Contents

1 Structure of Atom —Classical Mechanics

CHAPTER

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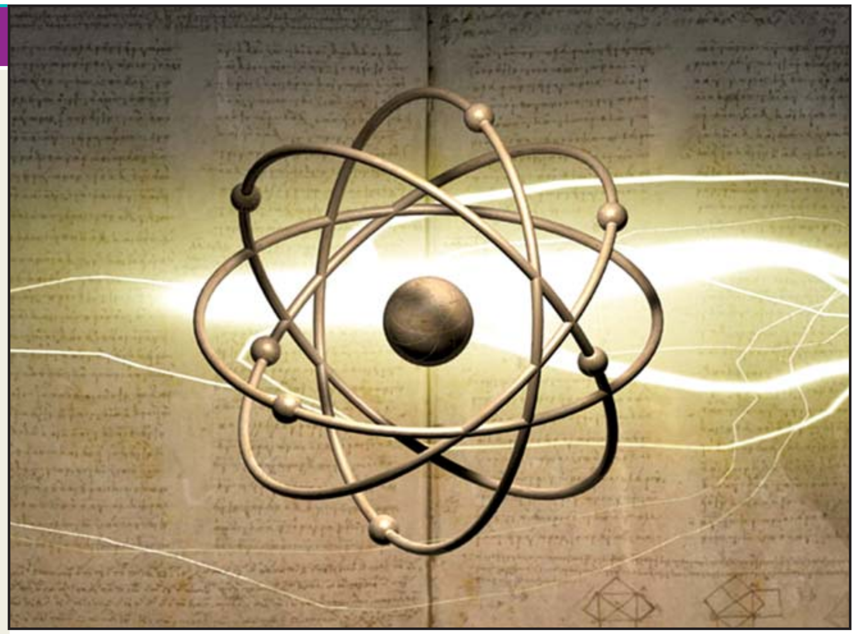
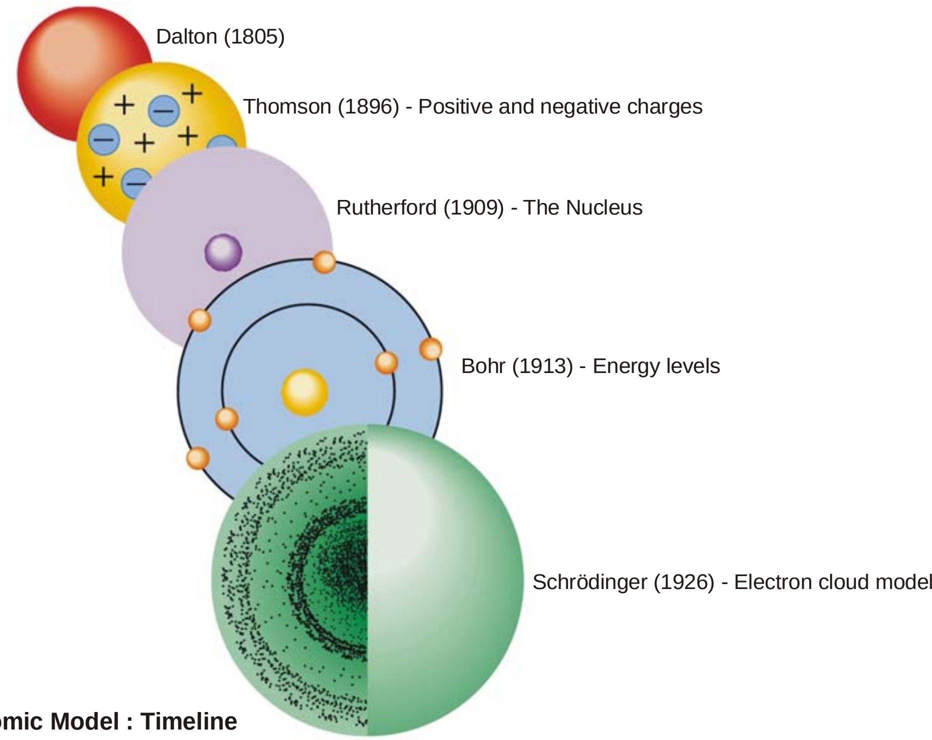


John Dalton (1805) considered that **all matter was composed of small particles called atoms.** He visualised the atom as a hard solid individual particle incapable of subdivision. At the end of the nineteenth century there accumulated enough experimental evidence to show that the atom is made of still smaller particles. These subatomic particles are called the **fundamental particles.** The number of subatomic particles now known is very large. For us, the three most important are the **proton, neutron and electron.** How these fundamental particles go to make the internal structure of the atom, is a fascinating story. The main landmarks in the evolution of atomic structure are :

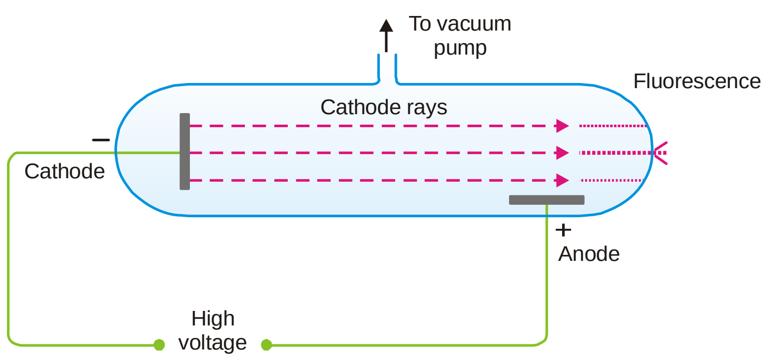
1896	J.J. Thomson's discovery of the electron and the proton
1909	Rutherford's Nuclear Atom
1913	Mosley's determination of Atomic Number
1913	Bohr Atom
1921	Bohr-Bury Scheme of Electronic Arrangement
1932	Chadwick's discovery of the neutron.



■ **Atomic Model : Timeline**

CATHODE RAYS – THE DISCOVERY OF ELECTRON

The knowledge about the electron was derived as a result of the study of the electric discharge in the **discharge tube** (J.J. Thomson, 1896). The discharge tube consists of a glass tube with metal electrodes fused in the walls (Fig. 1.1). Through a glass side-arm air can be drawn with a pump. The electrodes are connected to a source of high voltage (10,000 Volts) and the air partially evacuated. The electric discharge passes between the electrodes and the residual gas in the tube begins to glow. If virtually all the gas is evacuated from within the tube, the glow is replaced by faintly luminous 'rays' which produce fluorescence on the glass at the end far from the cathode. **The rays which proceed from the cathode and move away from it at right angles in straight lines are called Cathode Rays.**



■ **Figure 1.1**
Production of cathode rays.

PROPERTIES OF CATHODE RAYS

1. They travel in straight lines away from the cathode and cast shadows of metallic objects placed in their path.
2. Cathode rays cause mechanical motion of a small pin-wheel placed in their path. Thus they possess kinetic energy and must be material particles.
3. They produce fluorescence (a glow) when they strike the glass wall of the discharge tube.
4. They heat up a metal foil to incandescence which they impinge upon.
5. Cathode rays produce X-rays when they strike a metallic target.
6. Cathode rays are deflected by the electric as well as the magnetic field in a way indicating that they are streams of minute particles carrying negative charge.

By counterbalancing the effect of magnetic and electric field on cathode rays. Thomson was able to work out the ratio of the charge and mass (*e/m*) of the cathode particle. In SI units the value of *e/m* of cathode particles is – 1.76 × 18^8 coulombs per gram. As a result of several experiments, Thomson showed that the value of *e/m* of the cathode particle was the same regardless of both the gas and the metal of which the cathode was made. This proved that the particles making up the cathode rays were all identical and were constituent parts of the various atoms. Dutch Physicist H.A. Lorentz named them **Electrons.**

Electrons are also obtained by the action of X-rays or ultraviolet light on metals and from heated filaments. These are also emitted as β-particles by radioactive substances. Thus it is concluded that **electrons are a universal constituent of all atoms.**

MEASUREMENT OF *e/m* FOR ELECTRONS

The ratio of charge to mass (*e/m*) for an electron was measured by J.J. Thomson (1897) using the apparatus shown in Fig. 1.2.

Electrons produce a bright luminous spot at X on the fluorescent screen. Magnetic field is applied first and causes the electrons to be deflected in a circular path while the spot is shifted to Y. The radius of the circular path can be obtained from the dimensions of the apparatus, the current and number of turns in the coil of the electromagnet and the angle of deflection of the spot. An electrostatic field of known strength is then applied so as to bring back the spot to its original position. Then from the strength of the electrostatic field and magnetic field, it is possible to calculate the velocity of the electrons.

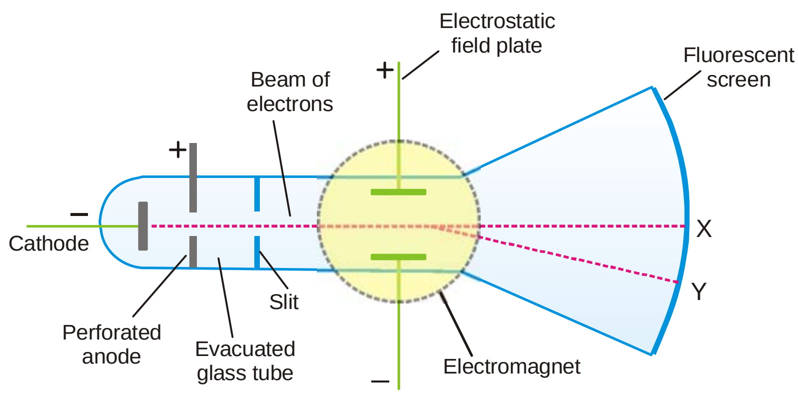


Figure 1.2
Measurement of *e/m* for electrons.

Equating magnetic force on the electron beam to centrifugal force.

$$Bev = \frac{mv^2}{r}$$

where B = magnetic field strength
v = velocity of electrons
e = charge on the electron
m = mass of the electron
r = radius of the circular path of the electron in the magnetic field.

This means

$$\frac{e}{m} = \frac{v}{Br} \qquad ...(1)$$

The value of r is obtained from the dimensions of the tube and the displacement of the electron spot on the fluorescent screen.

When the electrostatic field strength and magnetic field strength are counterbalanced,

$$Bev = Ee$$

where E is the strength of the electrostatic field.

Thus

$$v = \frac{E}{B} \qquad ...(2)$$

If E and B are known, v can be calculated and on substitution in equation (1), we get the value of e/m.

$$\frac{e}{m} = \frac{E}{B^2 r}$$

All the quantities on the right side of the equation can be determined experimentally. Using this procedure, the ratio e/m works out to be -1.76×10^8 per gram.

or e/m for the electron $= -1.76 \times 10^8$ coulomb/g

DETERMINATION OF THE CHARGE ON AN ELECTRON

The absolute value of the charge on an electron was measured by R.A. Milikan (1908) by what is known as the **Milikan's Oil-drop Experiment.** The apparatus used by him is shown in Fig. 1.3. He sprayed oil droplets from an *atomizer* into the apparatus. An oil droplet falls through a hole in the upper plate. The air between the plates is then exposed to X-rays which eject electrons from air molecules. Some of these electrons are captured by the oil droplet and it acquires a negative charge. When the plates are earthed, the droplet falls under the influence of gravity.

He adjusted the strength of the electric field between the two charged plates so that a particular oil drop remained suspended, neither rising nor falling. At this point, the upward force due to the negative charge on the drop, just equalled the weight of the drop. As the X-rays struck the air molecules, electrons are produced. The drop captures one or more electrons and gets a negative charge, Q. Thus,

$$Q = ne$$

where n = number of electrons and e = charge of the electron. From measurement with different drops, Milikan established that electron has the charge -1.60×10^{-19} coulombs.

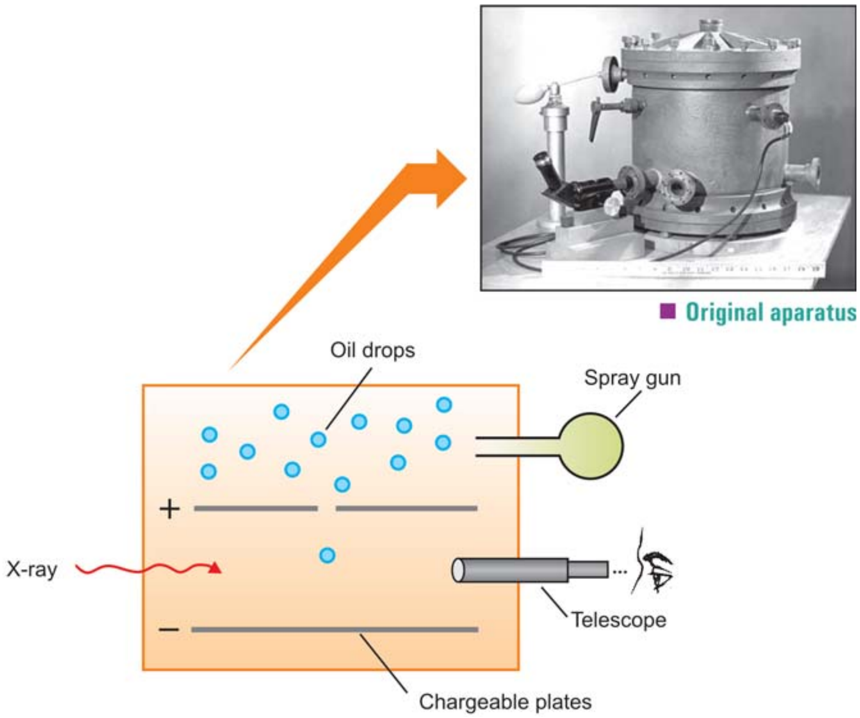


Figure 1.3
Milikan's apparatus for the Oil-drop experiment.

Mass of Electron

By using the Thomson's value of *e/m* and the Milikan's value of *e*, the absolute mass of an electron can be found.

$$e/m = -1.76 \times 10^{8} \text{ coulomb/g (Thomson)}$$
$$e = -1.60 \times 10^{-19} \text{ coulomb (Milikan)}$$

$$\therefore \quad \frac{e}{e/m} = \frac{1.60 \times 10^{-19}}{1.76 \times 10^{8}}$$

hence $m = 9.1 \times 10^{-28}$ g or 9.1×10^{-31} kg

Mass of an Electron relative to H

Avogadro number, the number of atoms in one gram atom of any element is 6.023×10^{23}. From this we can find the absolute mass of hydrogen atom.

Mass of 6.023×10^{23} atoms of hydrogen = 1.008 g

$$\therefore \quad \text{Mass of a hydrogen atom} = \frac{1.008}{6.023 \times 10^{23}} \text{ g}$$
$$= 1.67 \times 10^{-24} \text{ g}$$

But mass of electron $= 9.1 \times 10^{-28}$ g

$$\therefore \quad \frac{\text{mass of H atom}}{\text{mass of electron}} = \frac{1.67 \times 10^{-24}}{9.1 \times 10^{-28}}$$
$$= 1.835 \times 10^{3} = 1835$$

Thus an atom of hydrogen is 1835 times as heavy as an electron.

In other words, **the mass of an electron is $\frac{1}{1835}$th of the mass of hydrogen atom.**

DEFINITION OF AN ELECTRON

Having known the charge and mass of an electron, it can be defined as :

An electron is a subatomic particle which bears charge -1.60×10^{-19} coulomb and has mass 9.1×10^{-28} g.

Alternatively, an electron may be defined as :

A particle which bears one unit negative charge and mass 1/1835th of a hydrogen atom.

Since an electron has the smallest charge known, it was designated as unit charge by Thomson.

POSITIVE RAYS

In 1886 Eugen Goldstein used a discharge tube with a hole in the cathode (Fig. 1.4). He observed that while cathode rays were streaming away from the cathode, there were coloured rays produced simultaneously which passed through the perforated cathode and caused a glow on the wall opposite to the anode. Thomson studied these rays and showed that they consisted of particles carrying a positive charge. He called them **Positive rays.**

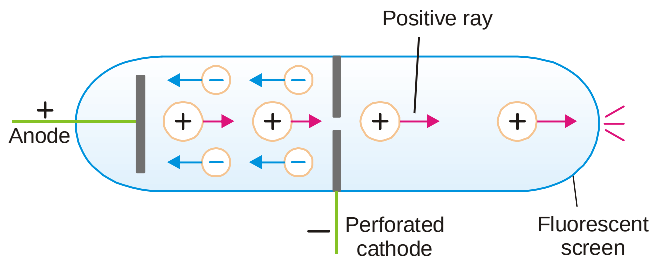


Figure 1.4
Production of Positive rays.

PROPERTIES OF POSITIVE RAYS

(1) They travel in a straight line in a direction opposite to the cathode.
(2) They are deflected by electric as well as magnetic field in a way indicating that they are positively charged.
(3) The charge-to-mass ratio (e/m) of positive particles varies with the nature of the gas placed in the discharge tube.
(4) They possess mass many times the mass of an electron.
(5) They cause fluorescence in zinc sulphide.

How are Positive rays produced ?

When high-speed electrons (cathode rays) strike molecule of a gas placed in the discharge tube, they knock out one or more electrons from it. Thus a positive ion results

$$M + e^- \longrightarrow M^+ + 2e^-$$

These positive ions pass through the perforated cathode and appear as positive rays. When electric discharge is passed through the gas under high electric pressure, its molecules are dissociated into atoms and the positive atoms (ions) constitute the positive rays.

Conclusions from the study of Positive rays

From a study of the properties of positive rays, Thomson and Aston (1913) concluded that atom consists of at least two parts :

(*a*) the electrons ; and

(*b*) a positive residue with which the mass of the atom is associated.

PROTONS

E. Goldstein (1886) discovered protons in the discharge tube containing hydrogen.

$$H \longrightarrow \underset{\text{proton}}{H^+} + e^-$$

It was J.J. Thomson who studied their nature. He showed that :

(1) The actual mass of proton is 1.672×10^{-24} gram. **On the relative scale, proton has mass 1 atomic mass unit (amu).**

(2) **The electrical charge of proton is equal in magnitude but opposite to that of the electron.** Thus proton carries a charge $+1.60 \times 10^{-19}$ coulombs or + 1 elementary charge unit.

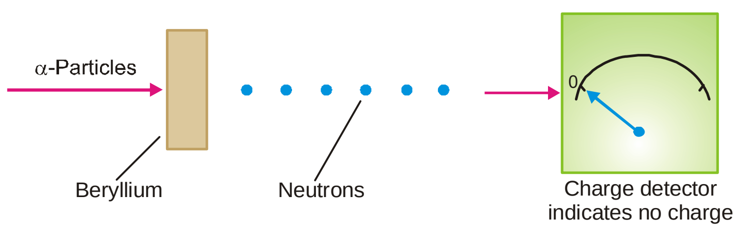
Since proton was the lightest positive particle found in atomic beams in the discharge tube, it was thought to be a unit present in all other atoms. Protons were also obtained in a variety of nuclear reactions indicating further that **all atoms contain protons.**

Thus **a proton is defined as a subatomic particle which has a mass of 1 amu and charge + 1 elementary charge unit.**

A proton is a subatomic particle which has one unit mass and one unit positive charge.

NEUTRONS

In 1932 Sir James Chadwick discovered the third subatomic particle. He directed a stream of alpha particles $\left({}^4_2\text{He}\right)$ at a beryllium target. He found that a new particle was ejected. It has almost the same mass (1.674×10^{-24} g) as that of a proton and has no charge.



■ **Figure 1.5**
α-Particles directed at beryllium sheet eject neutrons whereby the electric charge detector remains unaffected.

He named it *neutron.* The assigned relative mass of a neutron is approximately one atomic mass unit (amu). Thus :

A neutron is a subatomic particle which has a mass almost equal to that of a proton and has no charge.

The reaction which occurred in Chadwick's experiment is an example of artificial transmutation where an atom of beryllium is converted to a carbon atom through the nuclear reaction.

$${}^4_2\text{He} + {}^9_4\text{Be} \longrightarrow {}^{12}_6\text{C} + {}^1_0\text{n}$$

SUBATOMIC PARTICLES

We have hitherto studied the properties of the three principal fundamental particles of the atom, namely the *electron*, *proton*, and *neutron*. These are summarised in Table 1.1.

TABLE 1.1. CHARGE AND MASS OF ELECTRON, PROTON AND NEUTRON

Particle	Symbol	Mass		Charge	
		amu	grams	Units	Coloumbs
Electron	e^-	$\frac{1}{1835}$	9.1×10^{-28}	– 1	-1.60×10^{-19}
Proton	p^+	1	1.672×10^{-24}	+ 1	$+1.60 \times 10^{-19}$
Neutron	n or n^0	1	1.674×10^{-24}	0	0

Nearly all of the ordinary chemical properties of matter can be examined in terms of atoms consisting of electrons, protons and neutrons. Therefore for our discussion we will assume that atom contains only these three principal subatomic particles.

Other Subatomic Particles

Besides electrons, protons and neutrons, many other subatomic particles such as *mesons*, *positrons*, *neutrinos* and *antiprotons* have been discovered. A great deal of recent research is producing a long list of still other subatomic particles with names *quarks*, *pions* and *gluons*. With each discovery, the picture of atomic structure becomes increasingly complex. Fortunately, the three-particle (electron, proton, neutron) picture of the atom still meets the needs of the chemists.

ALPHA PARTICLES

Alpha particles are shot out from radioactive elements with very high speed. For example, they come from radium atoms at a speed of 1.5×10^7 m/sec. Rutherford identified them to be **di-positive helium ions,** He^{2+} or ${}^4_2He$. Thus an alpha particle has 2+ charge and 4 amu mass.

α-Particles are also formed in the discharge tube that contains helium,

$$He \longrightarrow He^{2+} + 2e^-$$

It has twice the charge of a proton and about 4 times its mass.

Conclusion

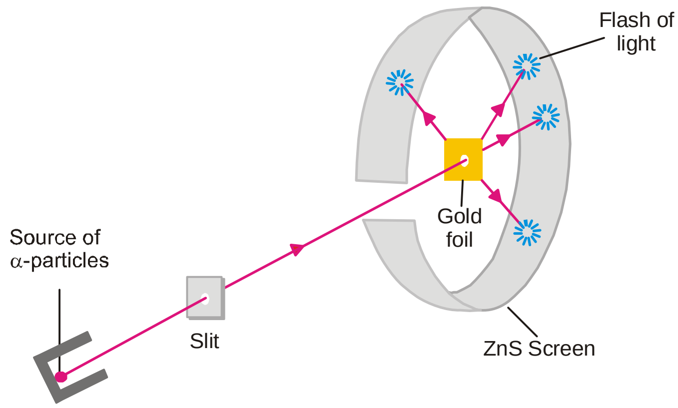
Though α-particle is not a fundamental particle of the atom (or subatomic particle) but because of its high energy $\left(\frac{1}{2}mv^2\right)$, Rutherford thought of firing them like bullets at atoms and thus obtain information about the structure of the atom.

(1) **He bombarded nitrogen and other light elements by α-particles when H^+ ions or protons were produced. This showed the presence of protons in atoms other than hydrogen atom.**

(2) **He got a clue to the presence of a positive nucleus in the atom as a result of the bombardment of thin foils of metals.**

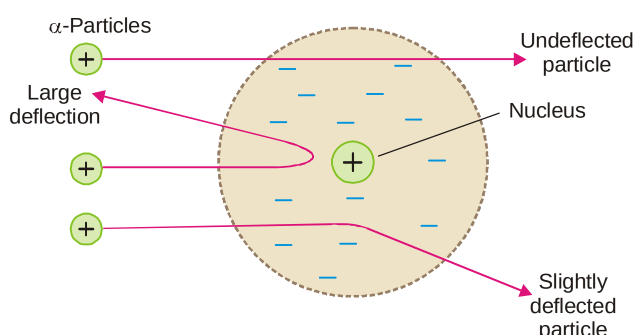
RUTHERFORD'S ATOMIC MODEL – THE NUCLEAR ATOM

Having known that atom contains electrons and a positive ion, Rutherford proceeded to perform experiments to know as to how and where these were located in the atom. In 1909 Rutherford and Marsden performed their historic **Alpha Particle-Scattering Experiment,** using the apparatus illustrated in Fig. 1.6. They directed a stream of very highly energetic α-particles from a radioactive source against a thin *gold foil* provided with a circular fluorescent zinc sulphide screen around it. Whenever an α-particle struck the screen, a tiny flash of light was produced at that point.



■ **Figure 1.6**
Rutherford and Marsden's α-particle scattering experiment.

Rutherford and Marsden noticed that most of the α-particles passed straight through the gold foil and thus produced a flash on the screen behind it. This indicated that gold atoms had a structure with plenty of empty space. To their great astonishment, tiny flashes were also seen on other portions of the screen, some time in front of the gold foil. This showed that gold atoms deflected or 'scattered' α-particles through large angles so much so that some of these bounced back to the source. Based on these observations, Rutherford proposed a model of the atom which is named after him. This is also called the **Nuclear Atom.** According to it :

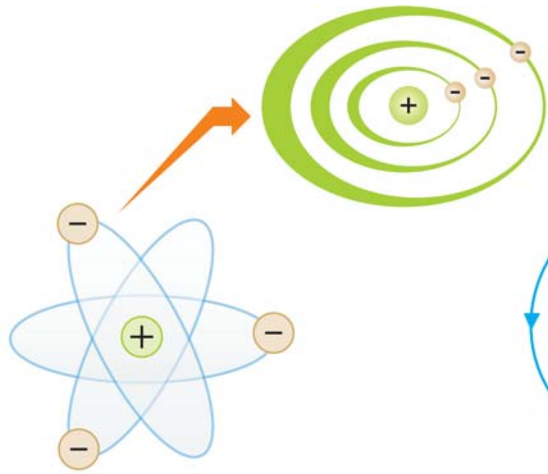


■ **Figure 1.7**
How nuclear atom causes scattering of α-particles.

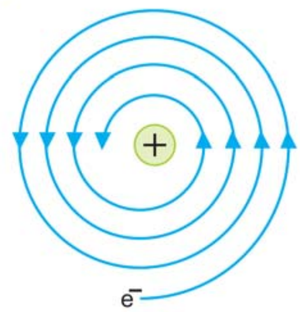
(1) **Atom has a tiny dense central core or the nucleus which contains practically the entire mass of the atom, leaving the rest of the atom almost empty.** The diameter of the nucleus is about 10^{-13} cm as compared to that of the atom 10^{-8} cm. If the nucleus were the size of a football, the entire atom would have a diameter of about 5 miles. It was this empty space around the nucleus which allowed the α-particles to pass through undeflected.

(2) **The entire positive charge of the atom is located on the nucleus, while electrons were distributed in vacant space around it.** It was due to the presence of the positive charge on the nucleus that α-particle (He^{2+}) were repelled by it and scattered in all directions.

(3) **The electrons were moving in orbits or closed circular paths around the nucleus like planets around the sun.**



■ **Figure 1.8**
Rutherford's model of atom ; electrons orbiting around nucleus.



■ **Figure 1.9**
Orbiting electron would radiate energy and spiral into the nucleus.

Weakness of Rutherford Atomic Model

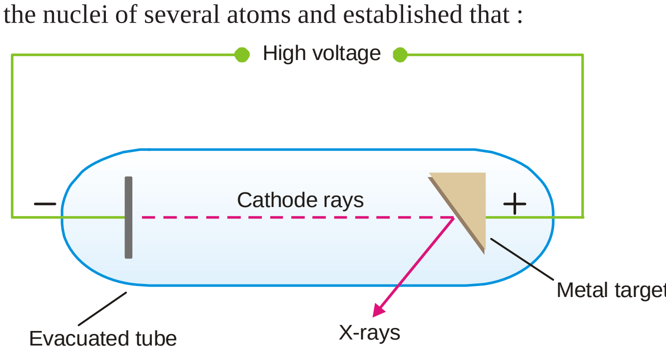
The assumption that electrons were orbiting around the nucleus was unfortunate. According to the classical electromagnetic theory if a charged particle accelerates around an oppositely charged particle, the former will radiate energy. If an electron radiates energy, its speed will decrease and it will go into spiral motion, finally falling into the nucleus. This does not happen actually as then the atom would be unstable which it is not. This was the chief weakness of Rutherford's Atomic Model.

MOSLEY'S DETERMINATION OF ATOMIC NUMBER

The discovery that atom has a nucleus that carries a positive charge raised the question : What is the magnitude of the positive charge? This question was answered by Henry Mosley in 1913.

Hitherto atomic number was designated as the 'position number' of a particular element in the Periodic Table. Mosley found that when cathode rays struck different elements used as anode targets in the discharge tube, characteristic X-rays were emitted. The wavelength of these X-rays decreases in a regular manner in passing from one element to the next one in order in the Periodic Table.

Mosley plotted the atomic number against the square root of the frequency of the X-rays emitted and obtained a straight line which indicated that atomic number was not a mere 'position number' but a fundamental property of the atom. He further made a remarkable suggestion that the wavelength (or frequency) of the emitted X-rays was related to the number of positive charges or protons in the nucleus. The wavelength changed regularly as the element that came next in the Periodic Table had one proton (one unit atomic mass) more than the previous one. Mosley calculated the number of units of positive charge on the nuclei of several atoms and established that :



■ **Figure 1.10**
Production of X-rays.

Atomic Number of an element is equal to the number of protons in the nucleus of the atom of that element.

Since the atom as a whole is electrically neutral, the atomic number (*Z*) is also equal to the number of extranuclear electrons. Thus hydrogen (H) which occupies first position in the Periodic Table has atomic number 1. This implies that it has a nucleus containing one proton (+ 1) and one extranuclear electron (– 1).

Now the term Atomic Number is often referred to as the **Proton Number.**

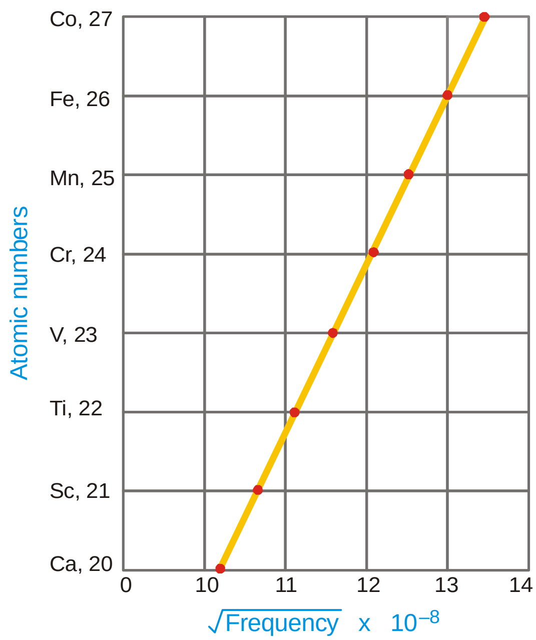


Figure 1.11
Mosley's plot of the square root of X-ray frequencies against atomic number for the elements calcium through cobalt.

WHAT IS MASS NUMBER ?

The total number of protons and neutrons in the nucleus of an atom is called the Mass Number, *A*, of the atom.

In situations where it is unnecessary to differentiate between protons and neutrons, these elementary particles are collectively referred to as **nucleons. Thus mass number of an atom is equal to the total number of nucleons in the nucleus of an atom.**

Obviously, the mass number of an atom is a whole number. Since electrons have practically no mass, the entire atomic mass is due to protons and neutrons, each of which has a mass almost exactly one unit. Therefore, **the mass number of an atom can be obtained by rounding off the experimental value of atomic mass (or atomic weight) to the nearest whole number.** For example, the atomic mass of sodium and fluorine obtained by experiment is 22.9898 and 26.9815 amu respectively. Thus their mass numbers are 23 for sodium and 27 for fluorine.

Each different variety of atom, as determined by the composition of its nucleus, is called a **nuclide.**

COMPOSITION OF THE NUCLEUS

Knowing the atomic number (*Z*) and mass number (*A*) of an atom, we can tell the number of protons and neutrons contained in the nucleus. By definition :

$$\text{Atomic Number, } Z = \text{Number of protons}$$
$$\text{Mass Number, } A = \text{Number of protons + Number of neutrons}$$

∴ The number of neutrons is given by the expression :

$$N = A - Z$$

SOLVED PROBLEM. Uranium has atomic number 92 and atomic weight 238.029. Give the number of electrons, protons and neutrons in its atom.

SOLUTION

Atomic Number of uranium = 92

∴ Number of electrons = 92

and Number of protons = 92

Number of neutrons (N) is given by the expression

$$N = A - Z$$

Mass Number (A) is obtained by rounding off the atomic weight

$$= 238.029 = 238$$

∴ $$N = 238 - 92 = 146$$

Thus uranium atom has 92 electrons, 92 protons and 146 neutrons.

The composition of nuclei of some atoms is given in Table 1.2.

TABLE 1.2. COMPOSITION OF THE NUCLEUS OF SOME ATOMS

Atom	Mass Number (A)	Atomic Number (Z)	COMPOSITION	
			Protons = Z	Neutrons = A – Z
Be	9	4	4	5
F	19	9	9	10
Na	23	11	11	12
Al	27	13	13	14
P	31	15	15	16
Sc	45	21	21	24
Au	197	79	79	118

QUANTUM THEORY AND BOHR ATOM

Rutherford model laid the foundation of the model picture of the atom. However it did not tell anything as to the position of the electrons and how they were arranged around the nucleus.

Rutherford recognised that electrons were orbiting around the nucleus. But according to the classical laws of Physics an electron moving in a field of force like that of nucleus, would give off radiations and gradually collapse into the nucleus. Thus Rutherford model failed to explain why electrons did not do so.

Neils Bohr, a brilliant Danish Physicist, pointed out that the old laws of physics just did not work in the submicroscopic world of the atom. He closely studied the behaviour of electrons, radiations and atomic spectra. In 1913 Bohr proposed a new model of the atom based on the modern Quantum theory of energy. With his theoretical model he was able to explain as to why an orbiting electron did not collapse into the nucleus and how the atomic spectra were caused by the radiations emitted when electrons moved from one orbit to the other. Therefore to understand the Bohr theory of the atomic structure, it is first necessary to acquaint ourselves with the nature of electromagnetic radiations and the atomic spectra as also the Quantum theory of energy.

Electromagnetic Radiations

Energy can be transmitted through space by electromagnetic radiations. Some forms of *radiant energy* are radio waves, visible light, infrared light, ultraviolet light, X-rays and γ-radiations.

Electromagnetic radiations are so named because they consist of waves which have electrical and magnetic properties. An object sends out energy waves when its particles move up and down or *vibrate* continuously. Such a vibrating particle causes an intermittent disturbance which constitutes a wave. A wave conveys energy from the vibrating object to a distant place. The wave travels at right angle to the vibratory motion of the object.

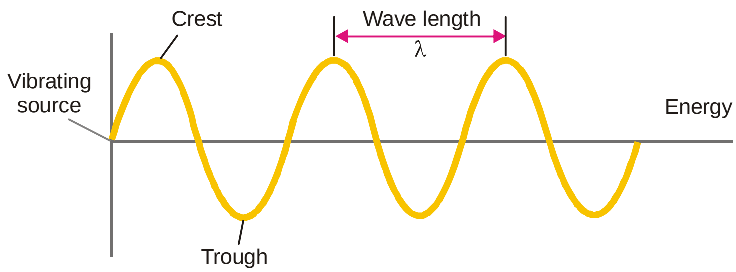


Figure 1.12
Illustration of wave motion caused by a vibrating source.

Waves similar to electromagnetic waves are caused when a stone is thrown in a pond of water. The stone makes the water molecules vibrate up and down and transmit its energy as waves on water surface. These waves are seen travelling to the bank of the pond.

A wave may be produced by the actual displacement of particles of the medium as in case of water or sound waves. However, electromagnetic waves are produced by a periodic motion of charged particles. Thus vibratory motion of electrons would cause a wave train of oscillating electric field and another of oscillating magnetic field. These electromagnetic waves travel through empty space with the speed or velocity of light.

Characteristics of Waves

A series of waves produced by a vibrating object can be represented by a wavy curve of the type shown in Fig. 1.12. The tops of the curve are called *crests* and the bottoms *troughs*. Waves are characterised by the following properties :

Wavelength

The wavelength is defined as the distance between two successive crests or troughs of a wave.

Wavelength is denoted by the Greek letter λ (lambda). It is expressed in centimetres or metres or in *angstrom* units. One angstrom, Å, is equal to 10^{-8} cm. It is also expressed in nanometers (1nm = 10^{-9} m). That is,

$$1\ \text{Å} = 10^{-8}\ \text{cm} = 10^{-10}\ \text{m} \qquad \text{or} \qquad 1\ \text{cm} = 10^{8}\ \text{Å and } 1\ \text{m} = 10^{10}\ \text{Å}$$
$$1\ \text{nm} = 10^{-9}\ \text{m}$$

Frequency

The frequency is the number of waves which pass a given point in one second.

Frequency is denoted by the letter ν (nu) and is expressed in *hertz* (hz).

It is noteworthy that **a wave of high frequency (*b*) has a shorter wavelength, while a wave of low frequency (*a*) has a longer wavelength.**

Speed

The speed (or velocity) of a wave is the distance through which a particular wave travels in one second.

Speed is denoted by c and it is expressed in cm per second. If the speed of a wave is c cm/sec, it means that the distance travelled by the wave in one second is c cm. Speed is related to frequency and wavelength by the expression

$$c = \nu\lambda$$

or $$\text{Speed} = \text{Frequency} \times \text{Wavelength}$$

The various types of electromagnetic radiations have different wavelengths and frequencies. As evident from Fig. 1.13, all types of radiations travel with the same speed or velocity. This velocity has been determined experimentally and it comes out to be 3×10^{10} cm/sec = 186,000 miles per second which is, in fact, the velocity of light.

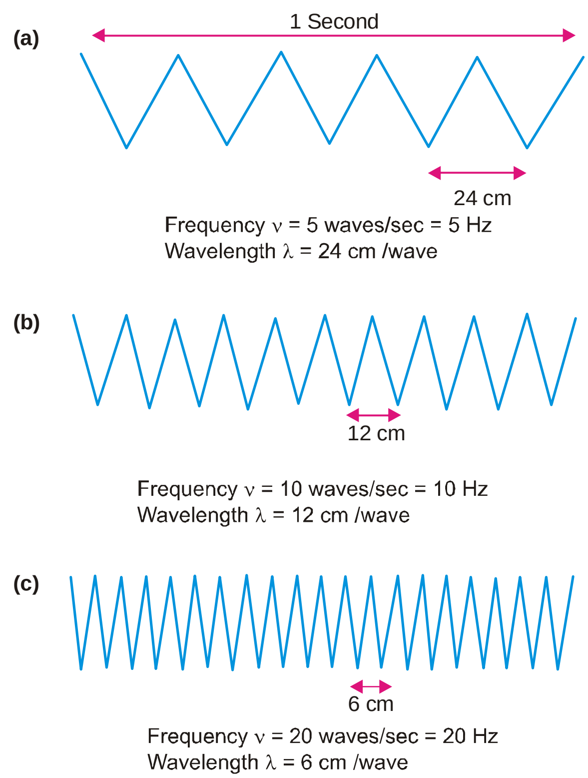


Figure 1.13
Waves of different wavelengths and frequencies.
In all three cases; velocity = λ x ν = 120 cm/sec.

Wave Number

Another quantity used to characterise radiation is the *wave number.* **This is reciprocal of the wavelength and is given the symbol $\bar{\nu}$ (nu bar).** That is,

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

The wave number is the number of wavelengths per unit of length covered. Its units are cm^{-1} or m^{-1}.

SOLVED PROBLEM. The wavelength of a violet light is 400 nm. Calculate its frequency and wave number.

SOLUTION. We know that

$$\text{frequency, } \nu = \frac{c}{\lambda}$$

Here $c = 3.0 \times 10^8$ m sec^{-1}; $\lambda = 400$ nm $= 400 \times 10^{-9}$ m

$$\nu = \frac{c}{\lambda} = \frac{3.0 \times 10^8 \text{ m sec}^{-1}}{400 \times 10^{-9} \text{ m}}$$

$$= \frac{3}{400} \times 10^{17} \text{ sec}^{-1}$$

$$= \frac{3000}{400} \times 10^{14} \text{ sec}^{-1}$$

$$= \mathbf{7.5 \times 10^{14}\ sec^{-1}}$$

Also, wave number $\bar{\nu} = \frac{1}{\lambda}$

$$\bar{\nu} = \frac{1}{400 \times 10^{-9} \text{ m}}$$

$$= \mathbf{25 \times 10^{5}\ m^{-1}}$$

SOLVED PROBLEM. The frequency of strong yellow line in the spectrum of sodium is 5.09×10^{14} sec^{-1}. Calculate the wavelength of the light in nanometers.

SOLUTION. We know that wavelength, $\lambda = \frac{c}{\nu}$

Here $c = 3.0 \times 10^8$ m sec^{-1}

$\nu = 5.09 \times 10^{14}$ sec^{-1} (given)

Wavelength $$\lambda = \frac{3.0 \times 10^8 \text{ m sec}^{-1}}{5.09 \times 10^{14} \text{ sec}^{-1}}$$

$$= \frac{3000}{5.09} \times 10^{-9} \text{ m}$$

$$= 589 \times 10^{-9} \text{ m}$$

$$= \mathbf{589\ nm} \qquad [\because\ 1 \text{ nm} = 10^{-9} \text{ m}]$$

SPECTRA

A spectrum is an array of waves or particles spread out according to the increasing or decreasing of some property. An increase in frequency or a decrease in wavelength represent an increase in energy.

THE ELECTROMAGNETIC SPECTRUM

Electromagnetic radiations include a range of wavelengths and this array of wavelengths is referred to as the *Electromagnetic radiation spectrum* or simply *Electromagnetic spectrum*. The electromagnetic spectrum with marked wavelengths is shown in Fig. 1.14.

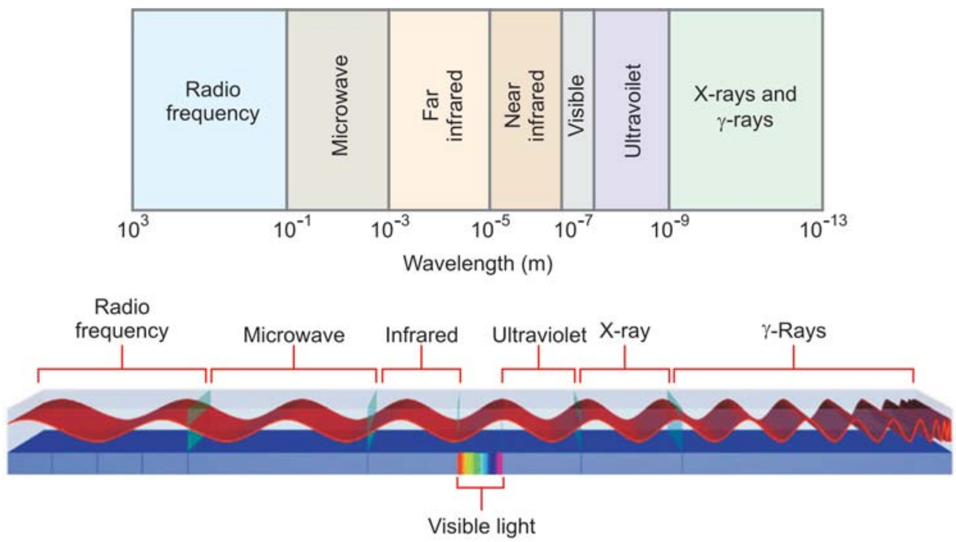


Figure 1.14
Electromagnetic spectrum. Wavelength boundaries of each region are approximate.

CONTINUOUS SPECTRUM

White light is radiant energy coming from the sun or from incandescent lamps. It is composed of light waves in the range 4000-8000 Å. Each wave has a characteristic colour. When a beam of white light is passed through a prism, different wavelengths are refracted (or bent) through different angles. When received on a screen, these form a continuous series of colour bands : violet, indigo, blue, green, yellow, orange and red (VIBGYOR). **This series of bands that form a continuous rainbow of colours, is called a Continuous Spectrum.**

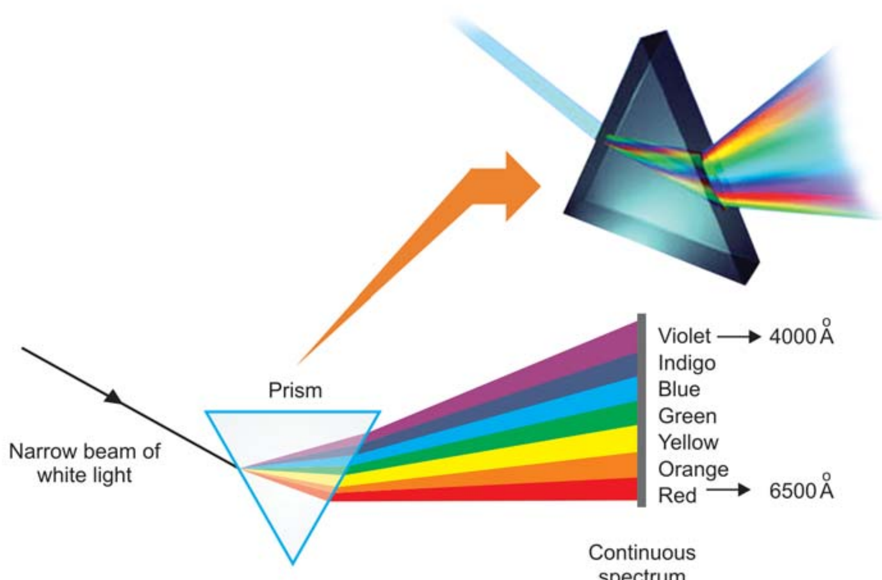
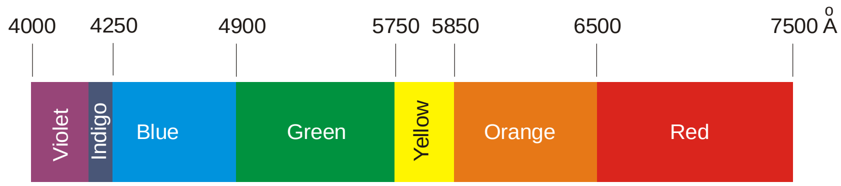


Figure 1.15
The continuous spectrum of white light.

The violet component of the spectrum has shorter wavelengths (4000 – 4250 Å) and higher frequencies. The red component has longer wavelengths (6500 – 7500 Å) and lower frequencies. The invisible region beyond the violet is called **ultraviolet region** and the one below the red is called **infrared region.**

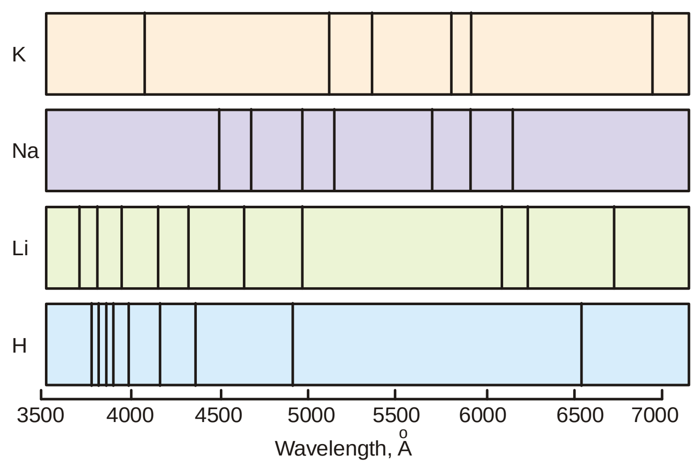
ATOMIC SPECTRA

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



■ **Figure 1.16**
Wavelength range of colour bands in Å of continuous spectrum.

For example, a Bunsen burner flame is coloured yellow by sodium salts, red by strontium and violet by potassium. In a discharge tube, neon glows orange-red, helium-pink, and so on. If we examine the emitted light with a **Spectroscope** (a device in which a beam of light is passed through a prism and received on a photograph), the spectrum obtained on the photographic plate is found to consist of bright lines (Fig. 1.18). **Such a spectrum in which each line represents a specific wavelength of radiation emitted by the atoms is referred to as the Line spectrum or Atomic Emission spectrum** of the element. The emission spectra of some elements are shown in Fig. 1.17. An individual line of these spectra is called a **Spectral line.**



■ **Figure 1.17**
Emission spectra of K, Na, Li and H.

When white light composed of all visible wavelengths, is passed through the cool vapour of an element, certain wavelengths may be absorbed. These absorbed wavelengths are thus found missing in the transmitted light. The spectrum obtained in this way consists of a series of dark lines which is referred to as the **Atomic Absorption spectrum** or simply **Absorption spectrum.** The wavelengths of the dark lines are exactly the same as those of bright lines in the emission spectrum. The absorption spectrum of an element is the reverse of emission spectrum of the element.

Atomic spectral lines are emitted or absorbed not only in the visible region of the electromagnetic spectrum but also in the infrared region **(IR spectra)** or in the ultraviolet region **(UV spectra).**

Since the atomic spectra are produced by emission or absorption of energy depending on the internal structure of the atom, each element has its own characteristic spectrum. Today spectral analysis has become a powerful method for the detection of elements even though present in extremely small amounts. The most important consequence of the discovery of spectral lines of hydrogen and other elements was that it led to our present knowledge of atomic structure.

ATOMIC SPECTRUM OF HYDROGEN

The emission line spectrum of hydrogen can be obtained by passing electric discharge through the gas contained in a discharge tube at low pressure. The light radiation emitted is then examined with the help of a **spectroscope.** The bright lines recorded on the photographic plate constitute the atomic spectrum of hydrogen (Fig. 1.18).

In 1884 J.J. Balmer observed that there were four prominent coloured lines in the visible hydrogen spectrum :

(1) a *red line* with a wavelength of 6563 Å.
(2) a *blue-green line* with a wavelength 4861 Å.
(3) a *blue line* with a wavelength 4340 Å.
(4) a *violet line* with a wavelength 4102 Å.

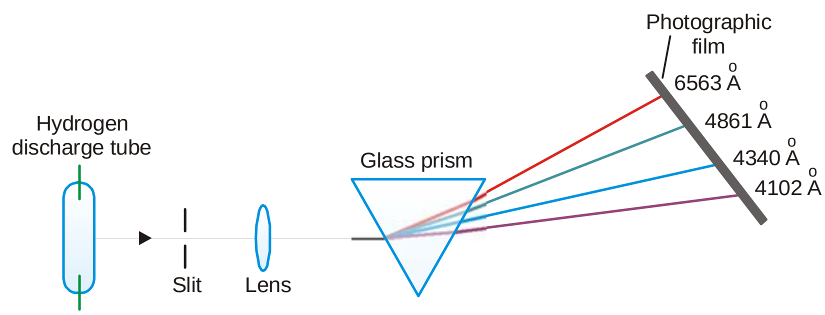


Figure 1.18
The examination of the atomic spectrum of hydrogen with a spectroscope.

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

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

where R is a constant called the **Rydberg Constant** which has the value 109, 677 cm^{-1} and $n = 3, 4,$ 5, 6 etc. That is, if we substitute the values of 3, 4, 5 and 6 for n, we get, respectively, the wavelength of the four lines of the hydrogen spectrum.

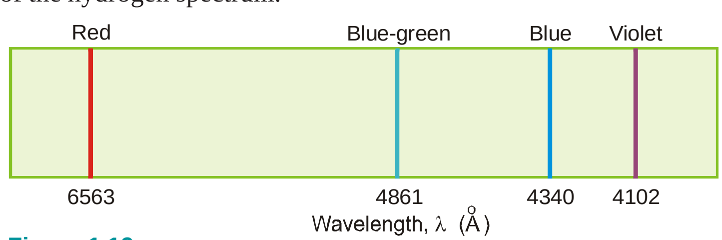


Figure 1.19
Balmer series in the Hydrogen spectrum.

In addition to Balmer Series, four other spectral series were discovered in the infrared and ultraviolet regions of the hydrogen spectrum. These bear the names of the discoverers. Thus in all we have **Five Spectral Series** in the atomic spectrum of hydrogen :

Name	Region where located
(1) Lyman Series	Ultraviolet
(2) Balmer Series	Visible
(3) Paschen Series	Infrared
(4) Brackett Series	Infrared
(5) Pfund Series	Infrared

Balmer equation had no theoretical basis at all. Nobody had any idea how it worked so accurately in finding the wavelengths of the spectral lines of hydrogen atom. However, in 1913 Bohr put forward his theory which immediately explained the observed hydrogen atom spectrum. Before we can understand Bohr theory of the atomic structure, it is necessary to acquaint ourselves with the quantum theory of energy.

QUANTUM THEORY OF RADIATION

The wave theory of transmission of radiant energy appeared to imply that energy was emitted (or absorbed) in continuous waves. In 1900 Max Planck studied the spectral lines obtained from hot-body radiations at different temperatures. According to him, light radiation was produced discontinuously by the molecules of the hot body, each of which was vibrating with a specific frequency which increased with temperature. Thus Planck proposed a new theory that a hot body radiates energy not in continuous waves but in small units of waves. The 'unit wave' or 'pulse of energy' is called **Quantum** (plural, *quanta*). In 1905 Albert Einstein showed that light radiations emitted by 'excited' atoms or molecules were also transmitted as particles or quanta of energy. These light quanta are called **photons.**

The general **Quantum Theory of Electromagnetic Radiation** in its present form may be stated as :

(1) **When atoms or molecules absorb or emit radiant energy, they do so in separate 'units of waves' called quanta or photons.** Thus light radiations obtained from energised or 'excited atoms' consist of a stream of photons and not continuous waves.

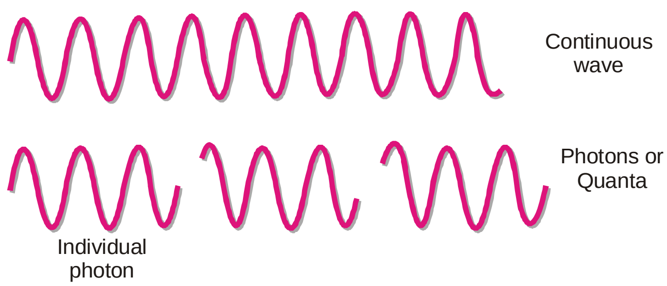


Figure 1.20
A continuous wave and photons.

(2) **The energy, *E*, of a quantum or photon is given by the relation**

$$E = h\nu \qquad ...(1)$$

where ν is the frequency of the emitted radiation, and h the **Planck's Constant.** The value of $h = 6.62 \times 10^{-27}$ erg sec. or 6.62×10^{-34} J sec.

We know that c, the velocity of radiation, is given by the equation

$$c = \lambda\nu \qquad ...(2)$$

Substituting the value of ν from (2) in (1), we can write

$$E = \frac{hc}{\lambda}$$

Thus **the magnitude of a quantum or photon of energy is directly proportional to the frequency of the radiant energy, or is inversely proportional to its wavelength, λ.**

(3) **An atom or molecule can emit (or absorb) either one quantum of energy ($h\nu$) or any whole number multiple of this unit.**

Thus radiant energy can be emitted as $h\nu$, $2h\nu$, $3h\nu$, and so on, but never as 1.5 $h\nu$, 3.27 $h\nu$, 5.9 $h\nu$, or any other fractional value of $h\nu$ *i.e.* $nh\nu$

Quantum theory provided admirably a basis for explaining the photoelectric effect, atomic spectra and also helped in understanding the modern concepts of atomic and molecular structure.

SOLVED PROBLEM. Calculate the magnitude of the energy of the photon (or quantum) associated with light of wavelength 6057.8 Å. (Å = 10^{-8} cm)

SOLUTION

(*a*) Calculation of Frequency :

$$\nu = \frac{c}{\lambda} = \frac{3.0 \times 10^{10}\,\text{cm sec}^{-1}}{6057.8 \times 10^{-8}\,\text{cm}}$$

$$= 4.952 \times 10^{14}\ \text{sec}^{-1}$$

(*b*) Calculation of Energy :

$$E = h\nu = (6.625 \times 10^{-27}\ \text{erg sec})\ (4.952 \times 10^{14}\ \text{sec}^{-1})$$

$$\mathbf{= 3.281 \times 10^{-12}\ erg}$$

PHOTOELECTRIC EFFECT

When a beam of light of sufficiently high frequency is allowed to strike a metal surface in vacuum, electrons are ejected from the metal surface. This phenomenon is known as **Photoelectric effect** and the ejected electrons **Photoelectrons.** For example, when ultraviolet light shines on Cs (or Li, Na, K, Rb) as in the apparatus shown in Fig 1.21, the photoelectric effect occurs.

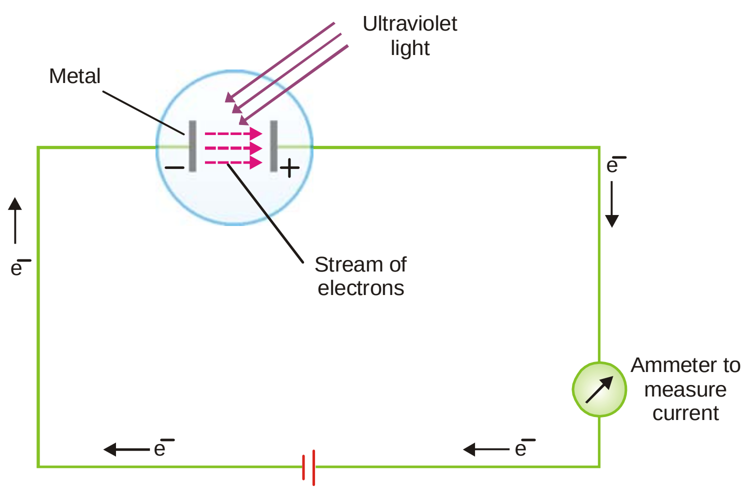


Figure 1.21
Apparatus for measuring the photoelectric effect. When ultraviolet light shines on the metal, the emitted electrons flow to the anode and the circuit is completed. This current can be measured with the help of an ammeter.

With the help of this photoelectric apparatus the following observations can be made :

(1) **An increase in the intensity of incident light does not increase the energy of the photoelectrons.** It merely increases their rate of emission.

(2) **The kinetic energy of the photoelectrons increases linearly with the frequency of the incident light (Fig. 1.22).** If the frequency is decreased below a certain critical value **(Threshold frequency, ν_0)**, no electrons are ejected at all.
The Classical Physics predicts that the kinetic energy of the photoelectrons should depend on the intensity of light and not on the frequency. Thus it fails to explain the above observations.

EINSTEIN'S EXPLANATION OF PHOTOELECTRIC EFFECT

In 1905 Albert Einstein, who was awarded Nobel Prize for his work on photons, interpreted the Photoelectric effect by application of the Quantum theory of light.

(1) A photon of incident light transmits its energy ($h\nu$) to an electron in the metal surface which escapes with kinetic energy $\frac{1}{2}mv^2$. **The greater intensity of incident light merely implies greater number of photons each of which releases one electron.** This increases the rate of emission of electrons, while the kinetic energy of individual photons remains unaffected.

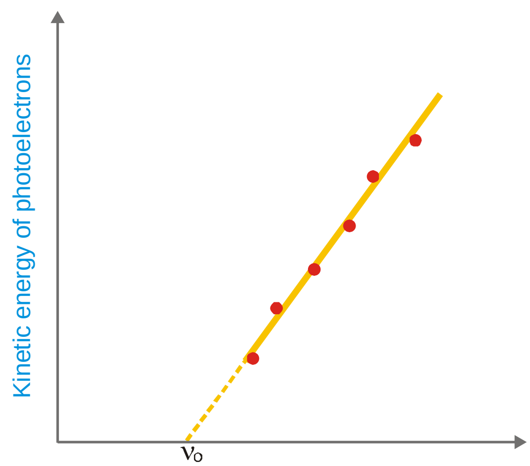


Figure 1.22
Kinetic energy of photoelectrons plotted against frequency of incident light.

(2) **In order to release an electron from the metal surface, the incident photon has first to overcome the attractive force exerted by the positive ion of the metal.** The energy of a photon ($h\nu$) is proportional to the frequency of incident light. The frequency which provides enough energy just to release the electron from the metal surface, will be the *threshold frequency*, ν_0. For frequency less than ν_0, no electrons will be emitted.

For higher frequencies $\nu > \nu_0$, a part of the energy goes to loosen the electron and remaining for imparting kinetic energy to the photoelectron. Thus,

$$h\nu = h\nu_0 + \frac{1}{2}mv^2 \quad ...(1)$$

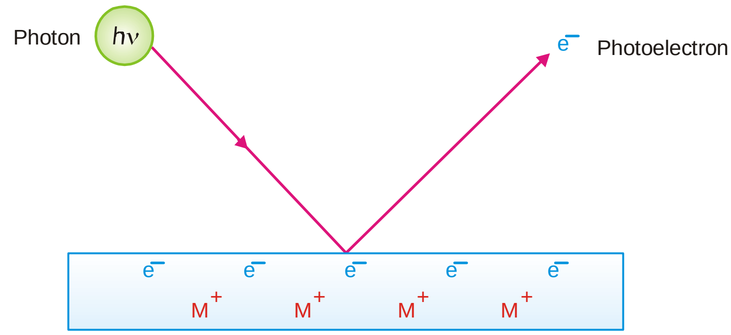


Figure 1.23
It needs a photon($h\nu$) to eject an electron with energy ½ mv^2.

Where $h\nu$ is the energy of the incoming photon, $h\nu_0$ is the minimum energy for an electron to escape from the metal, and $\frac{1}{2}mv^2$ is the kinetic energy of the photoelectron. $h\nu_0$ is constant for a particular solid and is designated as W, the **work function.** Rearranging equation (1)

$$\frac{1}{2}mv^2 = h\nu - W \qquad ...(2)$$

This is the equation for a straight line that was experimentally obtained in Fig. 1.22. Its slope is equal to h, the Planck's constant. The value of h thus found came out to be the same as was given by Planck himself.

SOLVED PROBLEM. What is the minimum energy that photons must possess in order to produce photoelectric effect with platinum metal? The threshold frequency for platinum is 1.3×10^{15} sec^{-1}.

SOLUTION

The threshold frequency (ν_0) is the lowest frequency that photons may possess to produce the photoelectric effect. The energy corresponding to this frequency is the minimum energy (E).

$$E = h\nu_0$$
$$= (6.625 \times 10^{-27} \text{ erg sec})\ (1.3 \times 10^{15} \text{ sec}^{-1})$$
$$= \mathbf{8.6 \times 10^{-12} \text{ erg}}$$

SOLVED PROBLEM. Calculate the kinetic energy of an electron emitted from a surface of potassium metal (work function = 3.62×10^{-12} erg) by light of wavelength 5.5×10^{-8} cm.

SOLUTION

$$\nu = \frac{c}{\lambda} \text{ where } c = \text{velocity of light } \left(3.0 \times 10^{10} \text{cm sec}^{-1}\right)$$

For $\lambda = 5.5 \times 10^{-8}$ cm

$$\nu = \frac{c}{\lambda} = \frac{3.0 \times 10^{10} \text{ cm sec}^{-1}}{5.5 \times 10^{-8} \text{ cm}} = 5.5 \times 10^{17} \text{ sec}^{-1}$$

$$\frac{1}{2}mv^2 = h\nu - W$$
$$= (6.6 \times 10^{-27} \text{ erg sec})\ (5.5 \times 10^{17} \text{ sec}^{-1}) - 3.62 \times 10^{-12} \text{ erg}$$
$$= 3.63 \times 10^{-9} \text{ erg} - 3.62 \times 10^{-12} \text{ erg}$$
$$= \mathbf{3.63 \times 10^{-9} \text{ erg}}$$

Thus the electron will be emitted with kinetic energy of 3.63×10^{-9} erg.

COMPTON EFFECT

In 1923 A.H. Compton provided one more proof to the quantum theory or the photon theory. He was awarded Nobel Prize in 1927 for his discovery of what is now called the **Compton Effect.** He demonstrated that : **When X-rays of wavelength λ' struck a sample of graphite, an electron was ejected and the X-rays scattered at an angle θ had longer wavelength λ.**

Explanation of Compton Effect

Compton said that it was like a ball hitting a stationary ball which is pushed away while the energy of the striking ball decreases. Thus he argued that light radiation (X-rays) consisted of particles (photons), as a continuous wave could not have knocked out the electron. **He visualised that a photon of incident light struck a stationary electron in graphite and hence lost some energy which resulted in the increase of wavelength.** This process could not have occurred unless light radiation consisted of particles or photons.

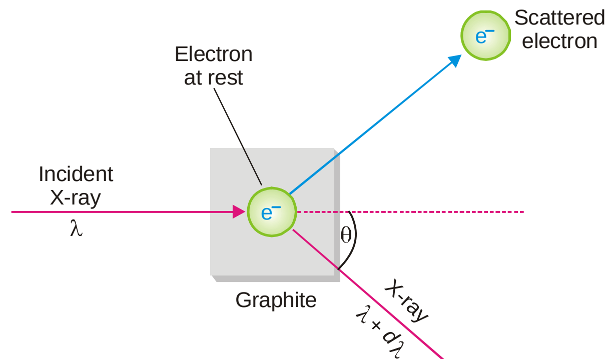


Figure 1.24
Compton scattering of X-rays.

By assuming photon-electron collisions to be perfectly elastic, Compton found that the shift in wavelength, $d\lambda$ was given by the expression

$$d\lambda = \frac{2h}{mc}\sin^2 \theta/2.$$

where h is Planck's constant, m the mass of an electron, c the velocity of light and θ the angle of scattering. The expression shows that $d\lambda$ is independent of the nature of the substance and wavelength of the incident radiation. Given the wavelength of a photon, one can calculate the momentum of the electron ejected.

BOHR MODEL OF THE ATOM

Rutherford's nuclear model simply stated that atom had a nucleus and the negative electrons were present outside the nucleus. It did not say anything as to how and where those electrons were arranged. It also could not explain why electrons did not fall into the nucleus due to electrostatic attraction. In 1913 Niels Bohr proposed a new model of atom which explained some of these things and also the emission spectrum of hydrogen. Bohr's theory was based on Planck's quantum theory and was built on the following postulates.

Postulates of Bohr's Theory

(1) **Electrons travel around the nucleus in specific permitted circular orbits and in no others.**

Electrons in each orbit have a definite energy and are at a fixed distance from the nucleus. The orbits are given the letter designation n and each is numbered 1, 2, 3, etc. (or K, L, M, etc.) as the distance from the nucleus increases.

(2) **While in these specific orbits, an electron does not radiate (or lose) energy.**

Therefore in each of these orbits the energy of an electron remains the same *i.e.* it neither loses nor gains energy. Hence the specific orbits available to the electron in an atom are referred to as **stationary energy levels** or simply **energy levels.**

(3) **An electron can move from one energy level to another by quantum or photon jumps only.**

When an electron resides in the orbit which is lowest in energy (which is also closest to the nucleus), the electron is said to be in the **ground state.** When an electron is supplied energy, it absorbs one quantum or photon of energy and jumps to a higher energy level. The electron then has potential energy and is said to be in an **excited state.**

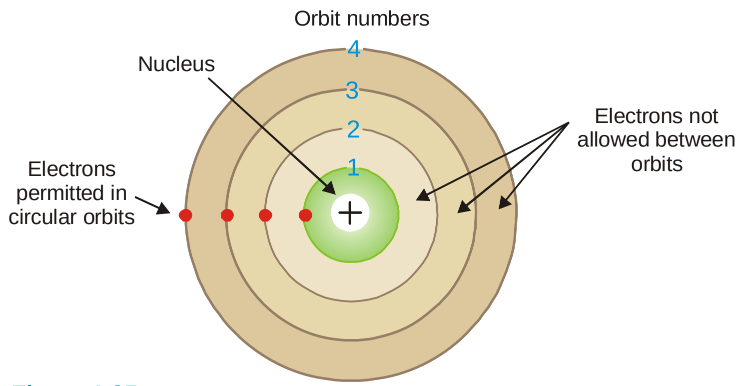


Figure 1.25
Circular electron orbits or stationary energy levels in an atom.

The quantum or photon of energy absorbed or emitted is the difference between the lower and higher energy levels of the atom

$$\Delta E = E_{high} - E_{low} = h\nu \qquad ...(1)$$

where h is Planck's constant and ν the frequency of a photon emitted or absorbed energy.

(4) **The angular momentum (mvr) of an electron orbiting around the nucleus is an integral multiple of Planck's constant divided by 2π.**

$$\text{Angular momentum} = mvr = n\frac{h}{2\pi} \qquad ...(2)$$

where m = mass of electron, v = velocity of the electron, r = radius of the orbit ; n = 1, 2, 3, etc., and h = Planck's constant.

By putting the values 1, 2, 3, etc., for n, we can have respectively the angular momentum

$$\frac{h}{2\pi}, \frac{2h}{2\pi}, \frac{3h}{2\pi}, \text{ etc.}$$

There can be no fractional value of $h/2\pi$. Thus *the angular momentum is said to be quantized.* The integer n in equation (2) can be used to designate an orbit and a corresponding energy level n is called the atom's **Principal quantum number.**

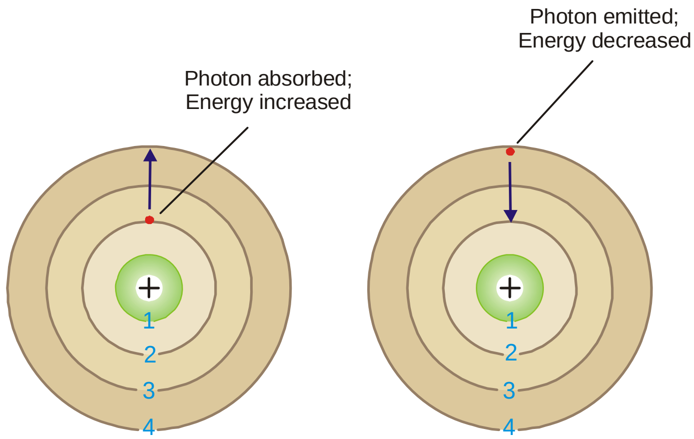


Figure 1.26
An electron absorbs a photon of light while it jumps from a lower to a higher energy orbit and a photon is emitted while it returns to the original lower energy level.

Using the above postulates and some classical laws of Physics, Bohr was able to calculate the radius of each orbit of the hydrogen atom, the energy associated with each orbit and the wavelength of the radiation emitted in transitions between orbits. The wavelengths calculated by this method were found to be in excellent agreement with those in the actual spectrum of hydrogen, which was a big success for the Bohr model.

Calculation of radius of orbits

Consider an electron of charge e revolving around a nucleus of charge Ze, where Z is the atomic number and e the charge on a proton. Let m be the mass of the electron, r the radius of the orbit and v the tangential velocity of the revolving electron.

The electrostatic force of attraction between the nucleus and the electron (Coulomb's law),

$$= \frac{Ze \times e}{r^2}$$

The centrifugal force acting on the electron

$$= \frac{mv^2}{r}$$

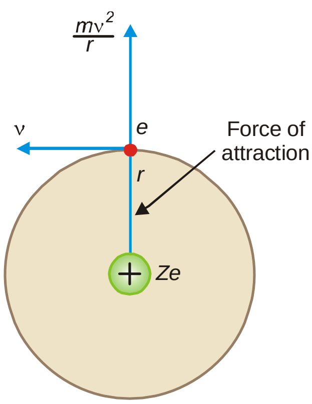


Figure 1.27
Forces keeping electron in orbit.

Bohr assumed that these two opposing forces must be balancing each other exactly to keep the electron in orbit. Thus,

$$\frac{Ze^2}{r^2} = \frac{mv^2}{r}$$

For hydrogen $Z = 1$, therefore,

$$\frac{e^2}{r^2} = \frac{mv^2}{r} \qquad ...(1)$$

Multiplying both sides by r

$$\frac{e^2}{r} = mv^2 \qquad ...(2)$$

According to one of the postulates of Bohr's theory, angular momentum of the revolving electron is given by the expression

$$mvr = \frac{nh}{2\pi}$$

or $$v = \frac{nh}{2\pi\, mr} \qquad ...(3)$$

Substituting the value of v in equation (2),

$$\frac{e^2}{r} = m\left(\frac{nh}{2\pi\, mr}\right)^2$$

Solving for r,

$$r = \frac{n^2h^2}{4\pi^2\, me^2} \qquad ...(4)$$

Since the value of h, m and e had been determined experimentally, substituting these values in (4), we have

$$r = n^2 \times 0.529 \times 10^{-8} \text{ cm} \qquad ...(5)$$

where n is the principal quantum number and hence the number of the orbit.

When $n = 1$, the equation (5) becomes

$$r = 0.529 \times 10^{-8} \text{ cm} = \alpha_0 \qquad ...(6)$$

This last quantity, α_0 called the first **Bohr radius** was taken by Bohr to be the radius of the hydrogen atom in the ground state. This value is reasonably consistent with other information on the size of atoms. When $n = 2, 3, 4$ etc., the value of the second and third orbits of hydrogen comprising the electron in the excited state can be calculated.

SOLVED PROBLEM. Calculate the first five Bohr radii.

SOLUTION

The equation (5) may be written as

$$r = n^2 \times 0.529 \times 10^{-8} \text{ cm}$$

$$n = 1\,;\, r = 1^2 \times 0.529 \times 10^{-8} = 0.529 \times 10^{-8} \text{ cm}$$

$$n = 2\,;\, r = 2^2 \times 0.529 \times 10^{-8} = 2.12 \times 10^{-8} \text{ cm}$$

$$n = 3\,;\, r = 3^2 \times 0.529 \times 10^{-8} = 4.76 \times 10^{-8} \text{ cm}$$

$$n = 4\,;\, r = 4^2 \times 0.529 \times 10^{-8} = 8.46 \times 10^{-8} \text{ cm}$$

$$n = 5\,;\, r = 5^2 \times 0.529 \times 10^{-8} = 13.2 \times 10^{-8} \text{ cm}$$

Energy of electron in each orbit

For hydrogen atom, the energy of the revolving electron, E is the sum of its kinetic energy $\left(\frac{1}{2}mv^2\right)$ and potential energy $\left(-\frac{e^2}{r}\right)$.

$$E = \frac{1}{2}mv^2 - \frac{e^2}{r} \qquad ...(7)$$

From equation (1)

$$mv^2 = \frac{e^2}{r}$$

Substituting the value of mv^2 in (7)

$$E = \frac{1}{2}\frac{e^2}{r} - \frac{e^2}{r}$$

or $$E = -\frac{e^2}{2r} \qquad ...(8)$$

Substituting the value of r from equation (4) in (8)

$$E = -\frac{e^2}{2} \times \frac{4\pi^2 me^2}{n^2 h^2}$$

$$= -\frac{2\pi^2 me^4}{n^2 h^2} \qquad ...(9)$$

Substituting the values of m, e, and h in (9),

$$E = \frac{-2.179 \times 10^{-11}}{n^2} \text{ erg/atom} \qquad ...(10)$$

or $$E = \frac{-2.179 \times 10^{-18}}{n^2} \text{ J per atom}$$

or $$E = \frac{-2.17 \times 10^{18} \times 6.02 \times 10^{23}}{n^2} \text{ J per mole}$$

or $$E = \frac{-1311.8}{n^2} \text{ kJ per mole}$$

or $$E = \frac{-313.3}{n^2} \text{ kcal per mole}$$

By using proper integer for n (quantum or orbit number), we can get the energy for each orbit.

SOLVED PROBLEM. Calculate the five lowest energy levels of the hydrogen atom.

SOLUTION

From equation (10)

$$E = \frac{-2.179 \times 10^{-11} \text{ erg/atom}}{n^2}$$

Therefore the energy associated with the first five energy levels (or orbits) is :

$n = 1$; $$E_1 = \frac{-2.179 \times 10^{-11}}{1^2} = -2.179 \times 10^{-11} \text{ erg/atom or } -1311.8 \text{ kJ mol}^{-1}$$

$n = 2$; $$E_2 = \frac{-2.179 \times 10^{-11}}{2^2} = -0.5448 \times 10^{-11} \text{ erg/atom or } -327.9 \text{ kJ mol}^{-1}$$

$n = 3$; $$E_3 = \frac{-2.179 \times 10^{-11}}{3^2} = -0.2421 \times 10^{-11} \text{ erg/atom or } -147.5 \text{ kJ mol}^{-1}$$

$n = 4$; $$E_4 = \frac{-2.179 \times 10^{-11}}{4^2} = -0.1362 \times 10^{-11} \text{ erg/atom or } -82.0 \text{ kJ mol}^{-1}$$

$n = 5$; $$E_5 = \frac{-2.179 \times 10^{-11}}{5^2} = -0.08716 \times 10^{-11} \text{ erg/atom or } -52.44 \text{ kJ mol}^{-1}$$

Significance of Negative Value of Energy

The energy of an electron at infinity is arbitrarily assumed to be zero. This state is called *zero-energy* state. When an electron moves and comes under the influence of nucleus, it does some work and spends its energy in this process. Thus the energy of the electron decreases and it becomes less than zero *i.e.* it acquires a negative value.

Bohr's Explanation of Hydrogen Spectrum

The solitary electron in hydrogen atom at ordinary temperature resides in the first orbit ($n = 1$) and is in the lowest energy state (ground state). When energy is supplied to hydrogen gas in the *discharge tube*, the electron moves to higher energy levels *viz*., 2, 3, 4, 5, 6, 7, etc., depending on the quantity of energy absorbed. From these high energy levels, the electron returns by jumps to one or other lower energy level. In doing so the electron emits the excess energy as a photon. This gives an excellent explanation of the various spectral series of hydrogen.

Lyman series is obtained when the electron returns to the ground state *i.e.*, $n = 1$ from higher energy levels ($n_2 = 2, 3, 4, 5$, etc.). Similarly, Balmer, Paschen, Brackett and Pfund series are produced when the electron returns to the second, third, fourth and fifth energy levels respectively as shown in Fig. 1.28.

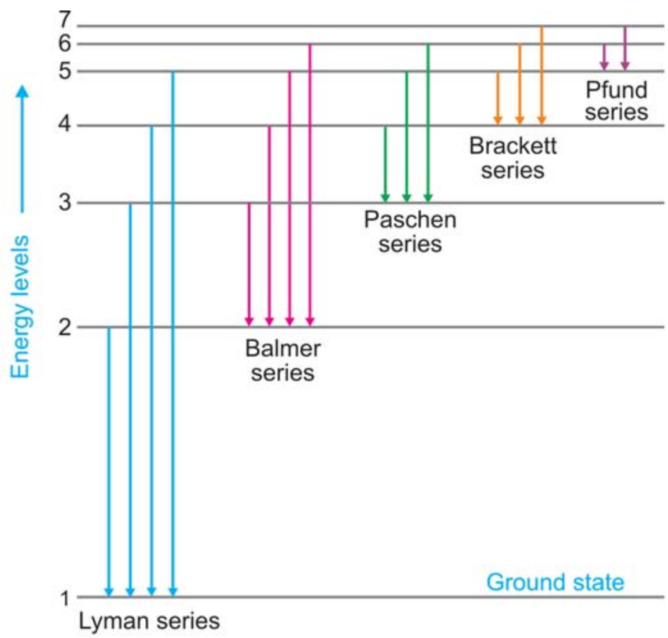


Figure 1.28
Hydrogen spectral series on a Bohr atom energy diagram.

TABLE 1.3. SPECTRAL SERIES OF HYDROGEN

Series	n_1	n_2	Region	Wavelength λ (Å)
Lyman	1	2, 3, 4, 5, etc.	ultraviolet	920-1200
Balmer	2	3, 4, 5, 6, etc.	visible	4000-6500
Paschen	3	4, 5, 6, 7, etc.	infrared	9500-18750
Brackett	4	5, 6, 7	infrared	19450-40500
Pfund	5	6, 7	infrared	37800-75000

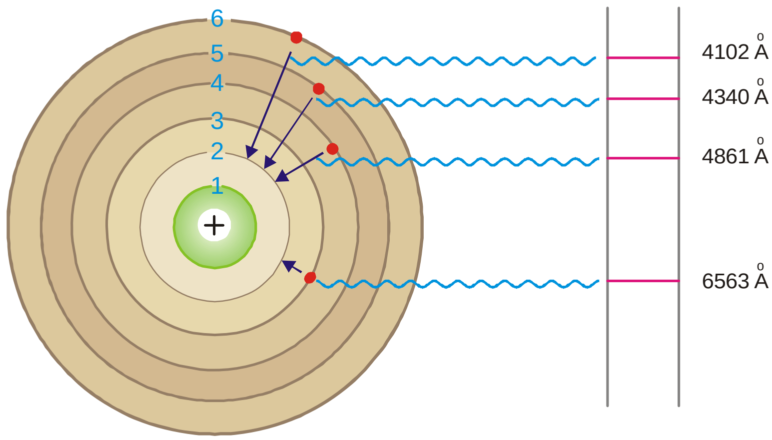


Figure 1.29
Explanation of spectral lines of hydrogen in visible region.

Value of Rydberg's constant is the same as in the original empirical Balmer's equation

According to equation (1), the energy of the electron in orbit n_1 (lower) and n_2 (higher) is

$$E_{n_1} = -\frac{2\pi^2 \, me^4}{n_1^2 \, h^2}$$

$$E_{n_2} = -\frac{2\pi^2 \, me^4}{n_2^2 \, h^2}$$

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

$$\Delta E = E_{n_2} - E_{n_1} = \frac{2\pi^2 me^4}{h^2}\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right] \qquad \text{...(1)}$$

According to Planck's equation

$$\Delta E = h\nu = \frac{hc}{\lambda} \qquad \text{...(2)}$$

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

$$\frac{hc}{\lambda} = \frac{2\pi^2 e^4 m}{h^2}\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$$

or

$$\frac{1}{\lambda} = \frac{2\pi^2 e^4 m}{h^3 c}\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$$

$$= R\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right] \qquad \text{...(3)}$$

where R is **Rydberg constant.** The value of R can be calculated as the value of e, m, h and c are known. It comes out to be 109,679 cm^{-1} and agrees closely with the value of Rydberg constant in the original empirical Balmer's equation (109,677 cm^{-1}).

Calculation of wavelengths of the spectral lines of Hydrogen in the visible region

These lines constitute the Balmer series when $n_1 = 2$. Now the equation (3) above can be written as

$$\frac{1}{\lambda} = 109679\left[\frac{1}{2^2} - \frac{1}{n_2^2}\right]$$

Thus the wavelengths of the photons emitted as the electron returns from energy levels 6, 5, 4 and 3 were calculated by Bohr. The calculated values corresponded exactly to the values of wavelengths of the spectral lines already known. This was, in fact, a great success of the Bohr atom.

SOLVED PROBLEM. Find the wavelength in Å of the line in Balmer series that is associated with drop of the electron from the fourth orbit. The value of Rydberg constant is 109,676 cm^{-1}.

SOLUTION

The wavelengths of lines in Balmer series are given by

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

where λ = wavelength, R (Rydberg constant) = 109,676 cm^{-1} ; $n = 4$.

$$\therefore \quad \frac{1}{\lambda} = 109676\left(\frac{1}{2^2} - \frac{1}{3^2}\right) = 109676\left(\frac{9-4}{36}\right)$$

$$= 109676 \times \frac{5}{36}$$

$$\lambda = \frac{36}{109676 \times 5} = 6.561 \times 10^{-5} \text{ cm}$$

$$\lambda \text{ in Å} = 6.561 \times 10^{-5} \times 10^{8} = 6561 \text{ Å}$$

$\therefore$ Wavelength of the spectral line is **6561 Å**

SHORTCOMINGS OF THE BOHR ATOM

(1) The great success of the Bohr theory was in its ability to predict lines in the hydrogen atom spectrum. But **it was spectacularly unsuccessful for every other atom containing more than one electron.**

(2) **We no longer believe in well-defined electron orbits as was assumed by Bohr.** In fact, in view of modern advances, like dual nature of matter, uncertainty principle, any mechanical model of the atom stands rejected.

(3) **Bohr's model of electronic structure could not account for the ability of atoms to form molecules through chemical bonds.** Today we only accept Bohr's views regarding quantization as nobody has explained atomic spectra without numerical quantization and no longer attempted description of atoms on classical mechanics.

(4) Bohr's theory could not explain the effect of magnetic field (Zeeman effect) and electric field (Stark effect) on the spectra of atoms.

SOMMERFELD'S MODIFICATION OF BOHR ATOM

When spectra were examined with spectrometers, each line was found to consist of several closely packed lines. The existence of these multiple spectral lines could not be explained on the basis of Bohr's theory. Sommerfeld modified Bohr's theory as follows. **Bohr considered electron**

orbits as circular but Sommerfeld postulated the presence of elliptic orbits also. An ellipse has a major and minor axis. A circle is a special case of an ellipse with equal major and minor axis. The angular momentum of an electron moving in an elliptic orbit is also supposed to be quantized. Thus only a definite set of values is permissible. It is further assumed that the angular momentum can be an integral part of $h/2\pi$ units, where h is Planck's constant. Or that,

$$\text{angular momentum} = \frac{kh}{2\pi}$$

where k is called the **azimuthal quantum number,** whereas the quantum number used in Bohr's theory is called the **principal quantum number.** The two quantum numbers n and k are related by the expression :

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

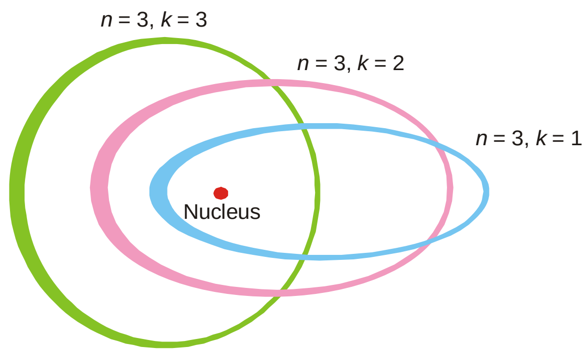


Figure 1.30
Sommerfeld orbits in hydrogen atom.

The values of k for a given value of n are $k = n - 1$, $n - 2$, $n - 3$ and so on. A series of elliptic orbits with different eccentricities result for the different values of k. When $n = k$, the orbit will be circular. In other words k will have n possible values (n to 1) for a given value of n. However, calculations based on wave mechanics have shown that this is incorrect and the Sommerfeld's modification of Bohr atom fell through.

ELECTRON ARRANGEMENT IN ORBITS

Having known that planetary electrons numerically equal to the atomic number are revolving about the atomic nucleus in closed orbits, the question arises as to how they are arranged in these orbits.

Langmuir Scheme

We are indebted to Langmuir for putting forward the first elaborate scheme of the arrangement of extranuclear electrons in 1919. His fundamental conception is that **the inert gases possess the most stable electron configuration and, therefore, contain complete electron orbits.** Since *helium* has two planetary electrons, the first orbit is considered fully saturated with 2 electrons. In the next inert gas *neon*, we have 10 planetary electrons and since 2 electrons would fully saturate the first orbit the remaining 8 will form the next stable orbit. Argon with atomic number 18 will similarly

ELECTRONIC CONFIGURATION OF ELEMENTS
(ATOMIC NUMBERS ARE GIVEN AFTER THE SYMBOLS OF THE ELEMENTS)

Group 0	Group 1		Group 2		Group 3		Group 4		Group 5		Group 6		Group 7		Group 8
	A	B	A	B	A	B	A	B	A	B	A	B	A	B	
	H 1 1												H 1 1		
He 2 2	Li 3 2, 1		Be 4 2, 2			B 5 2, 3		C 6 2, 4		N 7 2, 5		O 8 2, 6		F 9 2, 7	
Ne 10 2, 8	Na 11 2, 8, 1		Mg 12 2, 8, 2			Al 13 2, 8, 3		Si 14 2, 8, 4		P 15 2, 8, 5		S 16 2, 8, 6		Cl 17 2, 8, 7	
Ar 18 2, 8, 8	K 19 2, 8, 8, 1		Ca 20 2, 8, 8, 2		Sc 21 2, 8, 9, 2		Ti 22 2, 8, 10, 2		V 23 2, 8, 11, 2		Cr 24 2, 8, 12, 2		Mn 25 2, 8, 13, 2		Fe 26 2,8,14,2; Co 27 2,8,15,2; Ni 28 2,8,16,2
		Cu 29 2, 8, 17, 2		Zn 30 2, 8, 18, 2		Ga 31 2, 8, 18, 3		Ge 32 2, 8, 18, 4		As 33 2, 8, 18, 5		Se 34 2, 8, 18, 6		Br 35 2, 8, 18, 7	
Kr 36 2, 8, 18, 8	Rb 37 2, 8, 18, 8, 1		Sr 38 2, 8, 18, 8, 2		Y 39 2, 8, 18, 9, 2		Zr 40 2,8,18,10,2		Nb 41 2,8,18,11,2		Mo 42 2, 8,18,12,2		Tc 43 2,8,18,13,2		Ru 44 2,8,18 14,2; Rh 45 2,8,18 15,2; Pd 46 2,8,18 16,2
		Ag 47 2, 8, 18, 17, 2		Cd 48 2, 8, 18, 18, 2		In 49 2, 8, 18, 18, 3		Sn 50 2,8,18,18,4		Sb 51 2,8,18,18,5		Te 52 2,8,18,18,6		I 53 2,8,18,18,7	
Xe 54 2,8,18,18,8	Cs 55 2,8,18,18,8,1		Ba 56 2,8,18,18,8,2		La and Rare Earths (57-71) 2, 8, 18, 18, 9, 2 to 2,8,18,32,9,2		Hf 72 2, 8, 18, 32, 10, 2		Ta 73 2, 8, 18, 32, 11, 2		W 74 2, 8, 18, 32, 12, 2		Re 75 2, 8, 18, 32, 13, 2		Os 76 2,8,18, 32,14,2; Ir 77 2,8,18, 32,15,2; Pt 78 2,8,18, 32,16,2
		Au 79 2, 8, 18, 32, 17, 2		Hg 80 2, 8, 18, 32, 18, 2		TI 81 2, 8, 18, 32, 18, 3		Pb 82 2, 8, 18, 32, 18, 4		Bi 83 2, 8, 18, 32, 18, 5		Po 84 2, 8, 18, 32, 18, 6		At 85 2, 8, 18, 32, 18, 7	
Rn 86 2, 8, 18, 32, 18, 8	Fr 87 2, 8, 18, 32, 18, 8, 1		Ra 88 2, 8, 18, 32, 18, 8, 2		Ac 89 2, 8, 18, 32, 18, 9, 2		Th 90 2, 8, 18, 32, 19, 9, 2		Pa 91 2, 8, 18, 32, 20, 9, 2		U 92 2, 8, 18, 32 21, 9, 2				

have the similar arrangement 2, 8, 8. Proceeding in this manner the successive orbits would contain 2, 8, 8, 18, 32 electrons. Langmuir's scheme although quite correct for the first few elements, failed to explain the behaviour of higher elements.

Bohr-Bury Scheme

In 1921, Bury put forward a modification of Langmuir scheme which is in better agreement with the physical and chemical properties of certain elements. At about the same time as Bury developed his scheme on chemical grounds, Bohr (1921) published independently an almost identical scheme of the arrangement of extra-nuclear electrons. He based his conclusions on a study of the emission spectra of the elements. Bohr-Bury scheme as it may be called, can be summarised as follows :

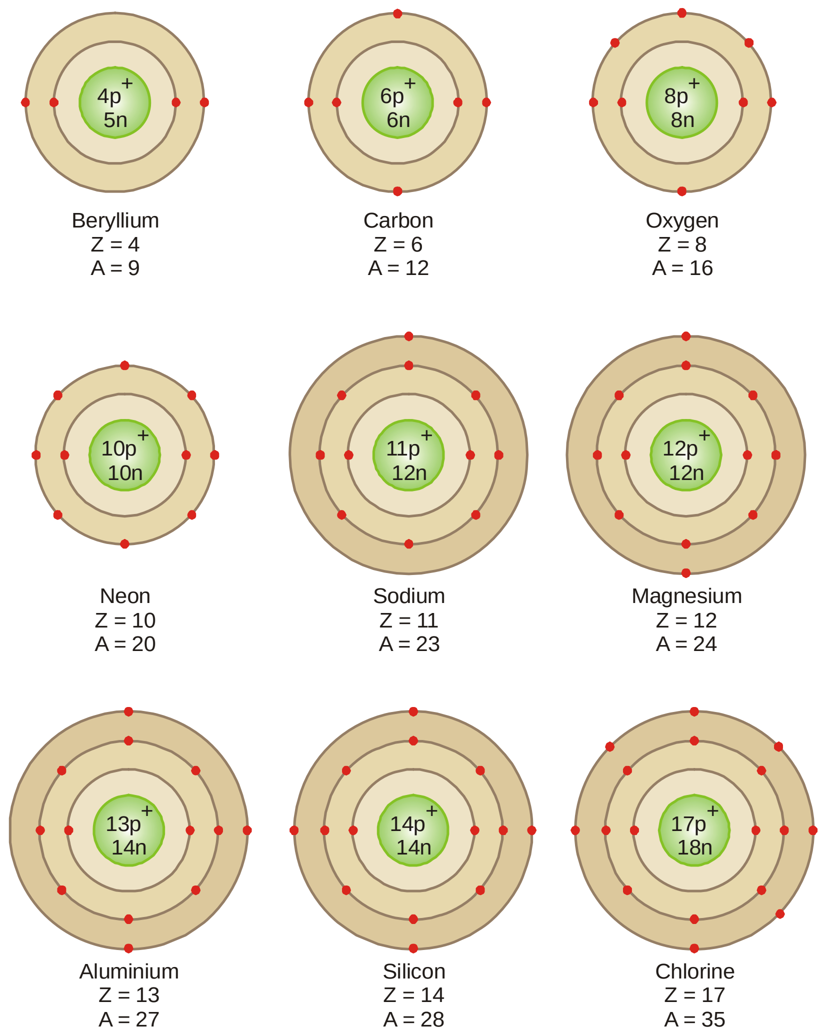


Figure 1.31
Representation of some atomic models and their electron configuration elucidating Bohr-Bury theory.

Rule 1. **The maximum number of electrons which each orbit can contain is $2 \times n^2$, where *n* is the number of orbit.**

The first orbit can contain $2 \times 1^2 = 2$; second $2 \times 2^2 = 8$; third $2 \times 3^2 = 18$; fourth $2 \times 4^2 = 32$, and so on.

Rule 2. **The maximum number of electrons in the outermost orbit is 8 and in the next-to-the outermost 18.**

Rule 3. **It is not necessary for an orbit to be completed before another commences to be formed. In fact, a new orbit begins when the outermost orbit attains 8 electrons.**

Rule 4. **The outermost orbit cannot have more than 2 electrons and next-to-outermost cannot have more than eight so long as the next inner orbit, in each case, has not received the maximum electrons as required by rule (1).**

According to Bohr-Bury scheme the configuration of the inert gases is given in the table below :

TABLE 1.4. ELECTRON CONFIGURATION OF INERT GASES

Inert Gas	Atomic Number	Electron Orbits					
		1st (K)	2nd (L)	3rd (M)	4th (N)	5th (O)	6th (P)
Helium (He)	2	2	–	–	–	–	–
Neon (Ne)	10	2	8	–	–	–	–
Argon (Ar)	18	2	8	8	–	–	–
Krypton (Kr)	36	2	8	18	8	–	–
Xenon (Xe)	54	2	8	18	18	8	–
Radon (Rn)	86	2	8	18	32	18	8

A complete statement of the electron configuration of elements elucidating the various postulates of Bohr-Bury scheme is given in the table on page 31 for ready reference.

ZEEMAN EFFECT

In 1896 Zeeman discovered that **spectral lines are split up into components when the source emitting lines is placed in a strong magnetic field.** It is called the Zeeman effect after the name of the discoverer. The apparatus used to observe Zeeman effect is shown in the Fig. 1.32.

It consists of electromagnets capable of producing strong magnetic field with pole pieces through which holes have been made lengthwise. Let a discharge tube or sodium vapour lamp emitting radiations be placed between the pole pieces. When the spectral lines are viewed axially through the hole in the pole pieces *i.e.*, parallel to the magnetic field, the line is found to split up into two components, one having shorter wavelength (higher frequency) and the other having higher wavelength (shorter frequency) than that of the original spectral line, which is no longer observable. The two

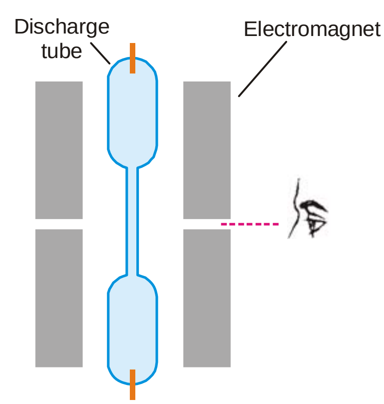


Figure 1.32
Zeeman effect.

lines are symmetrically situated around the position of the original line and the change in wavelength is termed the Zeeman shift (denoted as $d\lambda$). When viewed in a direction perpendicular to the applied field the lines split up into three, the central one having the same wavelength and frequency as that of the original line and the other two occupying the same position as observed earlier.

In order to explain Zeeman effect, let us consider motion of an electron in a particular orbit corresponding to its permitted angular momentum. The motion of the electron in an orbit is equivalent to a current in a loop of wire. If a current carrying loop of wire be placed in a magnetic field, it experiences a torque, and energy of the system depends upon the orientation of the loop with respect to magnetic field. The correct values of the energies are obtained if the components of the angular momentum of the electron along the direction of the magnetic field are restricted to the value

$$= m \times \frac{h}{2\pi}$$

where $m = 0, \pm 1, \pm 2, ...$ and so on. Corresponding to these values of m, a given line splits into as many lines. Hence for each frequency of a radiation emitted by the atom in the absence of magnetic field, there are several possible frequencies in the presence of it. This is, in fact, the cause of Zeeman Effect.

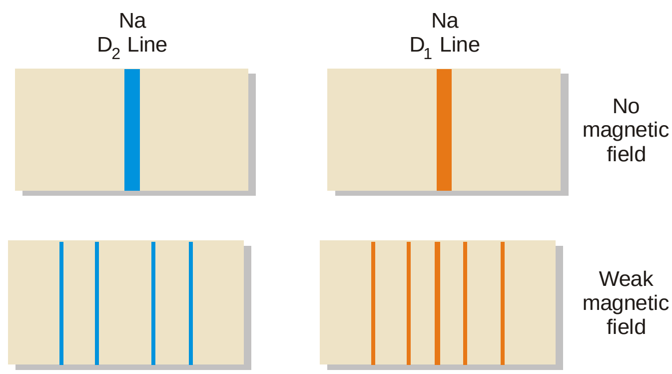


Figure 1.33
Splitting of the D_2 and D_1 lines in the sodium spectrum by a weak magnetic field (Illustration of Zeeman effect).

The shift in the frequency $d\lambda$ for each of the component lines is given by Lorentz's theoretically derived equation as

$$\text{Zeeman shift } d\lambda = \pm \frac{He\lambda^2}{4\pi mc}$$

where H is the strength of magnetic field, e the electronic charge, m the mass of electron, c the velocity of light and λ the wavelength of the original line in the absence of magnetic field. The equation can also be written as

$$\frac{e}{m} = \pm \frac{4\pi c d\lambda}{H\lambda^2}$$

The validity of the above equation can be tested experimentally by observing the Zeeman shift dλ for a given light source of known λ (say D-line of sodium) for a magnetic field of known strength H and calculating the value of e/m for the above equation. Lorentz found that the e/m of the electrons found by this method comes out to be the same as by any other method.

EXAMINATION QUESTIONS

1. Define or explain the following terms :

(*a*) Neutrons (*b*) Nucleons

(*c*) Atomic number (*d*) Mass Number

(*e*) Photoelectric effect (*f*) Threshold energy

2. Give an account of the experiment which led Rutherford to conclude that every atom has a positively charged nucleus which occupies a very small volume. What were the drawbacks of Rutherford's nuclear model of the atom? How did Bohr rectify the drawbacks of Rutherford model?

3. (*a*) State the postulates of Bohr's theory of the hydrogen atom. Derive an expression for the *n*th orbit of a hydrogen atom. Derive an expression for the radius of any orbit in the atom.

(*b*) Calculate the energy of transition involving $n_1 = 6$ to $n_2 = 3$ in a hydrogen atom, given that Rydberg constant $R = 109737.32$ cm^{-1} and $h = 6.63 \times 10^{-34}$ J sec.

Answer. (*b*) 1.818×10^{-19} J

4. (*a*) Discuss Bohr's model of an atom. Show how it successfully explains the spectra of hydrogen atom.

(*b*) Calculate the velocity of the electron in the first Bohr's orbit. ($h = 6.625 \times 10^{-27}$ erg sec; $r = 0.529$Å; $m = 9.109 \times 10^{-28}$ g)

Answer. (*b*) 2.189×10^{8} cm sec^{-1}

5. (*a*) Explain Mosley's contribution towards the structure of the atom.

(*b*) Give the defects of Rutherford's model of atom. What suggestions were given by Bohr to remove these defects?

6. Calculate the radius of the third orbit of hydrogen atom. ($h = 6.625 \times 10^{-27}$ erg sec; $r = 0.529$Å; $m = 9.109 \times 10^{-28}$ g; e = 4.8×10^{-10} esu)

Answer. (*b*) 4.763×10^{-8}

7. Calculate the wavelength of the first line in Balmer series of hydrogen spectrum. ($R = 109677$ cm^{-1})

Answer. 1215 Å

8. (*a*) How does Bohr's theory explain the spectrum of hydrogen atom?

(*b*) Calculate the wavelength associated with an electron moving with a velocity of 1×10^{8} cm sec^{-1}. Mass of an electron = 9.1×10^{-28} g

Answer. (*b*) 7.28×10^{-8} cm

9. A line at 434 nm in Balmer series of spectrum corresponds to a transition of an electron from the *n*th to 2nd Bohr orbit. What is the value of *n*?

Answer. $n = 5$

10. (*a*) Explain Rutherford's atomic model. What are its limitations?

(*b*) State and explain Ritz combination principle.

(*c*) Calculate the radius of third orbit of hydrogen atom. ($h = 6.625 \times 10^{-27}$ erg sec; $m = 9.1091 \times 10^{28}$g; $e = 4.8 \times 10^{-10}$ esu)

(*d*) Calculate the wavelength of first line in Balmer series of hydrogen spectrum. (R = Rydberg's constant = 109677 cm^{-1})

Answer. (*c*) 4.763×10^{-8} cm (*d*) 1215 Å

11. Describe various series in hydrogen spectrum and calculate energy levels of hydrogen atom.

12. Write Rutherford's experiment of scattering of α-particles and give the drawbacks of atomic model.

13. Write notes on :

(*a*) Merits and demerits of Bohr's theory (*b*) Assumptions of Bohr's atomic model

14. Based on Bohr's calculations, establish the energy expression of the rotating electron in hydrogen like atomic species.

15. Give an account of Bohr's theory of atomic structure and show how it explains the occurrence of spectral lines in the atomic spectra of hydrogen.

16. The electron energy in hydrogen atom is given by $E = -21.7 \times 10^{-12}/n^2$ ergs. Calculate the energy required to remove an electron completely from the $n = 2$ orbit. What is the longest wavelength (in cm) of light that can be used to cause this transition?

Answer. -5.42×10^{-12} erg; 3.67×10^{-5} cm

17. In a hydrogen atom, an electron jumps from 3rd orbit to first orbit. Find out the frequency and wavelength of the spectral line.

Answer. 1025.6 Å (*Agra BSc, 2000*)

18. The energy of the electron in the second and third orbits of the hydrogen atom is -5.42×10^{-12} erg and -2.41×10^{-12} erg respectively. Calculate the wavelength of the emitted radiation when the electron drops from third to second orbit.

Answer. 6600 Å (*Kolkata BSc, 2000*)

19. Calculate the wavelength in Å of the photon that is emitted when an electron in Bohr orbit $n = 2$ returns to the orbit $n = 1$ in the hydrogen atom. The ionisation potential in the ground state of hydrogen atom is 2.17×10^{-11} erg per atom.

Answer. 1220 Å (*Osmania BSc, 2000*)

20. What transition in the hydrogen spectrum would have the same wavelength as the Balmer transition $n = 4$ to $n = 2$ of He^+ transition?

Answer. $n = 2$ to $n = 1$ (*Baroda BSc, 2001*)

21. (*a*) State postulates of Bohr's theory of an atom and derive an expression for radius of Bohr orbit of hydrogen atom.

(*b*) Give any four limitations of Bohr's theory of an atom. (*Nagpur BSc, 2002*)

22. Describe Rutherford's model of the atom. How was it improved by Bohr? (*Arunachal BSc, 2002*)

23. Atomic hydrogen is excited to the 4th energy level from the ground state. Determine

(*a*) the number of lines emitted and

(*b*) the shortest wavelength present in the emission spectrum. (R_H = 109677 cm^{-1})

Answer. (*a*) 3; (*b*) 972.55 Å (*Vidyasagar BSc, 2002*)

24. Radius of the first Bohr orbit of H-atom is 0.529 Å. Find the radii of the first and second Bohr orbit of Li^{2+} ion.

Answer. (*a*) 0.1763 Å; (*b*) 0.7053 Å (*Vidyasagar BSc, 2002*)

25. If the energy difference between the ground state of an atom and its excited state is 4.4×10^{-19} J, what is the wavelength of the photon required to produce this transition?

Answer. 4.517×10^{-7} m (*Madras BSc, 2003*)

26. Calculate the wavelength and energy of radiations emitted for the electronic transition from infinity ($\propto$) to stationary state of the hydrogen atom. ($R = 1.09678 \times 10^7$ m^{-1}; $h = 6.625 \times 10^{-34}$ Joule sec and $c = 2.9979 \times 10^8$ m sec^{-1}) (*Gulbarga BSc, 2003*)

Answer. 9.11×10^{-6} m; 217.9×10^{-23} kJ

27. The energy transition in hydrogen atom occurs from $n = 3$ to $n = 2$ energy level. ($R = 1.097 \times 10^7$ m^{-1}).

(*a*) Calculate the wavelength of the emitted electron.

(*b*) Will this electron be visible?

(*c*) Which spectrum series does this photon belong to? (*Jadavpur BSc, 2003*)

28. Calculate the energy emitted when electrons of 1.0 g of hydrogen undergo transition giving the spectral line of lowest energy in the visible region of its atomic spectrum ($R = 1.1 \times 10^7$ m^{-1}; $c = 3 \times 10^8$ m sec^{-1}; $h = 6.62 \times 10^{-34}$ J sec)

Answer. 182.5 kJ (*Panjab BSc, 2004*)

29. In hydrogen atom the energy of the electron in first Bohr's orbit is -1312×10^5 J mol^{-1}. What is the energy required for the excitation of second Bohr's orbit ? (*Burdwan BSc, 2005*)

Answer. 9.84×10^5 J mol^{-1}

30. Calculate the wavelength in Å of the photon that is emitted when an electron in Bohr orbit $n = 2$ returns to the orbit $n = 1$ in the hydrogen atom. The ionisation potential in the ground state of hydrogen atom is 2.17×10^{-11} erg per atom. (*Kalayani BSc, 2005*)

Answer. 1220 Å

31. A line at 434 nm in Balmer series of spectrum corresponds to a transition of an electron from the *n*th to 2nd Bohr orbit. What is the value of n ? (*Gulbarga BSc, 2006*)

Answer. $n = 5$

32. The energy transition in hydrogen atom occurs from $n = 3$ to $n = 2$ energy level. ($R = 1.097 \times 10^7$ m^{-1}). (i) Calculate the wavelength of the emitted electron (ii) Will this electron be visible ? (iii) Which spectrum series does this photon belong to ? (*Vikram BSc, 2006*)

Answer. 6564 Å ; Yes ; Balmer series

33. The energy of the electron in the second and third Bohr orbits of the hydrogen atom is -5.42×10^{-12} erg and -2.41×10^{-12} erg respectively. Calculate the wavelength of the emitted radiation when the electron drops from third to second orbit. (*Calicut BSc, 2006*)

Answer. 6600 Å

MULTIPLE CHOICE QUESTIONS

1. Cathode rays are deflected by

(*a*) electric field only (*b*) magnetic field only
(*c*) electric and magnetic field (*d*) none of these

Answer. (*c*)

2. The e/m value for the particles constituting cathode rays is the same regardless of

(*a*) the gas present in cathode rays tube (*b*) the metal of which cathode was made
(*c*) both of these (*d*) none of these

Answer. (*c*)

3. The charge to mass ratio (e/m) of positive particles

(*a*) varies with the nature of gas in discharge tube
(*b*) is independent of the gas in discharge tube
(*c*) is constant
(*d*) none of the above

Answer. (*a*)

4. A sub atomic particle which has one unit mass and one unit positive charge is known as

(*a*) hydrogen atom (*b*) neutron
(*c*) electron (*d*) proton

Answer. (*d*)

5. Atomic number of an element is equal to the number of _______ in the nucleus of the atom.

(*a*) neutrons (*b*) protons
(*c*) both the neutrons and protons (*d*) electrons

Answer. (*b*)

6. The mass number of an atom is equal to the number of _______ in the nucleus of an atom

(*a*) protons (*b*) neutrons

(*c*) electrons (*d*) nucleons

Answer. (*d*)

7. If Z is the number of proton and A the number of nucleons, then the number of neutrons is an atom is given by

(*a*) A + Z (*b*) A – Z

(*c*) Z – A (*d*) none of these

Answer. (*b*)

8. The mass number and atomic number of Phosphorus atom are 31 and 15 respectively. The number of neutrons in the nucleus is

(*a*) 15 (*b*) 16

(*c*) 31 (*d*) 46

Answer. (*b*)

9. In a sodium atom (atomic number = 11 and mass number = 23), the number of neutrons is

(*a*) equal to the number of protons (*b*) less than the number of protons

(*c*) greater than the number of protons (*d*) none of these

Answer. (*c*)

10. Which of the following is not correct for electromagnetic waves?

(*a*) the wavelength is the distance between two successive crests

(*b*) the frequency is the number of waves which pass a given point in one second

(*c*) the velocity of a wave is the distance covered by the particular wave in one second

(*d*) all electromagnetic waves have equal wavelengths

Answer. (*d*)

11. Which of the following relations is not correct?

(*a*) $c = \lambda \times v$ (*b*) $\bar{\nu} = \frac{1}{\nu}$

(*c*) $\bar{\nu} = \frac{1}{\lambda}$ (*d*) $\lambda = c \div v$

Answer. (*b*)

12. The unit in which wave number is measured

(*a*) hertz (*b*) sec^{-1}

(*c*) nanometer (*d*) cm^{-1}

Answer. (*d*)

13. In the spectrum of hydrogen atom, the series which falls in ultraviolet region is

(*a*) Lyman series (*b*) Balmer series

(*c*) Paschen series (*d*) Brackett series

Answer. (*a*)

14. The Balmer series in the spectrum of hydrogen atom falls in

(*a*) ultraviolet region (*b*) visible region

(*c*) infrared region (*d*) none of these

Answer. (*b*)

15. The energy of a photon is given by the relation

(*a*) $E = \frac{h\,\nu}{\lambda}$ (*b*) $E = \frac{h\,c}{\lambda}$

(*c*) $E = \frac{h \times c}{\nu}$ (*d*) $E = \frac{\lambda \times c}{h}$

Answer. (*b*)

16. When a beam of light of sufficiently high frequency is allowed to strike a metal surface in vacuum, electrons are ejected from the metal surface. This phenomenon is called

(*a*) Black body radiation (*b*) Photoelectric effect

(*c*) Zeeman effect (*d*) Stark effect

Answer. (*b*)

17. In photoelectric effect, the kinetic energy of the photoelectrons increases linearly with the

(*a*) wavelength of the incident light (*b*) frequency of the incident light
(*c*) velocity of the incident light (*d*) none of these

Answer. (*b*)

18. The kinetic energy of the photoelectrons emitted from the metal surface is given by the relation (v_o is the threshold frequency and v is the frequency of incident light)

(*a*) $\frac{1}{2} m v^2 = hv - hv_o$ (*b*) $\frac{1}{2} mv^2 = hv + hv_o$
(*c*) $\frac{1}{2} mv^2 = hv$ (*d*) $\frac{1}{2} mv^2 = hv_o$

Answer. (*a*)

19. In Bohr's model of atom, the angular momentum of an electron orbiting around the nucleus is given by the relation

(*a*) $m\,v\,r = \dfrac{h}{2\pi}$ (*b*) $m\,v\,r = \dfrac{n\,h}{2\pi}$
(*c*) $m\,v\,r = \dfrac{n^2\,h^2}{4\pi}$ (*d*) $m\,v\,r = \dfrac{n\,h}{4\pi}$

Answer. (*b*)

20. The radius of first orbit in hydrogen atom according to Bohr's Model is given by the relation

(*a*) $r = \dfrac{h^2}{4\pi^2\,m\,e^2}$ (*b*) $r = \dfrac{h}{4\pi^2\,m\,e^2}$
(*c*) $r = \dfrac{h^2}{4\pi\,m\,e^2}$ (*d*) $r = \dfrac{h^2}{4\pi\,m\,e^4}$

Answer. (*a*)

21. The radius of first orbit in hydrogen atom is 0.529 Å. The radius of second orbit is given by

(*a*) ½ × 0.529 Å (*b*) 2 × 0.529 Å
(*c*) 4 × 0.529 Å (*d*) 8 × 0.529 Å

Answer. (*c*)

22. The energy of an electron in the first orbit in hydrogen atom is $-313.6/n^2$ kcal mol^{-1}. The energy of the electron in 3rd orbit is given by the relation

(*a*) $E_3 = \dfrac{-313.6}{3}$ kcal mol^{-1} (*b*) $E_3 = \dfrac{-313.6}{2}$ kcal mol^{-1}
(*c*) $E_3 = \dfrac{-313.6}{9}$ kcal mol^{-1} (*d*) $E_3 = -313.6 \times 3$ kcal mol^{-1}

Answer. (*c*)

23. Lyman series is obtained when the electrons from higher energy levels return to

(*a*) 1st orbit (*b*) 2nd orbit
(*c*) 3rd orbit (*d*) 4th orbit

Answer. (*a*)

24. A line in Pfund series is obtained when an electron from higher energy levels returns to

(*a*) 1st orbit (*b*) 3rd orbit
(*c*) 5th orbit (*d*) 6th orbit

Answer. (*c*)

25. The energy of an electron in Bohr's atom ________ as we move away from the nucleus

(*a*) remains the same (*b*) decreases
(*c*) increases (*d*) sometimes increases, sometimes decreases

Answer. (*c*)

26. When an electron drops from a higher energy level to a lower energy level, then

(*a*) the energy is absorbed (*b*) the energy is released
(*c*) the nuclear charge increases (*d*) the nuclear charge decreases

Answer. (*b*)

27. The spectrum of hydrogen atom is similar to that of

(*a*) H^+ ion (*b*) He^+ ion

(*c*) Li^+ ion (*d*) Na^+ ion

Answer. (*b*)

28. If *r* is the radius of first orbit, the radius of nth orbit of hydrogen atom will be

(*a*) $n^2 r$ (*b*) $n r$

(*c*) n/r (*d*) r/n

Answer. (*a*)

29. The ratio of radii of second and first orbit of hydrogen atom according to Bohr's model is

(*a*) 2:1 (*b*) 1:2

(*c*) 4:1 (*d*) 1:4

Answer. (*c*)

30. The spectrum of helium is expected to be similar to that of

(*a*) H-atom (*b*) Li atom

(*c*) Li^+ ion (*d*) Na^+ ion

Answer. (*c*)

31. Electromagnetic radiations with minimum wavelength is

(*a*) ultraviolet (*b*) X-rays

(*c*) infrared (*d*) radiowaves

Answer. (*b*)

32. Which of the following statements is false?

(*a*) electrons travel around the nucleus in specific permitted circular orbits

(*b*) an electron does not lose energy as long as it moves in its specified orbits

(*c*) an electron can jump from one energy level to another by absorbing or losing energy

(*d*) the angular momentum of an electron is not quantised

Answer. (*d*)

33. The idea of stationary orbits was first given by

(*a*) Rutherford (*b*) JJ Thomson

(*c*) Niels Bohr (*d*) Max Planck

Answer. (*c*)

34. The maximum number of electrons that can be accommodated in an orbit is

(*a*) $2n$ (*b*) n^2

(*c*) $2n^2$ (*d*) $2n + 1$

Answer. (*c*)

35. The maximum number of electrons is the outermost orbit is

(*a*) 2 (*b*) 8

(*c*) 18 (*d*) 32

Answer. (*b*)

36. When the source emitting lines is placed in a strong magnetic field the spectral lines are split into its components. This effect is called

(*a*) Compton effect (*b*) Zeeman effect

(*c*) Rydberg effect (*d*) Photoelectric effect

Answer. (*b*)

37. The number of electrons in the outermost shell of Potassium (at. no. 19) is

(*a*) 1 (*b*) 2

(*c*) 8 (*d*) 9

Answer. (*a*)

38. An atom of silicon with atomic number 14 has the following number of electrons in the outermost shell

(*a*) 1 (*b*) 2

(*c*) 4 (*d*) 8

Answer. (*c*)

39. Inert gases possess the most stable electronic configuration as they contain
(*a*) fully filled outermost shell (*b*) half filled outermost shell
(*c*) two electrons in the outermost shell (*d*) eight electrons in the outermost shell
Answer. (*d*)

40. The effect of electric field on the spectra of atoms is called
(*a*) Compton effect (*b*) Photoelectric effect
(*c*) Stark effect (*d*) Zeeman effect
Answer. (*c*)

41. Which one of the following species has the same number of electrons as an atom of Neon?
(*a*) O^{2-} (*b*) Na
(*c*) Mg (*d*) K^+
Answer. (*a*)

42. The energy of an electron in the first Bohr orbit for hydrogen is
(*a*) 13.6 eV (*b*) –13.6 eV
(*c*) 1.36 eV (*d*) –1.36 eV
Answer. (*b*)

43. The energy of hydrogen atom in its ground state is –13.6 eV. The energy of the level corresponding to $n = 3$ is
(*a*) – 4.53 eV (*b*) – 2.265 eV
(*c*) – 1.51 eV (*d*) none of these
Answer. (*c*)

44. $E_n = -1311.8$ kJ mol^{-1}. If the value of E is –52.44 kJ mol^{-1}, to which value 'n' corresponds?
(*a*) 2 (*b*) 3
(*c*) 4 (*d*) 5
Answer. (*d*)

45. The spectral line lies in the Lyman series. It corresponds to the radiation emitted by an electron jumping from higher energy sates to
(*a*) first energy state (*b*) second energy state
(*c*) third energy state (*d*) fifth energy state
Answer. (*a*)

46. The ground state of an atom corresponds to a state of
(*a*) maximum energy (*b*) minimum energy
(*c*) zero energy (*d*) negative energy
Answer. (*b*)

47. Balmer series in the spectrum of hydrogen atom lies in
(*a*) ultraviolet region (*b*) visible region
(*c*) infrared region (*d*) none of these
Answer. (*b*)

48. The spectrum of H-atom is expected to be similar to that of
(*a*) Li^+ (*b*) Na^+
(*c*) He^+ (*d*) K^+
Answer. (*c*)

49. An atom of Calcium (at. no. 20) contains ________ electrons in the third energy level.
(*a*) 2 (*b*) 8
(*c*) 10 (*d*) 18
Answer. (*b*)

50. Out of the following pairs of elements which has the same number of electrons in the outer most energy level?
(*a*) helium and lithium (*b*) boron and carbon
(*c*) carbon and nitrogen (*d*) lithium and hydrogen
Answer. (*d*)

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