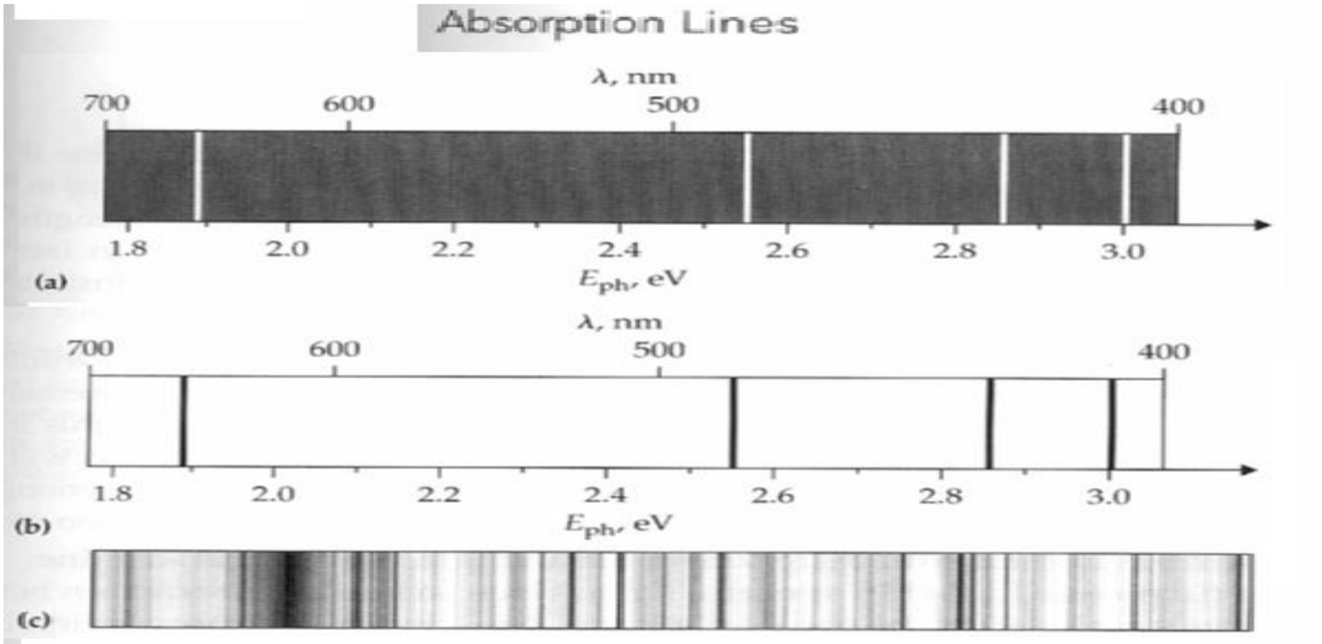
* * As in the case with a spectral emission, only certain wavelengths of light can be absorbed by the electrons

* * Wavelengths that correspond to photon energies that equal the difference in the energy levels.

- If we shine white light on a gas the atoms in the gas will absorb some wavelengths of light leaving dark lines at the particular wavelengths absorbed.

* The dark lines occur at the same wavelengths as the spectral emission lines for an atom.

The hydrogen absorption spectrum



● Absorption lines are an important tool for understand the composition of something from a distance.

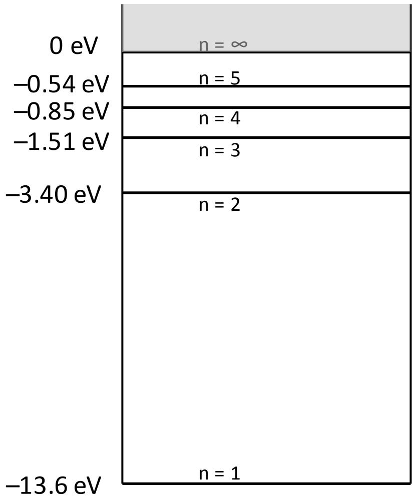
* * For example, star light shines through a nebula toward earth. Based on the absorption lines we can understand the atomic composition of the nebula.

Problems

1. Describe how the emission and absorption spectra of hydrogen are explained by the Bohr model of the atom.

2. What are the strengths of the Bohr model? What are the weaknesses of the Bohr model?

Use the energy level diagram for hydrogen to answer questions 5 to 11.



3. How much energy must a hydrogen electron in energy level n = 1 absorb in order to jump to energy level n = 2 and n = 3? (10.2 eV, 12.1 eV)

4. How does the total energy of photons emitted by an electron as it jumps back down to its ground state compare with the energy absorbed by the electron when it jumped to the higher level?

5. Why is a blue photon emitted when a hydrogen electron jumps from energy level n = 5 to n = 2, but a red photon is emitted when an electron jumps from level n = 3 to n = 2?

6. What is the ionization energy for the electron in hydrogen from its ground state?

7. What is the wavelength of a photon emitted when an electron in a hydrogen atom falls:

   A. From n = 4 to n = 2. (487 nm)

   B. From n = 5 to n = 1. (95.1 nm)

8. Electrons are accelerated through hydrogen gas at room temperature in a Franck-Hertz experiment by a potential difference of 12.3 V. What wavelengths of light can be expected to be emitted by the hydrogen? (122 nm, 103 nm, 657 nm)

9. What energy is needed to ionize hydrogen from the n=2 state? How likely is this to occur? Explain. (3.40 eV)

10. Use the energy level diagram below to answer the following questions.

n = ∞	0.000 eV
n = 9	-0.450 eV
n = 8	-0.570 eV
n = 7	-0.744 eV
n = 6	-1.013 eV
n = 5	-1.458 eV
n = 4	-2.278 eV
n = 3	-4.050 eV
n = 2	-9.113 eV
n = 1	-36.450 eV

11. What is the wavelength of the photon emitted when an electron falls from the sixth to second energy level? (153 nm)

12. What is the frequency of the photon emitted when an electron falls from n = 7 to n = 3? (7.987 x 10^{14} Hz)

13 What is the energy absorbed by an electron to jump from n = 1 to n = 8? (35.880 eV)

14. What is the ionization energy of this element?

16. Hydrogen atoms in states of high quantum number have been created in a lab. (a) Find the quantum number of the Bohr orbit in a hydrogen atom whose radius is 0.01 mm. (b) What is the energy of a hydrogen atom in this state?

Solution:

(a) $$n=\sqrt{\frac{r_n}{a_0}}=\sqrt{\frac{1.0\times10^{-5}m}{5.29\times10^{-11}}}=435$$

(b) $$E_n=\frac{E_1}{n^2}=\frac{-13.6eV}{(435)^2}=-7.19\times10^{-5}eV$$

16. Find the longest wavelength present in the Balmer series of hydrogen, corresponding to the Hα line.

In the Balmer series the quantum number of the final state is n_f=2. The longest wavelength corresponds to the smallest energy difference between energy levels. Hence the initial state must be n_i=3. Then

Solution:

$$\frac{1}{\lambda}=R(\frac{1}{n_f^2}-\frac{1}{n_i^2})=R(\frac{1}{2^2}-\frac{1}{3^2})=0.139R$$

$$\lambda=\frac{1}{0.139R}=6.56\times10^{-7}m;$$

This wavelength is near the red end of the visible spectrum.

19. Find the de Broglie wavelength of (a) a 46-g golf ball with a velocity of 30 m/s, and (b) an electron with a velocity of 10^7 m/s.

Solution:

Both speeds are nonrelativistic: *v«c*. Hence:

(a) $$\lambda=\frac{h}{mv}=\frac{6.63\times10^{-34}J\cdot s}{(0.046kg)(30m/s)}=4.8\times10^{-34}m$$

The wavelength of the golf ball is so small compared with its dimensions that we would not expect to find any wave aspect in its behavior.

(b) $$\lambda=\frac{h}{mv}=\frac{6.63\times10^{-34}J\cdot s}{(9.1\times10^{-31}kg)(10^7m/s)}=7.3\times10^{-11}m$$

The dimensions of atoms are comparable with this figure—the radius of the hydrogen atom, for instance, is 5.3×10^{-11} m. Thus, we need the wave properties of a moving electron to understand atomic structure and behavior.

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(b) $$\lambda=\frac{h}{mv}=\frac{6.63\times10^{-34}J\cdot s}{(9.1\times10^{-31}kg)(10^7m/s)}=7.3\times10^{-11}m$$

The dimensions of atoms are comparable with this figure—the radius of the hydrogen atom, for instance, is 5.3×10^{-11} m. Thus, we need the wave properties of a moving electron to understand atomic structure and behavior.

22. Using Balmer's formula, calculate the wave lengths of the first few lines of the visible regions of the hydrogen atomic spectrum n=3, n=4

Solution:

The first line is obtained by setting n= 3

$$\bar{\nu} = 109.680\left(\frac{1}{2^2} - \frac{1}{3^2}\right)\mathrm{Cm}^{-1}$$

$\bar{\nu}$ **=1.523x10^{4}Cm^{-1}**

$$\bar{\nu} = \frac{1}{\lambda}$$

λ= 6.564x10^{-5}Cm = 6564 Å

The next line is obtained by setting n=4

$$\bar{\nu} = 109.680\left(\frac{1}{2^2} - \frac{1}{4^2}\right)\ \mathrm{Cm}^{-1}$$

$\bar{\nu}$ **=2.056x10^{4}Cm^{-1}**

λ=4.863x10^{-5}Cm=4863 Å

The Balmer series occurs in the visible and near ultraviolet regions. There are lines in the hydrogen atomic spectrum in other regions; in fact there are series of lines similar to the Balmer series in the ultraviolet and in the infrared region.

The Rydberg formula accounts for all the lines in the hydrogen atomic spectrum. Rydberg accounted for all lines in the hydrogen atomic spectrum by generalizing the Balmer formula to

$$\bar{\nu} = 109.680\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)Cm^{-1} \qquad (n_2 > n_1) \quad \text{(1-15)}$$

This equation is called Rydberg formula.

The constant in Eq 1-15 is called Rydberg Constant

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

R_H is the Rydberg constant = 109.67 Cm^{-1}

23. Calculate the wavelength of the second line in the Paschen series and show that this line lies in the near infrared, that is, in the infrared region near the visible.

Solution:

In the paschen series, n_1=3 and n_2= 4, 5, 6… According to figure Thus the second line in the Paschen series is given by setting n_1=3 and n_2=5 in Eq. 1-15:

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

$$\bar{\nu} = 109.680 \left(\frac{1}{3^2} - \frac{1}{5^2} \right) \text{ Cm}^{-1}$$

$$\bar{\nu} = 7.799 \times 10^3 \text{Cm}^{-1} \qquad \because \quad \lambda = \frac{1}{\bar{\nu}}$$

$$\because \quad \lambda = 1.282 \times 10^{-4} \text{ Cm} = 12.820 \text{ Å}$$

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