UNIT 3

Atomic Structure

SYLLABUS

Fundamental particles, Rutherford's model of atom.

Nature of electromagnetic radiation, emission spectrum of hydrogen atom, concept of energy levels (orbitals), weaknesses of Bohr's model.

Modern concept of structure of atom (elementary idea only), idea of shells, subshells and orbitals the four quantum numbers, electronic configuration of elements, Aufbau principle (Pauli exclusion principle and Hund's rule).

SECTION—I

EARLIER DEVELOPMENTS ABOUT STRUCTURE OF ATOM

3.1. Subatiomic and Fundamental Particles

Although the credit for the first "atomic" theory is usually given to ancient Greeks, a landmark in the progress of chemistry took place with the advent of Dalton's atomic theory (discussed in Unit 1).

Dalton, a British school teacher, in 1808, proposed that matter was made up of extremely small, indivisible particles called atoms (*Greek, atoms* means *'uncut-able'*). The concept continued to hold grounds for a number of years. However, the researches done by various eminent scientists like J.J. Thomson, Goldstein, Rutherford, Chadwick, Bohr and others in the later half of the 19th century and in the beginning of the 20th century have established, beyond doubt, that atom was not the smallest indivisible particle but had a complex structure of its own and was made up of still smaller particles like electrons, protons, neutrons etc. At present, about 35 different **subatomic particles** are known but the three particles namely electron, proton and neutron are regarded as the **fundamental particles.**

The charge and mass of these fundamental particle are given in Table 3.1 below :

TABLE 3.1. Charge and mass of fundamental subatomic particles

Particle	Charge	Mass	
		kg	u
Electron	1—	$9{\cdot}10939 \times 10^{-31}$	0·000548596
Proton	1+	$1{\cdot}67262 \times 10^{-27}$	1·00727663
Neutron	0	$1{\cdot}67493 \times 10^{-27}$	1·0086654

One unit charge = $4{\cdot}80298 \times 10^{-10}$ e.s.u.

or $1{\cdot}60210 \times 10^{-19}$ coulombs

One u = 1/12th the mass of ^{12}C atom.

We shall now take up a systematic study of the discovery of these fundamental particles and other related discoveries which have been made from time to time.

3.2. Discovery of Electron— Study of Cathode Rays

The electrical nature of matter had been indicated in very early experiments on the production of frictional electricity (i.e. rubbing of glass or ebonite rods with silk or fur). This was further confirmed by the experiments on the electrolysis of substances by Davy, Stoney and Faraday in the first half of the nineteenth century. However, the discovery of electron came as a result of the study of conduction of electricity through gases as explained below :

William Crookes, in 1879, studied the conduction of electricity through gases at low pressure. For this purpose, he took a discharge tube which is a long glass tube, about 60 cm long, sealed at both the ends and fitted with two metal electrodes. It has a side tube fitted with a stop-cock (Fig. 3.1). This tube is connected to a vacuum pump and the pressure inside the discharge tube is reduced to as low as 0.01 mm. Now when a high voltage (nearly 10,000 volts) is applied between the electrodes, it is found that some invisible rays are emitted *from the cathode**. The presence of these rays is detected from the fact that the glass wall of the discharge tube opposite to the cathode begins to glow with a faint greenish light**. Obviously, this must be due to the bombardment of the walls by some rays emitted from the cathode. These rays were cathode rays.

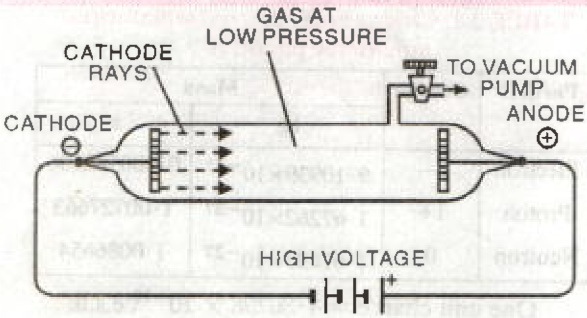

FIGURE 3.1. Discharge tube experiment – Production of cathode rays.

Properties of Cathode Rays. From the various experiments carried out by J.J. Thomson (1897) and others, the cathode rays have been found to possess the following properties :–

(*i*) They produce a sharp shadow of the solid object placed in their path (Fig. 3.2.). This shows that *cathode rays travel in straight lines*.

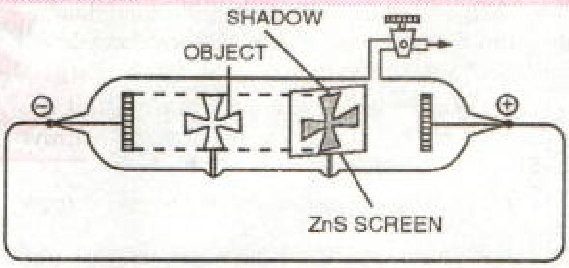

FIGURE 3.2. Production of a shadow of the solid object by cathode rays.

(*ii*) If a light paddle wheel (e.g. that of mica) mounted on an axle is placed in their path, the wheel begins to rotate (Fig. 3.3.). This shows that *cathode rays are made up of material particles*.

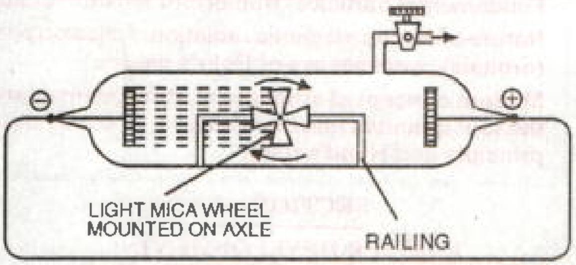

FIGURE 3.3. Rotation of light paddle wheel by cathode rays.

(*iii*) When an electric field is applied on the cathode rays, they are deflected towards the positive plate of the electric field (Fig. 3.4.). This shows that *cathode rays carry negative charge*.

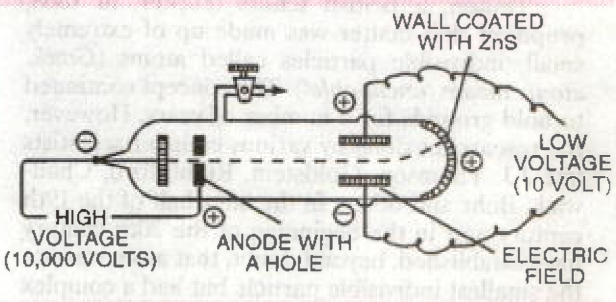

FIGURE 3.4. Deflection of cathode rays towards positive plate of the electric field.

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* It may be noted that when the gas pressure in the tube is 1 atmosphere, no electric current flows through the tube. This is because the gases are poor conductor of electricity.

** The television picture tube is a cathode ray tube in which a picture is produced due to fluorescence on the television screen coated with suitable material. Similarly, fluorescent light tubes are also cathode rays tubes coated inside with suitable materials which produce visible light on being hit with cathode rays.

Similarly, when a magnetic field is applied on the cathode rays, these rays are deflected in a direction which shows that they carry negative charge.

(*iv*) When cathode rays strike a metal foil, the latter becomes hot. This indicates that *cathode rays produce heating effect.*

(*v*) *They cause ionization of the gas through which they pass.*

(*vi*) *They produce X-rays when they strike against the surface of hard metals like tungsten, molybdenum etc.*

(*vii*) *They produce green fluorescence on the glass walls of the discharge tube as well as on certain other substances such as zinc sulphide.*

(*viii*) *They affect the photographic plates.*

(*ix*) *They possess penetrating effect* (i.e. they can easily pass through thin foils of metals). They are stopped only by the metal foils of greater thickness.

From the study of the various properties, as explained above, the two most important results are:

(*i*) Cathode rays are made up of material particles.

(*ii*) Cathode rays carry negative charge.

The negatively charged material particles constituting the cathode rays are called electrons.

Further experiments were carried out to determine the exact charge and mass of the electrons. Two types of experiments were carried out. These were

(*i*) *For determination of the ratio of charge/mass of electrons.* These experiments were carried out by **J.J. Thomson** (1897). He used different discharge tubes fitted with electrodes of different metals. He placed different gases in the tube. He found every time that the ratio of charge/mass of the electrons was the same. The value was found to be

$$\text{charge/mass} = e/m = 1 \cdot 76 \times 10^{8} \text{ coulombs/g}$$

(*ii*) *For determination of the charge on the electron.* The charge on the electron was found by **R.A. Millikan** (1917) with the help of his oil drop experiment. The value was found to be

$$\text{charge} = e = 1.60 \times 10^{-19} \text{ Coulombs}$$

$$\text{or } 4.8 \times 10^{-10} \text{ esu}$$

Thus the mass of the electron may be calculated from the values of e/m and e as follows :

$$\text{mass} = m = \frac{e}{e/m} = \frac{1 \cdot 60 \times 10^{-19}}{1 \cdot 76 \times 10^{8}}$$

$$= 9 \cdot 11 \times 10^{-28} \text{ g}^{*}$$

The charge, 1.60×10^{-19} coulombs, is the smallest measurable quantity of charge, and is called one unit. The mass, 9.11×10^{-28} g, is nearly 1/1837th of that of hydrogen atom. This can be easily calculated as follows :

1 g atom of hydrogen

$= 1 \cdot 008 \text{ g} = 6 \cdot 02 \times 10^{23}$ atoms

i.e. $6 \cdot 02 \times 10^{23}$ atoms of hydrogen weigh $= 1 \cdot 008$ g

$\therefore$ One atom of hydrogen weighs

$$= \frac{1 \cdot 008}{6 \cdot 02 \times 10^{23}} \text{ g} = 1 \cdot 67 \times 10^{-24} g$$

$$\therefore \frac{\text{Mass of H atom}}{\text{Mass of electron}} = \frac{1 \cdot 67 \times 10^{-24} g}{9 \cdot 11 \times 10^{-28} g} = 1833$$

Using more accurate values, the ratio comes out to the nearly 1837.

Hence the electron may be defined as follows:

An electron is that fundamental particle which carries one unit negative charge and has a mass nearly equal to 1/1837th of that of hydrogen atom.

Origin of Cathode Rays. The cathode rays are first produced from the material of the cathode and then from the gas inside the discharge tube due to bombardment of the gas molecules by the high speed electrons emitted first from the cathode.

Electron is a universal constituent of matter. In the discharge tube experiments, it is found that irrespective of nature of the gas taken inside the tube and the material of the electrodes, the ratio of charge/mass of the particles constituting the cathode rays (electrons) is the same. Similarly, the charge on each of these particles is also always the same. Since these particles are emitted first from the material of the cathode and then produced from the gas inside the tube as a result of the bombardment on the gas molecules by the high speed electrons emitted first from the cathode**, it is obvious that these particles i.e. electrons must be universal constituent of all matter. This is further supported by the following experiments in which

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*This is called Rest mass of the electron because it has been calculated assuming that the electron is moving with a velocity much less than the velocity of light.

** No electric current flows through vacuum.

the electrons emitted are found to have the same charge and mass : –

(*i*) By strongly heating certain metal filaments.

(*ii*) By exposing highly active metals like sodium and potassium to ultraviolet rays.

(*iii*) By exposing any form of matter to X-rays.

(*iv*) From radioactive substances in the form of β-rays.

3.3. Discovery o [illegible] on—Study of Anode Rays

Since the atom as a whole is electrically neutral and the presence of negatively charged particles in it was established, therefore it was thought that some positively charged particles must also be present in the atom. For this purpose, Goldstein in 1886, performed discharge tube experiments in which he took perforated cathode and a gas at low pressure was kept inside the tube, as before (Fig. 3.5.).

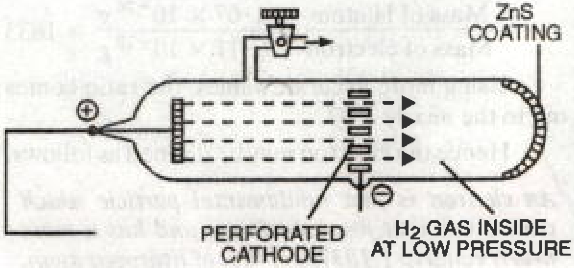

FIGURE 3.5. Production of Anode rays or Positive rays.

On passing high voltage between the electrodes, it was found that some rays were coming from the side of the anode which passed through the holes in the cathode and produced green fluorescence on the opposite glass wall coated with zinc sulphide. These rays were called *anode rays or canal rays or positive rays* (because they were found to carry positive charge).

Origin of Anode Rays. These rays are believed to be produced as a result of the knock out of the electrons from the gaseous atoms by the bombardment of high speed electrons of the cathode rays on them. Thus anode rays are not emitted from the anode but are produced in the space between the anode and the cathode.

Properties of Anode Rays. Using the same experimental methods, as described earlier for cathode rays, the anode rays were found to possess the following main properties : –

(*i*) *They travel in straight lines*. However their speed is much less than that of the cathode rays.

(*ii*) *They are made up of material particles*.

(*iii*) *They are positively charged*, as indicated by the direction of deflection of these rays in the electric and magnetic fields. That is why they are called 'positive rays.'

(*iv*) *Unlike cathode rays, the ratio, charge/mass (i.e. e/m) is found to be different for the particles constituting anode rays when different gases are taken inside the discharge tube*. In other words, the value of e/m depends upon the nature of the gas taken inside the discharge tube.

(*v*) *The value of the charge (e) on the particles constituting the anode rays is also found to depend upon the nature of the gas taken inside the discharge tube*. However, the charge on these particles is found to be a whole number multiple of the charge present on the electron. In other words, these positively charged particles may carry one, two or three units of positive charge, depending upon the number of electrons knocked out.

(*vi*) *The mass (m) of the particles constituting the anode rays is also found to be different for different gases taken in the discharge tube. However, its value is found to be nearly equal to that of the atom of the gas*.

Further, experiments revealed that when hydrogen gas is taken inside the discharge tube, the particles present in the anode rays have minimum mass i.e. lightest positively charged particles are produced. The charge on these particles is found to be same as that on the electron i.e. 1.6×10^{-19} coulombs or one unit. The ratio, charge/mass, for each of the particles is found to be 9.58×10^4 coulombs per gram. Hence the mass of each of these particles will be $= \frac{e}{e/m} = \frac{1{\cdot}6 \times 10^{-19}}{9{\cdot}58 \times 10^4}$

$= 1{\cdot}67 \times 10^{-24}$ g

This mass is nearly the same as that of the hydrogen atom. These particles were termed as **protons**. Hence

A proton may be defined as that fundamental particle which carries one unit positive charge and has a mass nearly equal to that of hydrogen atom.

It may be mentioned here that in case of any other gas taken inside the discharge tube, the mass of the positively charged particles was found to be nearly a whole number multiple of the mass of the proton. Hence it led to the belief that protons must be fundamental particles present in all atoms and that the atoms of gases other than hydrogen contained some whole number of protons.

After having established the presence of electrons and protons in the atom, the next problem before the scientists was to see how these particles were present within the atom. Two models of atom were proposed as discussed in the next sections.

Radioactivity. After the discovery of electron and proton, it was well established that atom is divisible and is made up of charged particles. This was further confirmed by the phenomenon of radioactivity, discovered by Becquerel in 1896.

Radioactivity is the phenomenon of spontaneous emission of radiations by certain elements like uranium, radium etc. The elements emitting such radiations are called radioactive elements.

The phenomenon can be observed by placing the radioactive element in a cavity made in a block of lead and applying electric or magnetic field on the radiations being emitted and then allowing them to fall on the photographic plate.

Three types of radiations are emitted as explained below:

(*i*) Those which are deflected slightly towards the negative plate and hence carry positive charge are called α-rays. The particles present in them are called α-particles. Each α-particle has charge = +2 units and mass = 4 u. Hence they are same as helium nuclei and are represented as ^4_2He.

(*ii*) Those which are deflected towards the positive plate to a larger extent and hence carry negative charge are called β-rays. The particles present in them are called β-particles. Each β-particle has same charge and mass as that of electron. Hence it is represented as $^{\ 0}_{-1}e$.

(*iii*) Those which remain undeflected are called γ-rays. They are simply electromagnetic radiations.

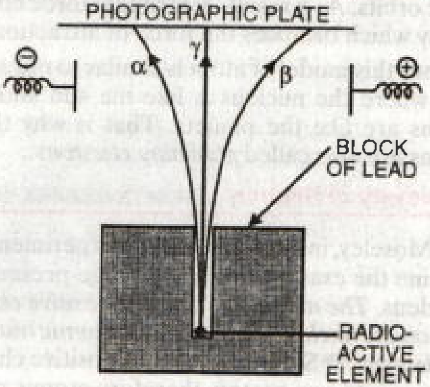

FIGURE 3.6. Effect of electric field on the radiations emitted from a radioactive element.

3.4. Thomson Model of Atom

J.J. Thomson, in 1904, proposed that an atom was a sphere of positive electricity in which were embedded number of electrons, sufficient to neutralize the positive charge (Fig. 3.7.). The stability of the atom was explained as a result of the balance between the repulsive forces between the electrons and their attraction towards the centre of the positive sphere. This model is compared with a water melon in which seeds are embedded or with a cake or pudding in which raisins (dried grapes/kishmish) are embedded. That is why this model is sometimes called **raisin pudding model.** However, this model could not satisfactorily explain the results of scattering experiments, carried out by Rutherford in 1911 and was rejected.

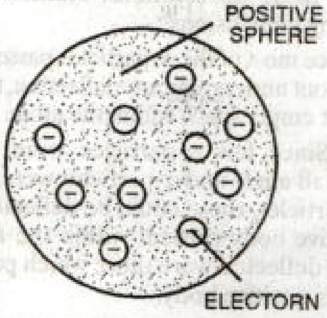

FIGURE 3.7. Thomson model of atom.

3.5. Rutherford's Model (Nuclear Model) of Atom—Discovery of Nucleus

Rutherford, in 1911, performed some scattering experiments in which he bombarded thin foils (nearly 100 nm thick) of metals like gold, silver, platinum or copper with a beam of fast moving α-particles*. The source of α-particles was radium, a radio-active substance, placed in a block of lead. Slits were used to get a fine beam (Fig. 3.8). The presence of α-particle at any point was detected with the help of a circular zinc sulphide screen. When an α-particle strikes this screen, a flash of light is given out.

From these experiments, he made the following observations :–

(*i*) Most of the α-particles (99.9 %) passed through the foil without undergoing any deflection.

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*An α-particle is a particle which carries two units of positive charge and has mass nearly four times that of a proton. In other words, these particles are nothing but helium nuclei.

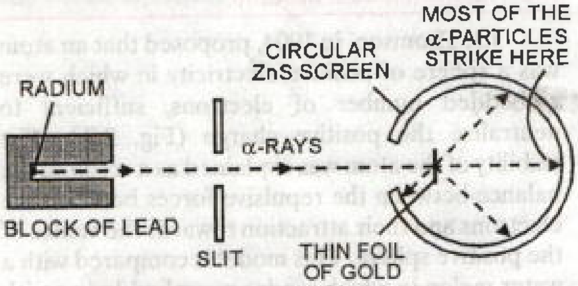

FIGURE 3.8. Rutherford's scattering experiments.

(*ii*) Few α-particles underwent deflection through small angles.

(*iii*) Very few (only one in 20,000) were deflected back i.e. through an angle greater than 90°.

From these observations, Rutherford drew the following conclusions :–

(*i*) Since most of the α-particles passed through the foil without undergoing any deflection, there must be sufficient empty space within the atom.

(*ii*) Since few α-particles were deflected through small angle and α-particles were positively charged particles, these could be deflected only by some positive body present within the atom. The α-particles deflected were those which passed very close to this positive body.

(*iii*) Since some α-particles were deflected back and α-particles are heavy particles, these could be deflected back only when they strike some heavier body inside the atom.

(*iv*) Since the number of α-particles deflected back is very very small, this shows that the heavy body present in the atom must be occupying a very very small volume.*

The small heavy positively charged body present within the atom was called **nucleus.**

In the light of the above results, the scattering of α-particles, according to Rutherford's model of atom, may be depicted as shown in Fig. 3.9.

Thus, according to Rutherford's model of atom, the atom consists of two parts :

(*i*) **Nucleus** which is very small in size, carries positive charge and in which the entire mass of the atom is concentrated.

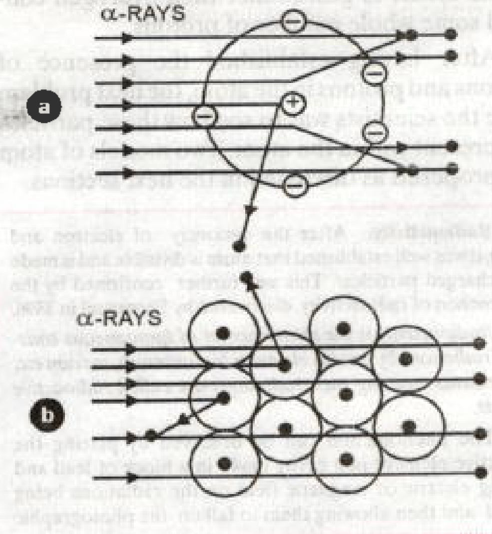

FIGURE 3.9. Scattering of α-particles by (a) a single atom (b) a group of atoms.

Since electrons have negligible mass, the mass of the atom is mainly due to protons. Hence protons must be present in the nucleus. The presence of positively charged protons in the nucleus also accounts for the positive charge on the nucleus.

(*ii*) Extra-nuclear part *i.e.* space around the nucleus in which the electrons were distributed.

To explain that the electrons do not fall into the nucleus as a result of attraction, Rutherford suggested that the electrons were not stationary, but were revolving around the nucleus in certain circular orbits. As a result, centrifugal force comes into play which balances the force of attraction.

Thus this model of atom is similar to our solar system where the nucleus is like the sun and the electrons are like the planets. That is why these electrons are also called *planetary electrons*.

3.6. Discovery of Neutron

Moseley, in 1913, performed experiments to determine the exact quantity of charge present on the nucleus. *The number of units of positive charge present on the nucleus was called the atomic number of the element.* ** Since each unit of positive charge corresponds to one proton, therefore atomic number was equal to the number of protons present in

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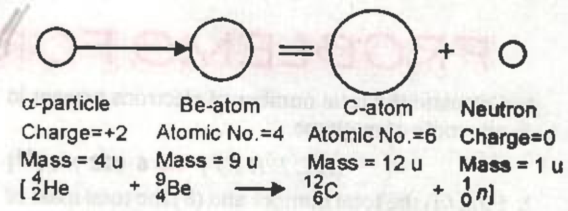
* From X-ray experiments, it has been found that radius of the atom is of the order of 10^{-10} *m* (Å) while the radius of the nucleus is of the order of 10^{-15} *m*. Thus nucleus is $10^{-15}/10^{-10}$ = 1/100,000th in size as compared to the total size of the atom. The difference in size can be visualized by suggesting that if nucleus were of the size of cricket ball, atom would have a radius of about 5 km.

** No two elements have the same atomic number. Hence atomic number is the most fundamental property of an element and is taken as the basis of classification of elements in the periodic chart.

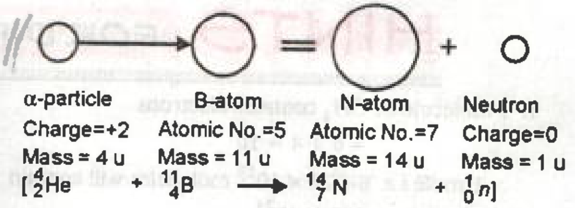
the nucleus. Further since each proton has one unit mass on the atomic mass scale, therefore the mass of the atom was calculated from the number of protons present in the nucleus (remembering that electrons have negligible mass). However, for any element (except hydrogen) this mass was found to be much less than the actual mass of the atom. This led to the idea that there must be some other particles present in the nucleus and that these particles should be neutral but should have considerable mass.

Chadwick, in 1932, performed some scattering experiments in which he bombarded some light elements like beryllium and boron with fast moving α-particles. He found that some new particles were emitted which carried no charge *i.e.*, were neutral but had a mass nearly equal to that of proton.* This particle was termed 'neutron'.

Hence a neutron may be defined as that fundamental particle which carries no charge but has a mass nearly equal to that of hydrogen atom or proton.



$$[\,^{4}_{2}\text{He} + {}^{9}_{4}\text{Be} \longrightarrow {}^{12}_{6}\text{C} + {}^{1}_{0}n\,]$$



$$[\,^{4}_{2}\text{He} + {}^{11}_{4}\text{B} \longrightarrow {}^{14}_{7}\text{N} + {}^{1}_{0}n\,]$$

In view of the discovery of neutron, Rutherford's model of atom was modified. The only modification was that the nucleus of the atom contained not only protons but also neutrons.

PROBLEMS ON MASS AND CHARGE OF FUNDAMENTAL PARTICLES

EXAMPLE 1. *Calculate the number of electrons which will together weigh one gram.* **(N.C.E.R.T.)**

Solution. Mass of one electron

$= 9\cdot11 \times 10^{-31}$ kg

i.e. $9\cdot11 \times 10^{-31}$ kg $= 1$ electron

$\therefore$ 1 g *i.e.* 10^{-3} kg

$$= \frac{1}{9\cdot11 \times 10^{-31}} \times 10^{-3} \text{ electrons}$$

$= \mathbf{1\cdot098 \times 10^{27}}$ **electrons.**

EXAMPLE 2. *Calculate the mass and charge of one mole of electrons.* **(N.C.E.R.T.)**

Solution. Mass of one electron

$= 9\cdot11 \times 10^{-31}$ kg

$\therefore$ Mass of one mole of electrons

$= (9\cdot11 \times 10^{-31}) \times (6\cdot022 \times 10^{23})$

$= \mathbf{5\cdot486 \times 10^{-7}}$ **kg**

Charge on one electron

$= 1\cdot602 \times 10^{-19}$ coulomb

$\therefore$ Charge on one mole of electrons

$= (1\cdot602 \times 10^{-19}) \times (6\cdot022 \times 10^{23})$

$= \mathbf{9\cdot65 \times 10^{4}}$ **coulombs.**

EXAMPLE 3. *Find (a) the total number and (b) the total mass of protons in 34 mg of NH_3 at S.T.P. (Assume the mass of proton $= 1\cdot6726 \times 10^{-27}$ kg)*

Will the answer change if temperature and pressure are changed ? **(N.C.E.R.T.)**

Solution. (*a*) 1 mol of NH_3 = 17 g NH_3

$= 6\cdot022 \times 10^{23}$ molecules of NH_3

$= (6\cdot022 \times 10^{23}) \times (7 + 3)$ protons

$= 6\cdot022 \times 10^{24}$ protons

$\therefore$ 34 mg *i.e.* $0\cdot034$ g NH_3

$$= \frac{6\cdot022 \times 10^{24}}{17} \times 0\cdot034$$

$= \mathbf{1\cdot2044 \times 10^{22}}$ **protons.**

(*b*) Mass of one proton

$= 1\cdot6726 \times 10^{-27}$ kg

$\therefore$ Mass of $1\cdot2044 \times 10^{22}$ protons

$= (1\cdot6726 \times 10^{-27}) \times (1\cdot2044 \times 10^{22})$ kg

$= \mathbf{2\cdot0145 \times 10^{-5}}$ **kg**

There is no effect of temperature and pressure.

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* Actual mass of the neutron $= 1.6749 \times 10^{-24}$ g

Actual mass of the proton $= 1.6726 \times 10^{-24}$ g

Thus the actual mass of neutron is slightly larger than that of proton.

PROBLEMS FOR PRACTICE

1. Calculate the total number of electrons present in one mole of methane. (N.C.E.R.T.) [Ans. $6 \cdot 022 \times 10^{24}$]

2. Find (*a*) the total number and (*b*) the total mass of neutrons in 7 mg of ^{14}C (Assume that the mass of neutron = $1 \cdot 675 \times 10^{-27}$ kg) (N.C.E.R.T.)
[Ans. (*a*) $2 \cdot 409 \times 10^{21}$ (*b*) $4 \cdot 035 \times 10^{-6}$ kg]

HINTS FOR DIFFICULT PROBLEMS

1. 1 molecule of CH_4 contains electrons
$= 6 + 4 = 10$
$\therefore$ 1 mole *i.e.* $6 \cdot 022 \times 10^{23}$ molecules will contain electrons $= 6 \cdot 022 \times 10^{24}$

2. 1 *g* atom of ^{14}C = 14 *g*
$= 6 \cdot 022 \times 10^{23}$ atoms
$= 6 \cdot 022 \times 10^{23} \times 8$ neutrons.

3.7. Atomic Number and Mass Number

Since the atom as a whole is electrically neutral, therefore the number of positively charged particles i.e. protons present in the atom must be equal to the number of negatively charged particles i.e. electrons present in it. This number is called **atomic number**. Hence

Atomic number of an element
= Total number of protons present in the nucleus
= Total number of electrons present in the atom

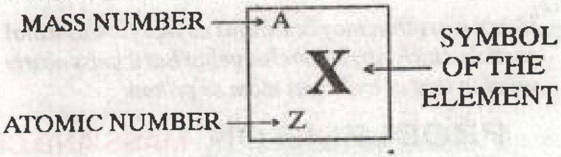
Atomic number is also known as **proton number** because the charge on the nucleus depends upon the number of protons.

Further, since the electrons have negligible mass, the entire mass of the atom is mainly due to protons and neutrons only. Since these particles are present in the nucleus, therefore they are collectively called **nucleons**. Further as each of these particles has one unit mass on the atomic mass scale, therefore the sum of the number of protons and neutrons will be nearly equal to the mass of the atom. This is called mass number. Hence

Mass number of an element = No. of protons + No. of neutrons.

The mass number of an element is nearly equal to the atomic mass of that element. However, the main difference between the two is that mass number is always a whole number whereas atomic mass is usually not a whole number.

The atomic number (Z) and mass number (A) of an element 'X' are usually represented alongwith the symbol of the element as



e.g. $^{23}_{11}Na$, $^{35}_{17}Cl$ and so on.

3.8. Nuclear Structure

Knowing the atomic number and mass number of an element, the number of electrons, protons and neutrons in the atom of the element can be calculated. Hence the composition of the nucleus can be known.

For example, if 'Z' represents the atomic number of an element and 'A' represents its mass number (or atomic mass rounded off to the nearest whole number), then

No. of electrons = No. of protons
= Atomic number (Z)

and No. of protons + No. of neutrons
= Mass number (A)

$\therefore$ No. of neutrons = Mass number (A) − Atomic number (Z)

e.g. (*i*) *For sodium,*

Atomic number (Z) = 11

Mass Number (A) = 23

No. of protons = No. of electrons = Z = 11

and No. of neutrons = A − Z
= 23 − 11 = 12

Thus the nucleus of sodium atom contains 11 protons and 12 neutrons

(*ii*) *For chlorine*, Atomic number (Z) = 17

Mass number (A) = 35

$\therefore$ No. of protons = No. of electrons = Z = 17

and No. of neutrons = A − Z = 35 − 17 = 18

Hence the nucleus of chlorine atom contains 17 protons and 18 neutrons.

Isotopes, Isobars, Isotones and Isoelectronics.

1. Isotopes. In some cases, atoms of the same element are found to contain the same number of protons but different number of neutrons. As a result, they have the same atomic number but different mass numbers.

Such atoms of the same element having same atomic number but different mass numbers are called isotopes.

For example, there are three isotopes of hydrogen having mass numbers, 1, 2 and 3 respectively and each of them having atomic number equal to 1. They are represented as ^1_1H, ^2_1H and ^3_1H and named as protium, deuterium (D) and tritium (T) respectively. Ordinary hydrogen is protium. Isotopes of other elements do not have special names. They are represented by simply indicating the values of A on the symbol. For example, isotopes of chlorine are written as ^{35}Cl and ^{37}Cl.

2. Isobars. Some atoms of different elements are found to have same mass number.

Such atoms of different elements which have same mass numbers (and of course different atomic numbers) are called isobars

e.g. $^{40}_{18}Ar$, $^{40}_{19}K$, $^{40}_{20}Ca$.

3. Isotones. It may be noted that isotopes differ in the number of neutrons only whereas isobars differ in the number of neutrons as well as protons. However some atoms of different elements are found to have the same number of neutrons.

Such atoms of different elements which contain the same number of neutrons are called isotones

e.g. $^{14}_{6}C$, $^{15}_{7}N$, $^{16}_{8}O$.

They differ in atomic number as well as mass number.

4. Isoelectronics.

The species (atoms or ions) containing the same number of electrons are called isoelectronic.

For example, O^{2-}, F^-, Na^+, Mg^{2+}, Al^{3+}, Ne all contain 10 electrons each and hence they are isoelectronic.

PROBLEMS ON NUCLEAR STRUCTURE

EXAMPLE 1. *Write the complete symbol for the atom with the given atomic number (Z) and atomic mass (A).*

(i) Z = 17, A = 35 (ii) Z = 92, A = 233
(iii) Z = 4, A = 9 (N.C.E.R.T.)

Solution. (*i*) $^{35}_{17}Cl$ (*ii*) $^{233}_{92}U$ (*iii*) $^{9}_{4}Be$.

EXAMPLE 2. *Find out the atomic number, mass number, number of protons, electrons and neutrons present in the element with the notation* $^{238}_{92}U$.

Solution. Atomic number (Z) = 92

Mass number (A) = 238

But we know that

No. of protons = No. of electrons = Atomic number (Z)

$\therefore$ No. of protons = 92

and No. of electrons = 92

Further, No. of neutrons = Mass number − Atomic number = A − Z = 238 − 92 = 146.

EXAMPLE 3. *The nuclear radius is of the order of 10^{-13} cm while atomic radius is of the order 10^{-8} cm. Assuming the nucleus and the atom to be spherical, what fraction of the atomic volume is occupied by the nucleus ?*

Solution. The volume of a sphere = $4\pi r^3/3$ where r is the radius of the sphere.

$\therefore$ Volume of the nucleus $= 4\pi r^3/3$.

$= 4\pi (10^{-13})^3/3 \text{ cm}^3$

Similarly, volume of the atom

$$= 4\pi r^3/3 = 4\pi\,(10^{-8})^3/3\ \text{cm}^3$$

∴ Fraction of the volume of atom occupied

$$\text{by the nucleus} = \frac{4\pi\,(10^{-13})^3/3\ \text{cm}^3}{4\pi\,(10^{-8})^3/3\ \text{cm}^3} = 10^{-15}$$

EXAMPLE 4. *Complete the following table :*

Particle	Mass No.	Atomic No.	Protons	Neutrons	Electrons
Nitrogen atom	—	—	—	7	7
Calcium ion	—	20	—	20	—
Oxygen atom	16	8	—	—	—
Bromide ion	—	—	—	45	36

Solution. For nitrogen atom.

No. of electrons = 7 (*Given*)

No. of neutrons = 7 (*Given*)

∴ No. of protons = Z = 7

(∵ atom is electrically neutral)

Atomic number = Z = 7

Mass No. (A) = No. of protons + No. of neutrons = 7 + 7 = 14

For calcium ion.

No. of neutrons = 20 (*Given*) ;

Atomic No. (Z) = 20 (*Given*)

∴ No. of protons = Z = 20 ;

No. of electrons in calcium atom = Z = 20

But in the formation of calcium ion, two electrons are lost from the extranuclear part according to the equation $Ca \rightarrow Ca^{2+} + 2e^-$ but the composition of the nucleus remains unchanged.

∴ No. of electrons in calcium ion = 20 − 2 = 18

Mass number (A) = No. of protons + No. of neutrons = 20 + 20 = 40.

For oxygen atom.

Mass number (A) = No. of protons + No. of neutrons = 16 (*Given*)

Atomic No. (Z) = 8 (*Given*)

No. of protons = Z = 8,

No. of electrons = Z = 8

No. of neutrons = A − Z = 16 − 8 = 8

For bromide ion. In the formation of bromide ion, one electron is added to the extranuclear part of the bromine atom according to the equation $Br + e^- \rightarrow Br^-$ but the composition of the nucleus remains unchanged.

Since the no. of electrons in bromide ion = 36 (*Given*)

No. of electrons in bromine atom = 36 − 1 = 35

Further since in the above reaction, nucleus of the bromine atom remains unchanged.

∴ No. of protons in the bromide ion = No. of protons in the bromine atom = 35.

Putting the values of the various vacant place as calculated above, in the table, we have

Particle	Mass No. (A)	Atomic No. (Z)	No. of protons (Z)	No. of Neutrons (A − Z)	No. of electrons (Z)
Nitrogen atom	7 + 7 = 14	7	7	7	7
Calcium ion	20 + 20 = 40	20	20	20	20 − 2 = 18
Oxygen atom	16	8	8	16 − 8 = 8	8
Bromide ion	45 + 35 = 80	35	36 − 1 = 35	45	36

EXAMPLE 5. *Calculate the percentage of higher isotope of neon which has atomic mass 20·2 and the isotopes have the mass numbers 20 and 22.*

Solution. Suppose $^{22}Ne = x\%$.

Then $^{20}Ne = (100 - x)\ \%$

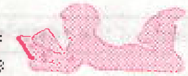
$$\therefore\ \frac{x \times 22 + (100 - x)\,20}{100} = 20\cdot2$$

or $22x + 2000 - 20x = 2020$

or $2x = 20$

or $x = 10$ *i.e.* $^{22}Ne = 10\%$

PROBLEMS FOR PRACTICE



1. Neutrons can be found in all atomic nuclei except in one case. Which is this atomic nucleus and what does it consist of ?
2. How many nucleons are present in an atom of Nobelium, $^{254}_{102}$No ? How many electrons are present in the atom? How many nucleons may be considered as neutrons ?
3. Complete the following table :

Particle	Atomic No.	Mass No.	No. of electrons	No. of protons	No. of neutrons
Sodium atom	11	—	—	—	12
Aluminium ion	—	27	10	—	—
Chloride ion	—	—	18	—	18
Phosphorus atom	—	31	—	15	—
Cuprous ion	—	—	28	—	35

4. Complete the following table :

Name of the particle	Mass No.	Atomic No.	Protons	No. of Electrons	Neutrons
Oxygen	—	—	8	—	8
Sodium ion	23	—	11	—	—
Bromine	—	—	—	35	45

5. Find the number of protons, electrons and neutrons in (*a*) $^{27}_{13}Al^{3+}$ (*b*) $^{15}_{8}O^{2-}$.
6. How many neutrons and protons are there in the following nuclei ?

$^{13}_{6}C$, $^{16}_{8}O$, $^{24}_{12}Mg$, $^{56}_{26}Fe$, $^{88}_{38}Sr$. *(N.C.E.R.T.)*

ANSWERS

1. The nucleus of hydrogen atom does not contain any neutrons. It consists of only one proton.
2. Nucleons = 254, electrons = 102 and neutrons = 254—102 = 152
3. Sodium atom : $Z = 11, p = e^- = 11$,

$A = p + n = 11 + 12 = 23$

Al^{3+} ion : $e^- = 10$. Hence e^- in Al = 13,

$\therefore \quad Z = p = 13$

$A = 27, \therefore \; n = 27 - 13 = 14$

Cl^- ion : $e^- = 18$. Hence e^- in Cl = 17

$\therefore \quad Z = p = 17$

$n = 18 \; \therefore \quad A = n + p = 18 + 17 = 35$

P atom : $A = 31, p = 15$. Hence $Z = e^- = 15$

$n = A - Z = 31 - 15 = 16$

Cu^+ ion : $e^- = 28$. Hence e^- in Cu = 29.

$Z = p = 29$

$n = 35 \; \therefore \quad A = n + p = 35 + 29 = 64$

Particle	Atomic No.	Mass No.	No. of electrons	No. of protons	No. of neutrons
Sodium	11	23	11	11	12
Aluminium ion	13	27	10	13	14
Chloride ion	17	35	18	17	18
Phosphorous atom	15	31	15	15	16
Cuprous ion	29	64	28	29	35

4.

Name of the particle	Mass No.	Atomic No.	Protons	No. of Electrons	Neutrons
Oxygen	16	8	8	8	8
Sodium ion	23	11	11	10	12
Bromine	80	35	35	35	45

5. (*a*) $p = 13, e^{-} = 10, n = 14$ (*b*) $p = 8, e^{-} = 10, n = 7$.

6. See Hints below.

HINTS FOR DIFFICULT PROBLEMS

5. For $^{27}_{13}\text{Al}$, $Z = p = e^{-} = 13$, $A = 27$,

$\therefore$ $n = A - Z = 27 - 13 = 14$,

e^{-} in $Al^{3+} = 13 - 3 = 10$

For $^{15}_{8}\text{O}$, $Z = p = e^{-} = 8$, $A = 15$

$\therefore$ $n = A - Z = 15 - 8 = 7$

e^{-} in $O^{2-} = 8 + 2 = 10$

6. $^{13}_{6}\text{C}$, $p = 6$, $n = 7$;

$^{16}_{8}\text{O}$, $p = 8$, $n = 8$;

$^{24}_{12}\text{Mg}$, $p = 12$, $n = 12$,

$^{56}_{26}\text{Fe}$, $p = 26$, $n = 56 - 26 = 30$;

$^{88}_{38}\text{Sr}$, $p = 38$, $n = 88 - 38 = 50$.

ADD TO YOUR KNOWLEDGE

1. It is believed that fundamental particles like protons and neutrons are made up by combination of elementary particles called **quarks.** These elementary particles (quarks) are believed to have fractional charges and certain properties like colour and flavour.

2. The rest mass of the electron is $9{\cdot}1095 \times 10^{-31}$ kg. On the atomic scale, the rest mass of the electron = 0·0005486 u. It is the mass possessed by the electron when it is moving with a velocity much smaller than the velocity of light. However, when it is moving with velocity v, its mass is given by $m = \dfrac{m_{\text{rest}}}{\sqrt{1-(v/c)^2}}$ where c is the velocity of light. Thus when the electron is moving with the velocity of light (so that $v = c$), its mass is infinite.

3. The radius, r of the nucleus of an atom is related to its mass number, A, according to the relation

$$r = R_0 A^{1/3} \qquad \text{where } R_0 \text{ is a constant having value} = 1{\cdot}4 \times 10^{-15}\ m.$$

4. The radius of the nucleus is of the order of $10^{-15}\ m$ while that of the atom is of the order of $10^{-10}\ m$. Thus nuclear radius is 1/100,000th of the atomic radius.

5. The volume of the nucleus is of the order of $10^{-45}\ m^3$ while that of the atom is $10^{-30}\ m^3$. Thus volume of the nucleus is 10^{-15} of that of the atom *i.e.* nucleus is very small in size as compared to atom.

6. The radii of the nuclei are usually expressed in terms of Fermis (1 Fermi = 10^{-13} cm = $10^{-15}\ m$)

The nuclear radii lie in the range of 1·5 to 6·5 Fermi.

7. The nucleus has very high density *i.e.* $10^{14}\ g/cm^3$ (or $10^{17}\ kg/m^3$ or 10^{8} tonnes/cm³) which is about 10^{12} times that of lead.

8. Mass of one mole of electron is nearly 0·55 mg.

9. Mass of neutron is slightly more than that of proton.

10. The concept of atomic number was introduced by **Moseley** in 1913. He found that when cathode rays hit the anticathode, the wavelength of the X-ray emitted is characteristic of the element bombarded.

11. Thomson was awarded 1966 Nobel prize in Physics while Rutherford was awarded 1908 Nobel prize in chemistry for studies on chemistry of radioactive substances.

• SECTION—II

EMISSION SPECTRA AND BOHR'S MODEL

3.9. Introduction

It is observed that all elements give characteristic line spectra (emission spectra) which could not be explained on the basis of Rutherford's nuclear model of atom. In order to understand line spectrum it is essential to understand the nature of light (or radiant energy) which in turn was explained first on the basis of 'Electromagnetic wave theory' and then by 'Planck's quantum theory'. Further, with the advent of Electromagnetic wave theory, it was found that Rutherford's model of atom suffered from a serious drawback. Hence a new model of atom, called Bohr's model of atom was put forward. This model of atom was able to explain the drawback of Rutherford's model of atom and the main lines of the hydrogen spectrum.

Now we shall take up a brief discussion of the above developments one by one.

3.10. Nature of Electromagnetic Radiation (Electromagnetic Wave Theory)

This theory was put forward by James Clark Maxwell in 1864. The main points of this theory are summed up as follows :

(*i*) The energy is emitted from any source (like the heated rod or the filament of a bulb through which electric current is passed) *continuously* in the form of radiations (or waves) and is called the *radiant energy*.

(*ii*) The radiations consist of electric and magnetic fields oscillating perpendicular to each other and both perpendicular to the direction of propagation of the radiation (Fig. 3.10).

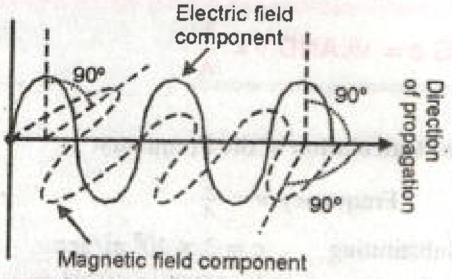


FIGURE. 3.10. Radiation consisting of electric and magnetic fields oscillating in planes perpendicular to each other and both perpendicular to the direction of propagation. They have same wavelength, frequency, speed and amplitude.

(*iii*) The radiations possess wave character and travel with the velocity of light (i.e. nearly 3×10^8 m/sec).

Because of the above characteristics, the radiations are called **Electromagnetic radiations** or **Electromagnetic waves.**

(*iv*) These waves do not require any material medium for propagation. For example, rays from the sun reach us through space which is a non-material medium.

Some important characteristics of a wave. The main characteristics of a wave are its wavelength (λ), frequency (ν) and velocity (c). These are defined as follows :

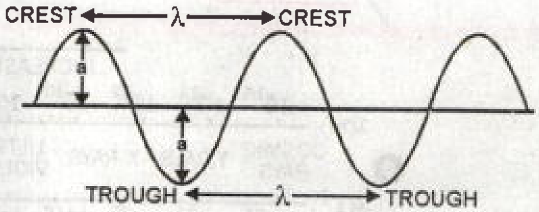


FIGURE 3.11. Some characteristics of a wave.

Wavelength *of a wave is defined as the distance between any two consecutive crests or troughs. It is represented by λ (lambda) and is expressed in Å or m or cm or nm (nanometer) or pm (picometer).*

$$1\ \text{Å} = 10^{-8}\ \text{cm} = 10^{-10}\ \text{m}$$

$$1\ \text{nm} = 10^{-9}\ \text{m},\quad 1\ \text{pm} = 10^{-12}\ \text{m}$$

Frequency *of a wave is defined as the number of waves passing through a point in one second. It is represented by ν (nu) and is expressed in Hertz (Hz) or cycles/sec or simply* sec^{-1} *or* s^{-1}.

$$1\ \text{Hz} = 1\ \text{cycle/sec}$$

Velocity *of a wave is defined as the linear distance travelled by the wave in one second. It is represented by c and is expressed in cm/sec or m/sec* ($m\,s^{-1}$).

Besides the above three characteristics, two other characteristics of a wave are amplitude and wave number.

Amplitude *of a wave is the height of the crest or the depth of the trough. It is represented by 'a' and is expressed in the units of length.*

Wave number is defined as the number of waves present in 1 cm length. Evidently, it will be equal to the reciprocal of the wavelength. It is represented by $\bar{\nu}$ (read as nu bar).

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

If λ is expressed in cm, $\bar{\nu}$ will have the units cm^{-1}.

Relationship between velocity, wavelength and frequency of a wave. As frequency is the number of waves passing through a point per second and λ is the length of each wave, hence their product will give the velocity of the wave. Thus

$$\boxed{c = \nu \times \lambda}$$

Electromagnetic spectrum. The different types of electromagnetic radiations differ only in their wavelengths and hence frequencies. Their *wavelengths* increase in the following order :–

Cosmic rays < γ – rays < X-rays < Ultra-violet rays < Visible < Infrared < Micro waves < Radio waves

When these electromagnetic radiations are arranged in order of their increasing wavelengths or decreasing frequencies, the complete spectrum obtained is called electromagnetic spectrum (Fig. 3.12).

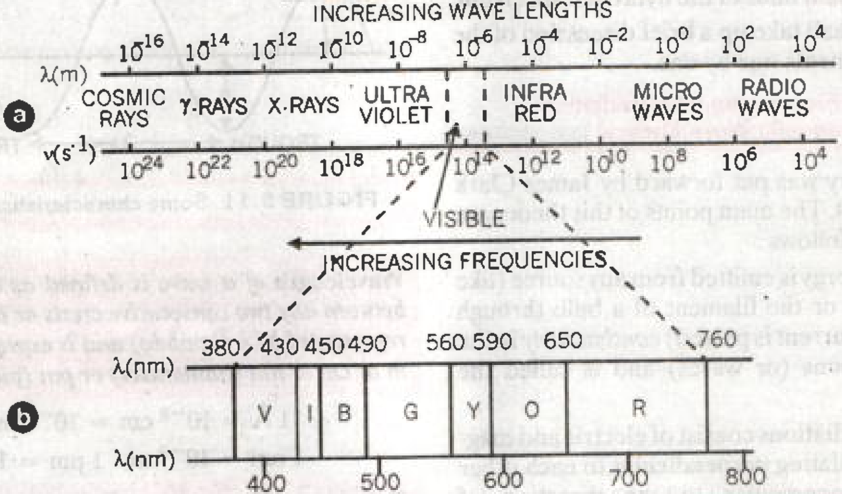


FIGURE 3.12. (a) Complete electromagnetic spectrum
(b) Spectrum of visible light.

PROBLEMS ON THE RELATIONS $c = \nu\lambda$ AND $\bar{\nu} = \frac{1}{\lambda}$

EXAMPLE 1. *Calculate (a) wave number and (b) frequency of yellow radiations having wavelength of 5800 Å.*

Solution. (*a*) Calculation of the wave number

Wave number $(\bar{\nu}) = 1/\lambda$

But $\lambda = 5800$ Å (Given)

$= 5800 \times 10^{-10}$ m

$$\therefore \quad \bar{\nu} = \frac{1}{5800 \times 10^{-10}\ \text{m}}$$

$$= 1{\cdot}72 \times 10^{6}\ \text{m}^{-1}$$

(*b*) Calculation of the Frequency

Frequency $\nu = \frac{c}{\lambda}$

Substituting $c = 3 \times 10^{8}$ m/sec

and $\lambda = 5800 \times 10^{-10}$ m

we get

$$\nu = \frac{3 \times 10^{8}\ \text{m/sec}}{5800 \times 10^{-10}\ \text{m}}$$

$= 5{\cdot}172 \times 10^{14}$ **sec^{-1} or cycles/sec or Hz.**

EXAMPLE 2. *A particular radio station broadcasts at a frequency of 1120 kHz (kilohertz). Another radio station broadcasts at a frequency of 98.7 MHz (Megahertz). What are the wavelengths of the radiations from each station ?*

Solution. **(*a*) Calculation of wavelength corresponding to a frequency of 1120 kHz.**

Wavelength, $\lambda = \frac{c}{\nu}$.

Substituting $c = 3 \times 10^8\ \text{ms}^{-1}$

and $\nu = 1120$ kHz. (Given)

$= 1120 \times 10^3$ cycles s^{-1}

(1 kHz = 10^3 cycles s^{-1})

$= 1120 \times 10^3\ \text{s}^{-1}$

we have $\lambda = \dfrac{3 \times 10^8\ \text{ms}^{-1}}{1120 \times 10^3\ \text{s}^{-1}}$

$= 267 \cdot 85$ m.

(*b*) Calculation of wavelength corresponding to a frequency of 98.7 MHz.

Wavelength, $\lambda = \frac{c}{\nu}$

Substituting $c = 3 \times 10^8\ \text{ms}^{-1}$

and $\nu = 98.7$ MHz

$= 98.7 \times 10^6$ cycles s^{-1}

(1 MHz = 10^6 cycles s^{-1})

we get, $\lambda = \dfrac{3 \times 10^8\ \text{ms}^{-1}}{98 \cdot 7 \times 10^6\ \text{s}^{-1}}$

$= 3 \cdot 0395$ m.

PROBLEMS FOR PRACTICE

1. Calculate the frequency of infrared radiations having wavelength, 3×10^6 nm. [Ans. $10^{11}\ \text{s}^{-1}$]
2. Calculate the range of frequencies of visible light from 3800 – 7600 Å. [Ans. $3 \cdot 95 \times 10^{14}$ to $7 \cdot 89 \times 10^{14}\ \text{s}^{-1}$]
3. How long would it take a radiowave of frequency, $6 \times 10^3\ \text{sec}^{-1}$ to travel from Mars to the Earth, a distance of 8×10^7 km ?
4. Calculate the wave number of radiations having a frequency of 4×10^{14} Hz. [Ans. $1 \cdot 33 \times 10^4\ \text{cm}^{-1}$]
5. Find the frequency of visible light with wavelength of 5000 Å. [Ans. $6 \times 10^{14}\ \text{sec}^{-1}$]
6. Yellow light emitted from a sodium lamp has a wavelength (λ) of 580 nm. Calculate the frequency (ν) and the wave number ($\bar{\nu}$) of the yellow light. [Ans. $5 \cdot 17 \times 10^{14}\ s^{-1}, 1 \cdot 72 \times 10^6\ m^{-1}$]
7. Calculate the wavelength, frequency and wave number of a light wave whose period is $2 \cdot 0 \times 10^{-10}\ s$. *(N.C.E.R.T.)* [Ans. $6 \cdot 0 \times 10^{-2}\ m, 5 \cdot 0 \times 10^9\ s^{-1}, 16 \cdot 66\ m^{-1}$]

HINTS FOR DIFFICULT PROBLEMS

1. $\lambda = 3 \times 10^6\ nm = (3 \times 10^6) \times 10^{-9}\ m$

$= 3 \times 10^{-3}\ m$

$$\nu = \frac{c}{\lambda} = \frac{3 \times 10^8\ ms^{-1}}{3 \times 10^{-3}\ m} = 10^{11}\ s^{-1}$$

2. $\lambda = 3800\ \text{Å} = 3800 \times 10^{-10}\ m = 3 \cdot 8 \times 10^{-7}\ m$

$$\nu = \frac{c}{\lambda} = \frac{3 \times 10^8\ ms^{-1}}{3 \cdot 8 \times 10^{-7}\ m} = 7 \cdot 89 \times 10^{14}\ s^{-1}$$

$\lambda = 7600\ \text{Å} = 7600 \times 10^{-10}\ m = 7 \cdot 6 \times 10^{-7}\ m$

$$\nu = \frac{c}{\lambda} = \frac{3 \times 10^8\ ms^{-1}}{7 \cdot 6 \times 10^{-7}\ m} = 3 \cdot 95 \times 10^{14}\ s^{-1}$$

3. All radiations in vacuum travel with the same speed, *i.e.*, $3 \times 10^8\ \text{m sec}^{-1}$

Distance to be travelled from Mars to the Earth = 8×10^7 km = $8 \times 10^7 \times 10^3$ m (1 km = 10^3 m)

$\therefore$ Time taken $= \dfrac{8 \times 10^7 \times 10^3}{3 \times 10^8}$

$= 2 \cdot 66 \times 10^2$ sec

$= 4$ min. 26 sec.

4. $\nu = 4 \times 10^{14}$ Hz (*i.e.* s^{-1}).

Wave number $\bar{\nu} = \frac{1}{\lambda} = \frac{\nu}{c}$

$$= \frac{4 \times 10^{14}\ s^{-1}}{3 \times 10^8\ ms^{-1}} = 1 \cdot 33 \times 10^6\ m^{-1}$$

or $\dfrac{4 \times 10^{14}\ s^{-1}}{3 \times 10^{10}\ \text{cm}\ s^{-1}} = 1 \cdot 33 \times 10^4\ \text{cm}^{-1}$

6. Similar to solved example 1.

7. Frequency (ν) $= \dfrac{1}{\text{Period}} = \dfrac{1}{2 \cdot 0 \times 10^{-10}}\ s^{-1}$

$= 5 \times 10^9\ s^{-1}$.

3.11. Limitations of Electromagnetic Wave Theory (Particle nature of electromagnetic radiation : Planck's Quantum Theory)

Electromagnetic wave theory was successful in explaining the properties of light such as interference, diffraction etc. but it could not explain the phenomena of 'Black body radiation', and 'Photoelectric effect' which could be explained only if electromagnetic waves are supposed to have particle nature. Each of these is briefly described below :

(1) Black body radiation. If any substance with high melting point (*e.g.* an iron bar) is heated, it first becomes red, then yellow and finally begins to glow with white light.

If the substance being heated is a black body (which is a perfect absorber and perfect radiator of energy) the radiation emitted is called black body radiation.

According to electromagnetic wave theory, the energy is emitted or absorbed continuously. Hence, the energy of any electromagnetic radiation is proportional to its intensity *i.e.* square of amplitude and is independent of its frequency or wavelength. Thus, according to the wave theory, the radiation emitted by the body being heated should have the same colour, although its intensity may vary as the heating is continued.

(2) Photoelectric effect. *When radiations with certain minimum frequency (v_0) strike the surface of a metal, the electrons are ejected from the surface of the metal* (Fig. 3.13). *This phenomenon is called photoelectric effect. The electrons emitted are called photo-electrons.*

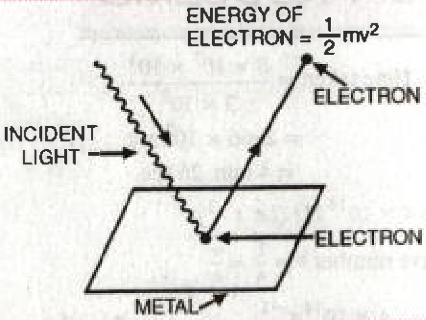


FIGURE 3.13. Photoelectric effect.

The apparatus used for studying the photoelectric effect is shown in Fig. 3.14. It consists of an evacuated tube fitted with metal surface to be exposed as cathode and a suitable detector as the anode and then connected to the external circuit as shown in the Fig. When light of sufficient energy is allowed to strike the surface of the metal, electrons are ejected which move towards the detector. By observing the amount of current flowing, the kinetic energy of the electrons can be determined.

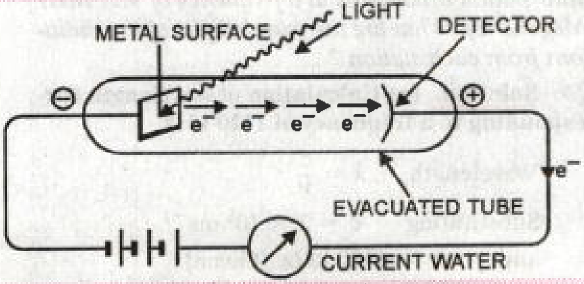


FIGURE 3.14. Apparatus for studying photoelectric effect.

However, the following three important facts are observed about the photoelectric effect :

(*i*) The electrons are ejected only if the radiation striking the surface of the metal has at least a minimum frequency (v_0). If the frequency is less than v_0, no electrons are ejected. This value (v_0) is called **Threshold Frequency.** *The minimum energy required to eject the electron (hv_0) is called* **work function (W_0)**.

(*ii*) The velocity (and hence the kinetic energy) of the electron ejected depends upon the frequency of the incident radiation and is independent of its intensity.

(*iii*) The number of photoelectrons ejected is proportional to the intensity of incident radiation.

The above observations cannot be explained by the Electromagnetic wave theory. According to this theory, since radiations are continuous, therefore it should be possible to accumulate energy on the surface of the metal, irrespective of its frequency and thus radiations of all frequencies should be able to eject electrons.

Similarly, according to this theory, the energy of the electrons ejected should depend upon the intensity of the incident radiation.

Planck's Quantum Theory. To explain the phenomena of 'Black body radiation' and 'Photoelectric effect,' Max Planck in 1900, put forward a theory known after his name as Planck's quantum theory. This theory was further extended by Einstein in 1905. The main points of this theory are as follows :–

(*i*) *The radiant energy is emitted or absorbed not continuously but discontinuously in the form of small discrete packets of energy.* Each such packet of energy is called a 'quantum'. In case of light, the quantum of energy is called a **'photon'**.

(*ii*) *The energy of each quantum is directly proportional to the frequency of the radiation**, i.e.

$$E \propto \nu$$

or $$\boxed{E = h\nu}$$

where h is a proportionality constant, called Planck's constant. Its value is approx. equal to $6 \cdot 626 \times 10^{-27}$ erg sec. or $6 \cdot 626 \times 10^{-34}$ joules sec.

(*iii*) *The total amount of energy emitted or absorbed by a body will be some whole number quanta.*

Hence $$E = nh\nu$$

where n is any integer.

To sum up, Planck's quantum theory postulates that light is made up of discrete particles called *photons*. At the same time, properties of light like interference, diffraction etc. can be explained if light is supposed to have wave character. In the light of these views, Einstein in 1905 proposed that *light has dual character.*

Explanation of Black body radiation and Photoelectric effect.

Explanation of Black Body Radiation. When some solid substance is heated, the atoms of the substance are set into oscillation and emit radiation of frequency, ν. Now, as heating is continued, more and more energy is being absorbed by the atoms and they emit radiations of higher and higher frequency. As red light has minimum frequency and yellow has higher frequency, therefore, the body on heating becomes first red, then yellow and so on.

Explanation of Photoelectric effect. Planck's quantum theory gives an explanation of the different points of the photoelectric effect as under :

(*i*) When light of some particular frequency falls on the surface of metal, the photon gives its entire energy to the electron of the metal atom. The electron will be dislodged or detached from the metal atom only if the energy of the photon is sufficient to overcome the force of attraction of the electron by the nucleus. That is why photoelectrons are ejected only when the incident light has a certain minimum frequency (threshold frequency ν_0).

(*ii*) If the frequency of the incident light (ν) is more than the threshold frequency (ν_0), the excess energy ($h\nu - h\nu_0$) is imparted to the electron as kinetic energy. *i.e.* K.E. of the ejected electron $= h\nu - h\nu_0$ or $\frac{1}{2} m v^2 = h\nu - h\nu_0$.

Hence greater is the frequency of the incident light, greater is the kinetic energy of the emitted electron**.

(*iii*) Increasing the intensity of light of a given frequency increases the number of photons but does not increase the energies of photons. Hence, when the intensity of light is increased, more electrons are ejected but the energies of these electrons are not altered.

REMEMBER

The energy acquired by an electron when it is accelerated through a potential difference of one volt is called one electron-volt (1 eV)

$$1 \text{ eV} = 1 \cdot 602 \times 10^{-19} \text{ J}$$

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*Thus in the visible light, as violet radiations have maximum frequency and the red radiations have minimum frequency, violet light has more energy than the red light. Similarly, the ultraviolet light has higher energy than the violet light and the infrared light has less energy than even the red light.

**If kinetic energy of the emitted photo-electrons is plotted against the frequency of the absorbed photons, a straight line of slope h is obtained (Fig. 3.15 *a*). If kinetic energy of the photoelectrons is plotted against intensity of the incident radiation (keeping frequency constant), a horizontal line is obtained as shown in Fig. 3.15 (*b*)

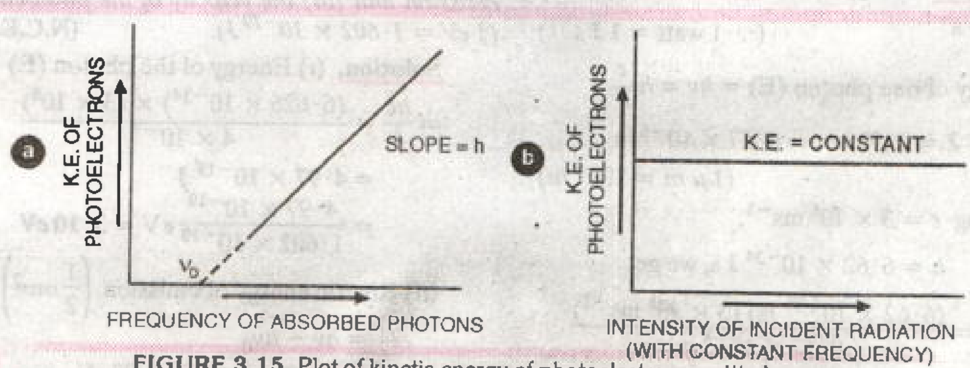


FIGURE 3.15. Plot of kinetic energy of photoelectrons emitted versus (a) frequency of absorbed photons (b) intensity of the incident radiation with constant frequency.

NUMERICAL PROBLEMS ON PLANCK'S QUANTUM THEORY AND PHOTOELECTRIC EFFECT

FORMULAS AND UNITS

(*i*) $E = h\nu, c = \nu\lambda$

where h = Planck's constant $= 6\cdot625 \times 10^{-34}$ joules sec.

ν = frequency in cycles/sec or sec^{-1}, E = energy in joules

c = velocity of light in $m\ \text{sec}^{-1} = 3\times10^{8}\ m\ \text{sec}^{-1}$

λ = wavelength in metres (m) $[1\text{Å} = 10^{-10}\ m]$

(*ii*) K.E. of the ejected electron, $\frac{1}{2}mv^2 = h\nu - h\nu_0$

where m = mass of the electron in kg,

v = velocity of the ejected electron in $m\ \text{sec}^{-1}$

ν_0 = threshold frequency in sec^{-1}, ν = incident frequency in sec^{-1}

EXAMPLE 1. *Calculate the frequency and energy of a photon of radiation having wavelength 6000Å.*

Solution. (*i*) Frequency $\nu = \frac{c}{\lambda}$

Substituting $c = 3 \times 10^8\ m\ \text{sec}^{-1}$

$\lambda = 6000\ \text{Å} = 6000 \times 10^{-10}\ m$

we get $\nu = \frac{3\times10^8}{6000\times10^{-10}} = \mathbf{5\times10^{14}\ sec^{-1}}$

(*ii*) Energy of the photon $E = h\nu$

Substituting $h = 6\cdot625 \times 10^{-34}$ joules sec

$\nu = 5 \times 10^{14}\ \text{sec}^{-1}$

we get $E = 6\cdot625 \times 10^{-34} \times 5 \times 10^{14}$

$= \mathbf{3\cdot3125 \times 10^{-19}}$ **joules.**

- **EXAMPLE 2.** *A 25 watt bulb emits monochromatic yellow light of wavelength of 0·57 μm. Calculate the rate of emission of quanta per second.* (N.C.E.R.T.)

Solution. Energy emitted by the bulb = 25 watt = $25\ \text{J s}^{-1}$ ($\because$ 1 watt = $1\ \text{J s}^{-1}$)

Energy of one photon (E) $= h\nu = h\frac{c}{\lambda}$

Here $\lambda = 0\cdot57\ \mu m = 0\cdot57 \times 10^{-6}\ m$ $(1\ \mu m = 10^{-6}\ m)$

Putting $c = 3 \times 10^8\ \text{ms}^{-1}$,

$h = 6\cdot62 \times 10^{-34}$ J s, we get

$$E = \frac{(6\cdot62\times10^{-34}\ \text{Js})\ (3\times10^8\ \text{ms}^{-1})}{0\cdot57\times10^{-6}\ m}$$

$= 3\cdot48 \times 10^{-19}$ J

$\therefore$ No. of photons emitted per sec

$$= \frac{25\ \text{Js}^{-1}}{3\cdot48\times10^{-19}\ \text{J}} = \mathbf{7\cdot18\times10^{19}}.$$

EXAMPLE 3. *Calculate the kinetic energy of the electron ejected when yellow light of frequency $5\cdot2 \times 10^{14}\ \text{sec}^{-1}$ falls on the surface of potassium metal. Threshold frequency of potassium is $5 \times 10^{14}\ \text{sec}^{-1}$.*

Solution. K.E. of the ejected electron is given by

$\frac{1}{2}mv^2 = h\nu - h\nu_0 = h(\nu - \nu_0)$

$= 6\cdot625 \times 10^{-34}\ (5\cdot2 \times 10^{14} - 5\cdot0 \times 10^{14})$

$= 6\cdot625 \times 10^{-34} \times 0\cdot2 \times 10^{14}$ joules

$= \mathbf{1\cdot325 \times 10^{-20}}$ **joules.**

EXAMPLE 4. *A photon of wavelength 4×10^{-7} m strikes on metal surface, the work function of the metal being 2·13 eV. Calculate (i) the energy of the photon (eV) (ii) the kinetic energy of the emission and (iii) the velocity of the photoelectron (1 eV = $1\cdot602 \times 10^{-19}$ J).* (N.C.E.R.T.)

Solution. (*i*) Energy of the photon (E) $= h\nu$

$$= \frac{hc}{\lambda} = \frac{(6\cdot626\times10^{-34})\times(3\times10^8)}{4\times10^{-7}}$$

$= \mathbf{4\cdot97 \times 10^{-19}\ J}$

$$= \frac{4\cdot97\times10^{-19}}{1\cdot602\times10^{-19}}\ \text{eV} = \mathbf{3\cdot10\ eV}$$

(*ii*) Kinetic energy of emission $\left(\frac{1}{2}mv^2\right)$

$= h\nu - h\nu_0$

$= 3\cdot10 - 2\cdot13 = \mathbf{0\cdot97\ eV}$

$$(iii)\ \frac{1}{2}mv^2 = 0\cdot97\,eV$$

$$= 0\cdot97 \times 1\cdot602 \times 10^{-19}\ J$$

$$i.e.\ \frac{1}{2} \times (9\cdot11 \times 10^{-31}\ kg) \times v^2 = 0\cdot97 \times 1\cdot602 \times 10^{-19}\ J$$

$$\text{or}\quad v^2 = 0\cdot341 \times 10^{12} = 34\cdot1 \times 10^{10}$$

$$\text{or}\quad v = \mathbf{5\cdot84 \times 10^5\ ms^{-1}}.$$

EXAMPLE 5. *Electrons are emitted with zero velocity from a metal surface when it is exposed to radiation of wavelength 6800 Å. Calculate the threshold frequency and work function (W_0) of the metal.* **(N.C.E.R.T.)**

Solution. Threshold wavelength (λ_0)

$$= 6800\ \text{Å} = 6800 \times 10^{-10}\ m$$

$$\text{As } c = \nu\lambda \therefore \nu_0 = \frac{c}{\lambda_0} = \frac{3\cdot0 \times 10^8\ ms^{-1}}{6800 \times 10^{-10}\ m}$$

$$= 4\cdot41 \times 10^{14}\ s^{-1}$$

Work function $(W_0) = h\nu_0$

$$= (6\cdot626 \times 10^{-34}\ Js)\ (4\cdot41 \times 10^{14}\ s^{-1})$$

$$= \mathbf{2\cdot92 \times 10^{-19}\ J}$$

EXAMPLE 6. *When electromagnetic radiation of wavelength 300 nm falls on the surface of sodium, electrons are emitted with a kinetic energy of $1\cdot68 \times 10^5\ J\ mol^{-1}$. What is the minimum energy needed to remove an electron from sodium ? What is the maximum wavelength that will cause a photoelectron to be emitted ?* **(N.C.E.R.T.)**

Solution. Energy of a photon of radiation of wavelength 300 nm will be

$$E = h\nu = h\frac{c}{\lambda}$$

$$= \frac{(6\cdot626 \times 10^{-34}\ Js)\ (3\cdot0 \times 10^8\ ms^{-1})}{(300 \times 10^{-9}\ m)}$$

$$= 6\cdot626 \times 10^{-19}\ J$$

∴ Energy of 1 mole of photons

$$= (6\cdot626 \times 10^{-19}\ J) \times (6\cdot022 \times 10^{23}\ mol^{-1})$$

$$= 3\cdot99 \times 10^5\ J\ mol^{-1}$$

As $E = E_0 + K.E.$ of photoelectrons emitted.

∴ Minimum energy (E_0) required to remove 1 mole of electrons from sodium = E − K.E.

$$= (3\cdot99 - 1\cdot68)\ 10^5\ J\ mol^{-1}$$

$$= 2\cdot31 \times 10^5\ J\ mol^{-1}$$

∴ Minimum energy required to remove one

$$\text{electron} = \frac{2\cdot31 \times 10^5\ J\ mol^{-1}}{6\cdot022 \times 10^{23}\ mol^{-1}} = \mathbf{3\cdot84 \times 10^{-19}\ J}.$$

The wavelength corresponding to this energy can be calculated as follows :

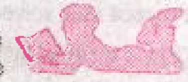
$$E = h\nu = h\frac{c}{\lambda}$$

$$\therefore \lambda = \frac{hc}{E} = \frac{(6\cdot626 \times 10^{-34}\ Js)\ (3\cdot0 \times 10^8\ ms^{-1})}{3\cdot84 \times 10^{-19}\ J}$$

$$= 5\cdot17 \times 10^{-7}\ m = 517 \times 10^{-9}\ m = \mathbf{517\ nm}$$

which corresponds to the green light.

PROBLEMS FOR PRACTICE



1. What is the energy of a mole of photons of radiations whose frequency is 4×10^{14} Hz ? **[Ans. 159·6 kJ mol^{-1}]**
2. Which has a higher energy : a photon of red light with a wavelength of 7500 Å or a photon of green light with a wavelength of 5250 Å ? **[Ans. Green]**
3. In the ultraviolet region of the atomic spectrum of hydrogen, a line is obtained at 1026 Å. Calculate the energy of photon of this wavelength ($h = 6\cdot626 \times 10^{-34}$ J-sec). **[Ans. 1·937 × 10^{-18} J]**
4. In the infrared region of the atomic spectrum of hydrogen, a line is obtained at 3802 cm^{-1}. Calculate the energy of this photon ($h = 6\cdot626 \times 10^{-34}$ J sec). **[Ans. 7·56 × 10^{-20} J]**
5. A 100 watt bulb emits monochromatic light of wavelength 400 nm. Calculate the number of photons emitted per second by the bulb. *(N.C.E.R.T.)* **[Ans. 2·01 × 10^2]**
6. Find the energy of each of the photons which
   (*i*) corresponds to light of frequency 3×10^{15} Hz
   (*ii*) have wavelength of 0·50 Å. *(N.C.E.R.T.)*
   [Ans. (*i*) 1·988 × 10^{-18} J (*ii*) 3·98 × 10^{-15} J]
7. What is the number of photons of light with a wavelength of 4000 pm that provide 1 J of energy ? *(N.C.E.R.T.)* **[Ans. 2·01 × 10^{16} protons]**
8. Light of wavelength 4000 Å falls on the surface of cesium. Calculate the energy of the photo-electron emitted. The critical wavelength for photoelectric effect in cesium is 6600 Å. **[Ans. 1·95 × 10^{-19} joule]**

PRACTICE PROBLEMS CONTD.

9. What is the ratio between the energies of two radiations, one with a wavelength of 6000 Å and the other with 2000 Å [1 Å = 10^{-10} *m*] ? [Ans. $\frac{1}{3}$]

10. The threshold energy for photo-electric emission of electrons from a metal is $3 \cdot 056 \times 10^{-15}$ joule. If light of 4000 Å wave length is used, will the electrons be ejected or not ? ($h = 6 \cdot 63 \times 10^{-34}$ Joule sec). [Ans. No]

11. Electromagnetic radiation of wavelength 242 nm is just sufficient to ionize the sodium atom. Calculate the ionization energy of sodium in kJ mol^{-1}.

(*N.C.E.R.T.*) [Ans. $494 \cdot 5$ kJ mol^{-1}]

12. Calculate the wavelength of a photon in Angstrom units having energy of one electron volt.

[Ans. $12 \cdot 40 \times 10^3$ Å]

HINTS FOR DIFFICULT PROBLEMS

1. $E = Nh\nu$

$= (6 \cdot 023 \times 10^{23})(6 \cdot 626 \times 10^{-34}\ \text{Js})(4 \times 10^{14}\ s^{-1})$

$= 159 \cdot 6 \times 10^3\ \text{J mol}^{-1} = 159 \cdot 6\ \text{kJ mol}^{-1}$

2. $E = h\nu = h\frac{c}{\lambda}$. Thus $E \propto \frac{1}{\lambda}$

3. $E = h\nu = h\frac{c}{\lambda}$

$$= \frac{(6 \cdot 626 \times 10^{-34}\ \text{Js})(3 \times 10^8\ ms^{-1})}{(1026 \times 10^{-10}\ m)}$$

$= 1 \cdot 937 \times 10^{-18}$ J

4. $\bar{\nu} = 3802\ \text{cm}^{-1}$, $E = h\nu = h\frac{c}{\lambda} = hc\bar{\nu}$

$= (6 \cdot 626 \times 10^{-34}\ \text{Js})(3 \times 10^{10}\ \text{cm}\ s^{-1}) \times (3802\ \text{cm}^{-1}) = 7 \cdot 56 \times 10^{-20}$ J

5. $1\ nm = 10^{-9}\ m$

Proceed as in solved example 2.

6. (*ii*) $\lambda = 0 \cdot 50 \times 10^{-10}\ m$,

$E = h\nu = h\frac{c}{\lambda}$

$$= \frac{(6 \cdot 626 \times 10^{-34})(3 \times 10^8)}{0 \cdot 50 \times 10^{-10}}\ \text{J}$$

$= 3 \cdot 98 \times 10^{-15}$ J.

7. $1\ pm = 10^{-12}\ m$. Proceed as in solved example 2.

10. Electrons will be ejected only if the energy of incident light is greater than the threshold energy.

Energy of the incident light $= h\nu = h\frac{c}{\lambda}$

$$= \frac{6 \cdot 63 \times 10^{-34} \times 3 \times 10^8}{4000 \times 10^{-10}}\ \text{J}$$

$= 4 \cdot 97 \times 10^{-19}$ J.

11. $E = Nh\nu = Nh\frac{c}{\lambda}$

$$= \frac{(6 \cdot 02 \times 10^{23}) \times (6 \cdot 626 \times 10^{-34}) \times (3 \times 10^8)}{242 \times 10^{-9}}$$

$= 4 \cdot 945 \times 10^5\ \text{J mol}^{-1}$

$= 494 \cdot 5\ \text{kJ mol}^{-1}$.

12. $E = 1\ eV = 1 \cdot 609 \times 10^{-19}$ J.

$E = h\nu = h\frac{c}{\lambda}$ or $\lambda = \frac{hc}{E}$

$$= \frac{(6 \cdot 62 \times 10^{-34}\ \text{Js})(3 \times 10^8\ \text{ms}^{-1})}{1 \cdot 602 \times 10^{-19}\ \text{J}}$$

$= 12 \cdot 40 \times 10^{-7}\ m = 12 \cdot 40 \times 10^3$ Å.

3.12. Study of Emission and Absorption Spectra

We have studied above that the electromagnetic spectrum consists of radiations of different wave lengths and frequencies. An instrument used to separate the radiations of different wavelengths (or frequencies) is called *spectroscope* or a *spectrograph*. A spectroscope consists of a prism or a diffraction grating for the dispersion of radiations and a telescope to examine the emergent radiations with the human eye. However, if in a spectroscope, the telescope is replaced by a photographic film, the instrument is called a spectrograph and the *photograph (or the pattern) of the emergent radiation recorded on the film is called a spectrogram or simply a spectrum of the given radiation The branch of science dealing with the study of spectra is called* **spectroscopy.**

The spectra are broadly classified into (*i*) Emission spectra and (*ii*) Absorption spectra. These are briefly explained below : –

1. Emission spectra. When the radiation emitted from some source e.g. from the sun or by passing electric discharge through a gas at low pressure or by heating some substance to high temperature etc. is passed directly through the prism and then received on the photographic plate, the spectrum obtained is called 'Emission spectrum'.

Depending upon the source of radiation, the emission spectra are mainly of two types :

(*i*) **Continuous spectra** When white light from any source such as sun, a bulb or any hot glowing body is analysed by passing through a prism, it is observed that it splits up into seven different wide bands of colours from violet to red, (like rainbow), as shown in Fig. 3.16. These colours are so continuous that each of them merges into the next. Hence the spectrum is called continuous spectrum.

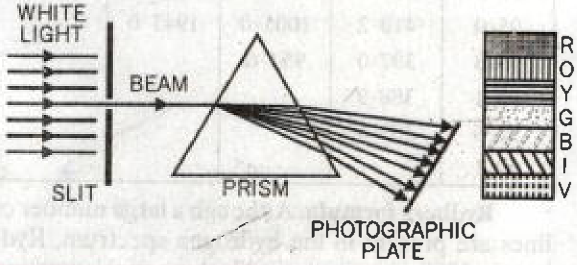


FIGURE 3.16. Continuous spectrum of white light.

It may be noted that on passing through the prism, red colour with the longest wavelength is deviated least while violet colour with shortest wavelength is deviated the most.

(*ii*) **Line spectra** When some volatile salt (*e.g.*, sodium chloride) is placed in the Bunsen flame (Fig. 3.17*a*) or an electric discharge is passed through a gas at low pressure (Fig. 3.17*b*), light is emitted. The colour of light emitted depends upon the nature of substance. For example, sodium or its salts emit yellow light while potassium or its salts give out violet light. If this light is resolved in a spectroscope, it is found that no continuous spectrum is obtained but some isolated coloured lines are obtained on the photographic plate separated from each other by dark spaces. This spectrum is called *'Line emission spectrum'* or simply *Line spectrum*.

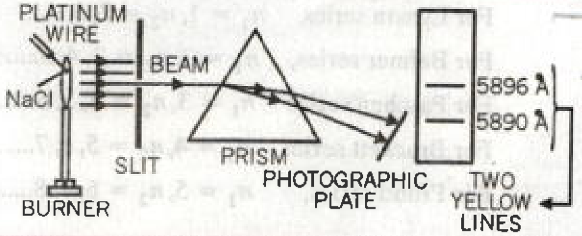


FIGURE 3.17(a). Line spectrum produced from a volatile salt placed in a flame.

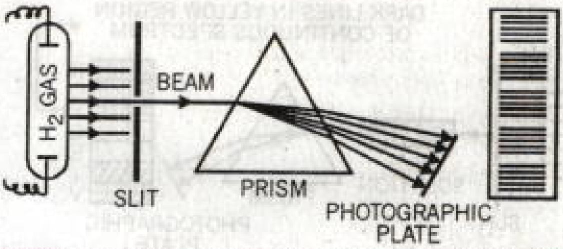


FIGURE 3.17(b). Line spectrum produced from light emitted by discharge tube.

Each line in the spectrum corresponds to a particular wavelength. Further, it is observed that each element gives its own characteristic spectrum, differing from those of all other elements. For example, sodium always gives two yellow lines (corresponding to wavelengths 5890 and 5896 Å). Hence the spectra of the elements are described as their *finger prints* differing from each other like the finger prints of the human beings*.

Further, it will be discussed later that the line spectra are obtained as a result of absorption and subsequent emission of energy by the electrons in the individual atoms of the element. Hence the line spectrum is also called **atomic spectrum.**

2. Absorption spectra When white light from any source is first passed through the solution or vapours of a chemical substance and then analysed by the spectroscope, it is observed that some dark lines are obtained in the otherwise continuous spectrum (Fig. 3.18). These dark lines are supposed to result from the fact that when white light (containing radiations of many wavelengths) is passed through the chemical substance, radiations

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*Spectroscopic methods have helped in the discovery of a number of elements e.g. helium in the sun and Rb, Cs, Tl, In, Ga and Sc in their minerals.

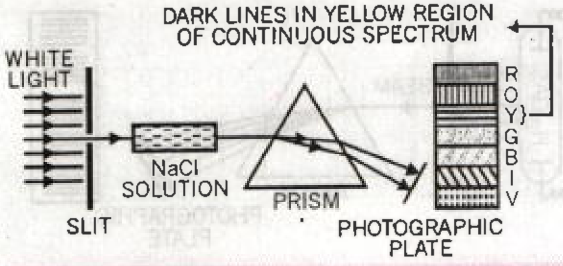

FIGURE 3.18. Production of absorption spectrum.

of certain wavelengths are absorbed, depending upon the nature of the element. Further it is observed that the dark lines are at the same place where coloured lines are obtained in the emission spectra for the same substance. This shows that the wavelengths absorbed were same as were emitted in the emission spectra. The spectrum thus obtained is, therefore, called *'absorption spectrum'*.

Difference between emission spectra and absorption spectra. The main points of difference between emission and absorption spectra are summed up in the table below :

EMISSION SPECTRUM	ABSORPTION SPECTRUM
1. Emission spectrum is obtained when the radiation from the source are directly analysed in the spectroscope.	1. Absorption spectrum is obtained when the white light is first passed through the substance and the transmitted light is analysed in the spectroscope.
2. It consists of bright coloured lines separated by dark spaces.	2. It consists of dark lines in the otherwise continuous spectrum.
3. Emission spectrum can be continuous spectrum (if source emits white light) or discontinuous *i.e.* line spectrum if source emits some coloured radiation.	3. Absorption spectrum is always discontinuous spectrum consisting of dark lines.

Emission spectrum of Hydrogen When hydrogen gas at low pressure is taken in the discharge tube and the light emitted on passing electric discharge is examined with a spectroscope, the spectrum obtained is called the emission spectrum of hydrogen (Fig. 3.17*b*). It is found to consist of a large number of lines which are grouped into different series, named after the discoverers.* The names of these series and the regions in which they are found to lie are given in the Fig. 3.18.

The wavelengths of different lines in each of these series are given in Table 3.2.

TABLE 3.2. Wavelengths (in nm) of various lines in the different series

LYMAN SERIES	BALMER SERIES	PASCHEN SERIES	BRACKETT SERIES	PFUND SERIES
121·6	656·3	1875·1	4050·0	7451·0
102·6	486·1	1281·8	2630·0	4652·0
97·3	434·0	1093·8	2166·0	3740·0
95·0	410·2	1005·0	1945·0	
93·8	397·0	954·6		
93·1	388·9			
92·6	383·5			
91·1				

Rydberg formula. Although a large number of lines are present in the hydrogen spectrum, Rydberg in 1890 gave a very simple theoretical equation for the calculation of the wavelengths of these lines. The equation gives the calculation of wave numbers ($\bar{\nu}$) of the lines by the formula $\bar{\nu} = R\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$

where R is a constant, called **Rydberg constant**** and has a value equal to 109,677 cm^{-1} or $1{\cdot}097 \times 10^7 \, m^{-1}$, n_1 and n_2 are whole numbers and for a particular series n_1 is constant and n_2 varies. For example,

For Lyman series, $n_1 = 1, n_2 = 2, 3, 4....$

For Balmer series, $n_1 = 2, n_2 = 3, 4, 5.....$

For Paschen series $n_1 = 3, n_2 = 4, 5, 6......$

For Brackett series $n_1 = 4, n_2 = 5, 6, 7.......$

For Pfund series, $n_1 = 5, n_2 = 6, 7, 8.....$

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* Hydrogen being the lightest element, the number of lines produced in the spectrum is minimum. As the gases with higher molecular masses are taken, the spectra become more and more complex.

**If the formula is written for frequency i.e. $\nu = R\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$, the value of Rydberg constant, $R = 3{\cdot}29 \times 10^{15}$ cycles/sec. $\left(\because \bar{\nu} = \frac{1}{\lambda} = \frac{\nu}{c} \text{ or } \nu = c\,\bar{\nu}\right)$

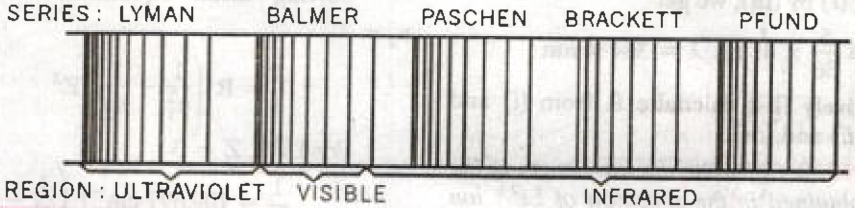


FIGURE 3.19. Emission or atomic spectrum of hydrogen.

The above expression is called ***Rydberg formula***.

For H-like particles, the formula is $\bar{\nu} = R\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) Z^2$ when Z is the atomic number of the H-like particle.

When $n_1 = 2$, the expression given above is called ***Balmer's formula*** as it was first put forward by Balmer in 1885 to explain the series of lines bearing his name (i.e. lines in the visible region).

Limiting line. The limiting line of any spectral series in the hydrogen spectrum is the line when n_2 in the Rydberg's formula is infinity *i.e.* $n_2 = \infty$.

PROBLEMS ON RYDBERG FORMULA/BALMER FORMULA

EXAMPLE 1. *Calculate the frequency and the wavelength of the radiation in nanometers emitted when an electron in the hydrogen atom jumps from third orbit to the ground state. In which region of the electromagnetic spectrum will this line lie ?*

(Rydberg constant = 109, 677 cm^{-1})

Solution. According to Rydberg formula,

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

Here $R = 109{,}677 \text{ cm}^{-1}$

$n_2 = 3$

$n_1 = 1$ (for ground state)

$$\therefore \bar{\nu} = 109{,}677\left(\frac{1}{1^2} - \frac{1}{3^2}\right) \text{cm}^{-1}$$

$$= 109{,}677 \times \frac{8}{9} \text{ cm}^{-1} = 97490 \cdot 7 \text{ cm}^{-1}$$

$$\lambda = \frac{1}{\bar{\nu}} = \frac{1}{97490 \cdot 7} \text{ cm} = 103 \times 10^{-7} \text{ cm}$$

$$= 103 \times 10^{-9} \text{ m} = \mathbf{103 \text{ nm}}$$

$$\nu = \frac{c}{\lambda} = \frac{3 \times 10^8 \text{ ms}^{-1}}{103 \times 10^{-9} \text{ m}} = \mathbf{2 \cdot 91 \times 10^{15} \text{ s}^{-1}}$$

The wavelength, as calculated above, lies in the ultraviolet region. Otherwise too, as the jump is on the 1st orbit, the line will belong to Lyman series and hence lie in the **ultraviolet region**.

EXAMPLE 2. *The wavelength of the first line in the Balmer series is 656 nm. Calculate the wavelength of the second line and the limiting line in Balmer series.*

Solution. According to Rydberg's formula

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

For the Balmer series, $n_1 = 2$ and for the 1st line, $n_2 = 3$

$$\therefore \frac{1}{656} = R\left(\frac{1}{2^2} - \frac{1}{3^2}\right) = R \times \left(\frac{1}{4} - \frac{1}{9}\right)$$

$$= R \times \frac{5}{36} = \frac{5R}{36} \quad \text{...(i)}$$

For the second line, $n_1 = 2, n_2 = 4$

$$\therefore \frac{1}{\lambda} = R\left(\frac{1}{2^2} - \frac{1}{4^2}\right) = R\left(\frac{1}{4} - \frac{1}{16}\right)$$

$$= R \times \frac{3}{16} = \frac{3R}{16} \quad \text{...(ii)}$$

Dividing (*i*) by (*ii*), we get

$$\frac{\lambda}{656} = \frac{5}{36} \times \frac{16}{3} \text{ or } \lambda = \mathbf{485 \cdot 9 \text{ nm}}$$

For the limiting line, $n_1 = 2, n_2 = \infty$

$$\therefore \frac{1}{\lambda} = R\left(\frac{1}{2^2} - \frac{1}{\infty^2}\right) = \frac{R}{4} \quad \text{...(iii)}$$

Dividing (*i*) by (*iii*), we get

$$\frac{\lambda}{656} = \frac{5}{36} \times 4 \quad \text{or} \quad \lambda = 364\cdot4 \text{ nm}$$

Alternatively first calcualte R from (*i*) and substitute in (*ii*) and (*iii*).

EXAMPLE 3. *Calculate the wavelength of the spectral line obtained in the spectrum of Li^{2+} ion when the transition takes place between two levels whose sum is 4 and the difference is 2.*

Solution. Suppose the transition takes place between levels n_1 and n_2.

Then $n_1 + n_2 = 4$ and $n_2 - n_1 = 2$

Solving these equations, we get $n_1 = 1$, $n_2 = 3$

$$\therefore \quad \frac{1}{\lambda} = R\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) Z^2$$

For Li^{2+}, Z = 3

$$\therefore \quad \frac{1}{\lambda} = 109{,}677 \text{ cm}^{-1} \left(\frac{1}{1^2} - \frac{1}{3^2}\right) \times 3^2$$

$$= 109{,}677 \times \left(\frac{1}{1} - \frac{1}{9}\right) \times 9 \text{ cm}^{-1}$$

$$= 109677 \times 8 \text{ cm}^{-1}$$

$$\text{or} \quad \lambda = \frac{1}{109677 \times 8} \text{ cm} = 1\cdot14 \times 10^{-6} \text{ cm.}$$

PROBLEMS FOR PRACTICE

1. What is the wavelength of the light emitted when the electron in a hydrogen atom undergoes transition from an energy level with $n = 4$ to an energy level with $n = 2$? What is the colour corresponding to this wavelength ? (Rydberg constant = 109,677 cm^{-1}) *(N.C.E.R.T.)* [Ans. **486 nm, Blue**]
2. Calculate the wavelength from the Balmer formula when $n = 3$. [Ans. **656 nm**]
3. Calculate the wavelength of the spectral line in Lyman series corresponding to $n_2 = 3$. [Ans. **102·6 nm**]

HINTS FOR DIFFICULT PROBLEMS

1. $$\bar{\nu} = R\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) = 109677\left(\frac{1}{2^2} - \frac{1}{4^2}\right) \text{cm}^{-1}$$

$$= 20564\cdot4 \text{ cm}^{-1}$$

$$\lambda = \frac{1}{\bar{\nu}} = \frac{1}{20564\cdot4 \text{ cm}^{-1}}$$

$$= 486 \times 10^{-7} \text{ cm} = 486 \times 10^{-9}\, m$$

$$= 486\, nm$$

2. $$\bar{\nu} = R\left(\frac{1}{2^2} - \frac{1}{n_2^2}\right) = 109677\left(\frac{1}{2^2} - \frac{1}{3^2}\right) \text{cm}^{-1}$$

$$= 15232\cdot9 \text{ cm}^{-1}$$

$$\lambda = \frac{1}{\bar{\nu}} = \frac{1}{15232\cdot9 \text{ cm}^{-1}} = 656 \times 10^{-7} \text{ cm}$$

$$= 656 \times 10^{-9}\, m = 656\, nm$$

3. For Lyman series, $n_1 = 1$ $\therefore$ $\bar{\nu} = R\left(\frac{1}{1^2} - \frac{1}{3^2}\right)$

$$= 109677 \times \frac{8}{9} = 97490\cdot7 \text{ cm}^{-1}$$

$$\lambda = \frac{1}{\bar{\nu}} = \frac{1}{97490\cdot7 \text{ cm}^{-1}}$$

$$= 102\cdot6 \times 10^{-7} \text{ cm}$$

$$= 102\cdot6\, nm$$

3.13. Drawback of Rutherford's Model

According to Rutherford's model, an atom consists of a small, heavy positively charged nucleus in the centre and the electrons were revolving around it. This model was compared with the solar system in which the planets were revolving around the sun and continue to move in their fixed circular paths because the force of attraction was balanced by the centrifugal force. However, there are some important differences between the two. Firstly, whereas the electrons and the nuclei are microscopic particles, the sun and the planets were big bodies and hence Newtonian laws of motion do not apply to the motion of microscopic particles.* Secondly, whereas the electrons and the nucleus were charged particles, the sun and the planets did not carry any charge. According to Maxwell's electromagnetic theory, whenever a charged particle like electron is revolving in a field of force like that of the nucleus, it loses energy continuously in

---

*This gave rise to a new branch of physics, called Quantum Mechanics.

the form of electromagnetic radiations. This is because when a particle is revolving, it undergoes acceleration due to change in direction even if the speed remains constant. Thus the orbit of the revolving electron will keep on becoming smaller and smaller, following a spiral path as shown in Fig. 3.20. and ultimately the electron should fall into the nucleus. In other words, the atom should collapse. However, this actually does not happen and the atom is quite stable.

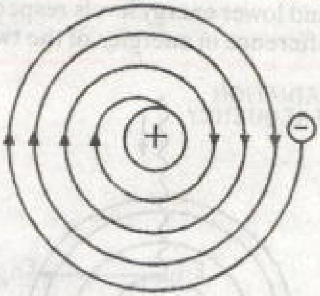


FIGURE 3.20. Continuous loss of energy by revolving electron.

Another limitation of Rutherford's model, as already mentioned in the beginning of sec. 3.9. was its inability to explain the atomic spectra of the elements.

3.14. Bohr's Model of Atom

To overcome the drawback of Rutherford's model of atom and to explain the line spectrum of hydrogen, Neils Bohr, a Danish physicist in 1913 proposed a new model of atom based upon Planck's quantum theory. This new model is called Bohr's model of atom.

1. Postulates of Bohr's Model of Atom. The main postulates of Bohr's model of atom are as follows :–

(*i*) An atom consists of a small, heavy positively charged nucleus in the centre and the electrons revolve around it in circular orbits.

(*ii*) Out of a large number of circular orbits theoretically possible around the nucleus, the electrons revolve only in those orbits which have a *fixed* value of *energy*. Hence these orbits are called **energy levels** *or* **stationary states.** The word stationary does not mean that the electrons are stationary but it means that the energy of the electron revolving in a particular orbit is fixed and does not change with time. The different energy levels are numbered as 1, 2, 3, 4....etc. or designated as K, L, M, N, O, P.....etc. starting from the shell closest to the nucleus.

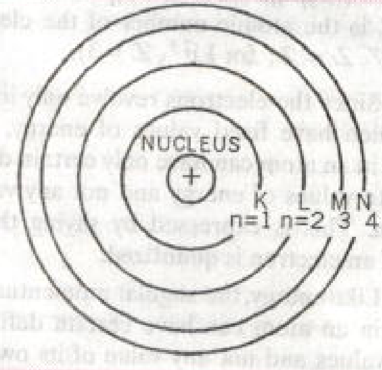


FIGURE 3.21. Circular orbits (energy levels/stationary states) around the nucleus.

The energies of the different stationary states in case of hydrogen atom are given by the expression (called *Bohr formula*)

$$\boxed{E_n = -\frac{2\pi^2 me^4}{n^2h^2}}\ ^*$$

Substituting the values of *m* (mass of the electron), *e* (charge on the electron) and *h* (Planck's constant), we get

$$\boxed{\begin{aligned} E_n &= -\frac{21\cdot8\times10^{-19}}{n^2}\ \text{J/atom} \\ &= -\frac{13\cdot6}{n^2}\ \text{eV/atom} \\ &\qquad (\because 1\ eV = 1\cdot6022\times10^{-19}\ \text{J}) \\ &= -\frac{1312}{n^2}\ \text{kJ mol}^{-1} \end{aligned}}$$

where n = 1, 2, 3.....etc. stand for 1st, 2nd, 3rd....etc. level respectively. Thus the 1st energy level ($n = 1$) which is closest to the nucleus has lowest energy. The energy of the levels increases as we move outwards starting from the 1st level (K-level). Thus the energies of the various levels are in the order :

---

*$E_n \propto \frac{1}{n^2}$ or $E_n = -R_H\left(\frac{1}{n^2}\right)$. The proportionality constant is called Rydberg constant (R_H). It has value equal to $21\cdot8\times10^{-19}$ J. For H-like particles, $E_n = -\frac{2\pi^2 m Z^2 e^4}{n^2 h^2}$ *i.e.* $E_n \propto \frac{Z^2}{n^2}$

1st < 2nd < 3rd < 4th.........and so on
or K < L < M < N..........and so on.

For H-like particle *e.g.* He^+, Li^{2+} etc. (containing one electron only), the expression for energy is

$$E_n = -\frac{2\pi^2 m Z^2 e^4}{n^2 h^2} = -\frac{1312\, Z^2}{n^2} \text{ kJ mol}^{-1}$$

where Z is the atomic number of the element (For He^+, Z = 2 ; for Li^{2+}, Z = 3).

(*iii*) Since the electrons revolve only in those orbits which have fixed values of energy, hence electrons in an atom can have only certain definite or discrete values of energy and not any value of their own. This is expressed by saying that the energy of an electron is **quantized.**

(*iv*) Like energy, the angular momentum of an electron in an atom can have certain definite or discrete values and not any value of its own. The only permissible values of angular momentum are given by the expression.*

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

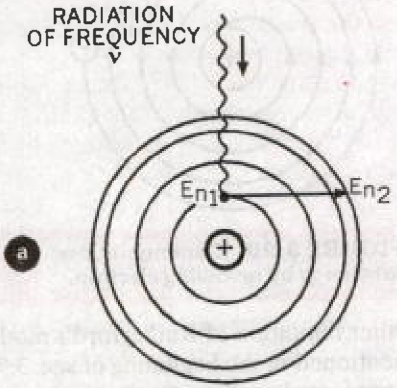
i.e. angular momentum of the electron is an integral multiple of $h/2\pi$. Here m is the mass of the electron, v is the tangential velocity of the revolving electron, r is the radius of the orbit, h is the Planck's constant and n is any integer. In other words, the angular momentum of the electron can be $h/2\pi$ $2h/2\pi$ $3h/2\pi$ .....etc. This means that *like energy, the angular momentum of an electron in an atom is also* **quantized.**

(*v*) When the electrons in an atom are in their lowest (normal) energy state, they keep on revolving in their respective orbits without losing energy because energy can neither be lost nor gained continuously. This state of atom is called **normal** or **ground state.**

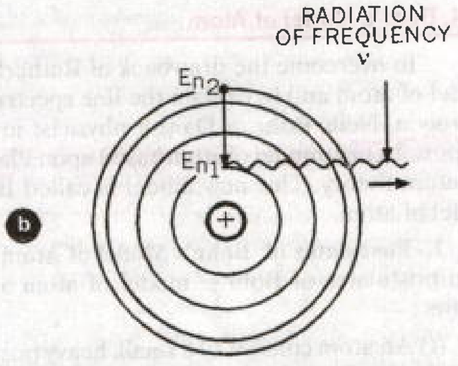
(*vi*) Energy is emitted or absorbed only when the electrons jump from one orbit to the other. For example, when energy is supplied to an atom by subjecting it to electric discharge or high temperature, an electron in the atom may jump from its normal energy level (ground state) to some higher energy level by absorbing a definite amount of energy (Fig. 3.22(*a*). This state of atom is called **excited state.** Since the life time of the electron in the excited state is short, it immediately jumps back to the lower energy level by emitting energy in the form of light of suitable frequency or wavelength (Fig. 3.22(*b*)). The amount of energy emitted or absorbed is given by the difference of energies of the two energy levels concerned, i.e.,

$$\Delta E = E_2 - E_1$$

where E_2 and E_1 are the energies of the electron in the higher and lower energy levels respectively and ΔE is the difference in energies of the two levels.



Energy is absorbed when an electron jumps from a lower energy level to some higher energy



Energy is emitted when an electron jumps from a higher energy level to some lower energy level.

FIGURE 3.22. Energy changes during electronic jumps.

Further, since each energy level is associated with a certain definite amount of energy, therefore, energy is always emitted or absorbed in certain

---

*Angular momentum = Moment of inertia × Angular velocity = $I \times \omega$.
But $I = m_e r^2$ and $\omega = v/r$ where v is linear velocity.
∴ Angular momentum $= m_e r^2 \times v/r = m_e v r$.

discrete quantities called quantas or photons and not any value. This means that the energy of the electron cannot change gradually and continuously but changes abruptly as the electron jumps from one energy level to the other.

In other words, we can state that for a change of electronic energy, the electron has to jump and not to flow from one energy level to the other.

2. Electronic Energy as Negative Energy. In the formula for the energy of the electron ($E_n = -1312/n^2$), we observe that it has a negative value.

The concept of negative energy of the electron may be explained as follows :

When the electron is at distance infinity from the nucleus, there is no force of attraction on the electron by the nucleus. Hence the energy of the electron at distance infinity from the nucleus is taken as zero.* As the electron moves towards the nucleus, it experiences a force of attraction by the nucleus. As a result, some energy is given out. Since its value was already zero, hence now it becomes negative. Further, as the electron comes more and more close to the nucleus, the attraction increases and more energy is released. Hence the energy of the electron becomes less and less. This explains why the energy decreases as we move from the outer to the inner levels.

Alternatively, the energy of the atom in the ionized state is taken as zero. When electron is added up into the ion, attraction takes place, energy is released. Since it was already zero, hence it becomes negative.

3. Quantization of Electronic Energy – The Key Concept of Bohr's Theory. The most important postulate of Bohr's theory is the concept of quantization of electronic energy. By quantization we mean that a quantity cannot change gradually and continuously to have any arbitrary value but changes only abruptly and discontinuously to have certain definite or discrete values. To understand the concept of quantization, let us consider an interesting example. When we travel in a taxi, we find that the pointer of the speedometer of the taxi moves gradually and continuously since the speed of the taxi can have any arbitrary value depending upon the acceleration. On the other hand, the fare meter only moves abruptly and discontinuously in multiples of one rupee. This is due to the reason that the fare meter has been designed to have only certain specific values in multiples of one rupee. Thus, we conclude that the fare of a taxi is quantized but the speed is not. Similarly, in case of an atom, Bohr postulated that electrons revolve around the nucleus in certain fixed circular orbits in which they can continue revolving without gaining or losing energy. This means that the energy of the electron cannot change continuously but can have only definite values. Thus, we can say that the *energy of an electron is quantized*.

4. Usefulness of Bohr's Model. The main advantages of Bohr's model are as under :

(i) It explains the stability of the atom. According to Bohr's theory, *an electron cannot lose energy as long as it stays in a particular orbit*. Therefore, the question of losing energy continuously and falling into the nucleus does not arise.

(ii) It explains the line spectrum of hydrogen. The most remarkable success of the Bohr's theory is that it provides a satisfactory explanation for the line spectrum of hydrogen.

According to Bohr's theory, an electron neither emits nor absorbs energy as long as it stays in a particular orbit. However, when an atom is subjected to electric discharge or high temperature, an electron in the atom may jump from the normal energy level, *i.e., ground state* to some higher energy level, *i.e., excited state*. Since the lifetime of the electron in the excited state is short, it returns to some lower energy level or even to the ground state in one or more jumps. During each such jump, energy is emitted in the form of a photon of light of a definite wavelength or frequency.

The frequency (ν) of the photon of light thus emitted depends upon the energy difference of the two energy levels concerned and is given by the expression, $E_2 - E_1 = h\nu$ or $\nu = \dfrac{E_2 - E_1}{h}$

where E_2 is the energy of higher energy level and E_1 is the energy of the lower energy level and h is the Planck's constant.

Now, frequency is related to the wavelength as $\nu = c/\lambda$ where c is the velocity of light.

$$\therefore \qquad \nu = \frac{c}{\lambda} = \frac{E_2 - E_1}{h}$$

$$\text{or} \qquad \lambda = \frac{hc}{E_2 - E_1}$$

---

*At infinite distance, the electron is considered as a free electron at rest, where its energy is taken as zero. The energy of the electron in an atom is lower than the energy of free electrons at rest. Hence it is negative.

Corresponding to the frequency or wavelength of each photon emitted, there appears a line in the spectrum. The frequencies (or wavelengths) of the spectral lines calculated with the help of above equations are found to be in good agreement with the experimental values. Thus Bohr's theory elegantly explains the line spectrum of hydrogen and hydrogen like particles (like He^+, Li^{2+}, Be^{3+}, etc.)

5. Simultaneous appearance of a large number of lines in the hydrogen spectrum. Although an atom of hydrogen contains only one electron, yet its atomic spectrum consists of a large number of lines which have been grouped into five series, i.e., Lyman, Balmer, Paschen, Brackett and Pfund. This may be explained as follows :

Any given sample of hydrogen gas contains a large number of molecules. When such a sample is heated to a high temperature or an electric discharge is passed, the hydrogen molecules split into hydrogen atoms. The electrons in different hydrogen atoms absorb different amounts of energies and are excited to different energy levels. For example, the electrons in some atoms are excited to second energy level (L), while in others they may be promoted to third (M), fourth (N), fifth (O) energy levels and so on. Since the lifetime of electrons in these excited states is very small, they return to some lower energy level or even to the ground state in one or more jumps. The various possibilities by which the electrons jump back from various excited states are shown in Fig. 3.23.

Thus different excited electrons adopt different routes to return to various lower energy levels or the ground state. As a result, they emit different amounts of energies and thus produce a large number of lines in the atomic spectrum of hydrogen.

For example, when the electron jumps from energy levels higher than $n = 1$, i.e., $n = 2, 3, 4, 5, 6$.....etc. to $n = 1$ energy level, the group of lines produced is called *Lyman series*. These lines lie in the *ultraviolet region*.

Similarly, the group of lines produced when electron jumps from 3rd, 4th, 5th or any higher energy level to 2nd energy level, is called *Balmer series*. These lines lie in the *visible region*.

In a similar way, *Paschen series* is obtained by the electronic jumps from 4th, 5th or any higher energy level to the 3rd energy level. Similarly, Brackett series results from electronic transitions from 5th, 6th or any higher energy level to the 4th energy level. Lastly, the *Pfund series* originates by electronic jumps from 6th, 7th or any higher energy level to 5th energy level. The spectral lines of the last three series lie in the *infrared region*.

To sum up

Lyman series : From $n = 2, 3, 4$ .... to $n = 1$

Balmer series : From $n = 3, 4, 5$ .... to $n = 2$

Paschen seires : From $n = 4, 5, 6$ .... to $n = 3$

Brackett series : From $n = 5, 6, 7$ .... to $n = 4$

Pfund series : From $n = 6, 7, 8$ .... to $n = 5$

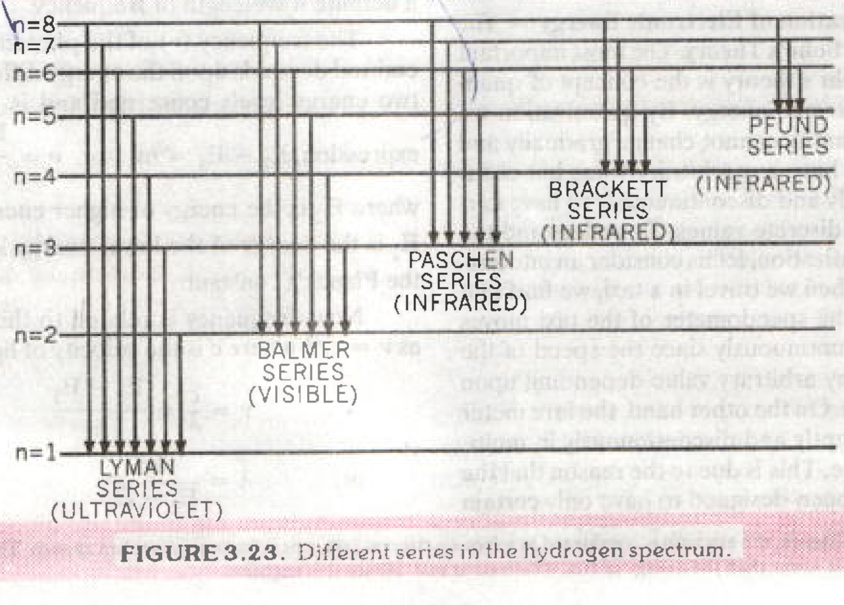


FIGURE 3.23. Different series in the hydrogen spectrum.

3.15. Weaknesses of Bohr's Model of Atom

Bohr's model of atom suffers from the following weaknesses or limitations.

(*i*) *Inability to explain line spectra of multi-electron atoms*. Bohr's theory was successful in explaining the line spectra of hydrogen atom and hydrogen like particles, containing single electron only. However, it failed to explain the line spectra of multi-electron atoms. When spectroscopes with better resolving powers were used, it was found that even in case of hydrogen spectrum, each line was split up into a number of closely spaced lines (called *fine structure*) which could not be explained by Bohr's model of atom.

(*ii*) *Inability to explain splitting of lines in the magnetic field (Zeeman effect) and in the electric field (Stark effect)*. In the production of line spectrum, if the source emitting the radiation is placed in a magnetic field or in an electric field, it is observed that each spectral line splits up into a number of lines. The splitting of spectral lines in the magnetic field is called *Zeeman effect* while the splitting of spectral lines in the electric field is called *Stark effect*. Bohr's model of atom was unable to explain this splitting of spectral lines.

(*iii*) *Inability to explain the three dimensional model of atom*. According to Bohr's model of atom, the electrons move along certain circular paths in one plane. Thus *it gives a flat model of atom*. But now it is well established that the atom is three dimensional and not flat, as had been suggested by Bohr.

(*iv*) *Inability to explain the shapes of molecules*. Now it is well known that in covalent molecules, the bonds have directional characteristics (i.e., atoms are linked to each other in particular directions) and hence they possess definite shapes. Bohr's model is unable to explain it.

(*v*) *Inability to explain de Broglie concept of dual character of matter and Heisenberg's uncertainty principle*. Bohr's model of atom is unable to explain the following :

(*i*) *de Broglie concept of dual character of matter*. According to this concept, an electron behaves not only as a particle but also as a wave. Bohr, however, considered electrons only as *discrete particles*.

(*ii*) *Heisenberg's uncertainty principle*. According to this principle, the position and momentum of a small particle like electron cannot be determined simultaneously with absolute accuracy. However, according to Bohr, the electron moves along a fixed circular path.

These will be studied in detail at the + 2 level.

Ionization energy of hydrogen and hydrogen-like particles. *Ionization energy is the energy required to remove the electron completely from the atom so as to convert it into a positive ion.* This means that it is the energy absorbed by the electron in the ground state so as to jump to $n = \infty$. Thus for H-atom, as

$$E_n = -\frac{21\cdot8 \times 10^{-19}}{n^2}\ \text{J atom}^{-1}$$

or $$-\frac{1312}{n^2}\ \text{kJ mol}^{-1}$$

$$\therefore \text{I.E.} = E_\infty - E_1$$

$$= 0 - (-21\cdot8 \times 10^{-19}\ \text{J atom}^{-1})$$

$$= 21\cdot8 \times 10^{-19}\ \text{J atom}^{-1}$$

or $$= 0 - (-1312\ \text{kJ mol}^{-1}) = +1312\ \text{kJ mol}^{-1}$$

For H-like particles,

$$E_n = -\frac{21\cdot8 \times 10^{-19}}{n^2} Z^2\ \text{J atom}^{-1}$$

or $$-\frac{1312}{n^2} Z^2\ \text{kJ mol}^{-1}$$

$$\therefore \text{I.E.} = E_\infty - E_1 = 0 - (\text{IE}_H Z^2)$$

$$= Z^2 \times \text{I.E.}_H$$

For example, for He^+, Z = 2,

$\therefore$ I.E. = 4 × I.E._H

and for Li^{2+}, Z = 3, I.E. = 9 × I.E._H

In fact ionization energy of He^+ is the second ionization energy of He atom and ionization energy of Li^{2+} is the third ionization energy of Li atom.

PROBLEMS ON BOHR'S MODEL

EXAMPLE 1. *Calculate the wavelength of the radiation emitted when an electron in a hydrogen atom undergoes a transition from 4th energy level to the 2nd energy level. In which part of the electromagnetic spectrum does this line lie ?*

Solution. For hydrogen atom

$$E_n = -\frac{21\cdot8 \times 10^{-19}}{n^2}\ \text{J atom}^{-1}$$

Energy emitted when the electron jumps from $n = 4$ to $n = 2$ will be given by

$$\Delta E = E_4 - E_2$$

$$= 21\cdot8 \times 10^{-19}\left(\frac{1}{2^2} - \frac{1}{4^2}\right)$$

$$= 21\cdot8 \times 10^{-19} \times \frac{3}{16} = 4\cdot0875 \times 10^{-19}\ \text{J}$$

The wavelength corresponding to this energy can be calculated using the expression

$$E = h\nu = h\cdot\frac{c}{\lambda} \qquad (\because\ c = \nu\lambda)$$

so that $\lambda = \dfrac{hc}{E}$

$$= \frac{(6\cdot626 \times 10^{-34}\text{J sec})\,(3 \times 10^8\ \text{m sec}^{-1})}{(4\cdot0875 \times 10^{-19}\ \text{J})}$$

$$= 4\cdot863 \times 10^{-7}\ \text{m} = 4863\ \text{Å (or 486.3 nm)}$$

It lies in the visible region.

EXAMPLE 2. *How much energy is required to ionise a hydrogen atom if the electron occupies fifth orbit ? Compare your answer with the ionisation energy of hydrogen atom i.e. the energy required to remove the electron from first orbit.* **(N.C.E.R.T.)**

Solution. $E_n = -\dfrac{21\cdot8 \times 10^{-19}}{n^2}$ J atom^{-1}

For ionization from 5th orbit, $n_1 = 5, n_2 = \infty$

$$\therefore \Delta E = E_2 - E_1 = -21\cdot8 \times 10^{-19}\left(\frac{1}{n_2^2} - \frac{1}{n_1^2}\right)$$

$$= 21\cdot8 \times 10^{-19}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

$$= 21\cdot8 \times 10^{-19}\left(\frac{1}{5^2} - \frac{1}{\infty}\right)$$

$$= \mathbf{8\cdot72 \times 10^{-20}\ J}$$

For ionization from 1st orbit, $n_1 = 1, n_2 = \infty$

$$\Delta E = 21\cdot8 \times 10^{-19}\left(\frac{1}{1^2} - \frac{1}{\infty}\right)$$

$$= \mathbf{21\cdot8 \times 10^{-19}\ J}$$

EXAMPLE 3. *Calculate the velocity of electron in the first Bohr orbit of hydrogen atom. Given that Bohr radius = 0·529 Å,*

Planck's constant, h = 6·626 × 10^{-34} Js,

mass of electron = 9·11 × 10^{-31} kg and

1 J = 1 kg m^{2}s^{-2}

Solution. $m\,v\,r = \dfrac{nh}{2\pi}$ or $v = \dfrac{nh}{2\pi mr}$

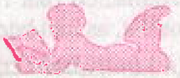
$$= \frac{(1)\,(6\cdot626 \times 10^{-34}\ \text{Js})}{2 \times 3\cdot14 \times (9\cdot11 \times 10^{-31}\ \text{kg}) \times (0\cdot529 \times 10^{-10}\ m)}$$

$$= 2\cdot188 \times 10^6\ \text{Js kg}^{-1}\ m^{-1}$$

But $1\ \text{J} = 1\ \text{kg}\ m^2\ s^{-2}$*

Hence $v = \mathbf{2\cdot189 \times 10^6\ ms^{-1}}$

PROBLEMS FOR PRACTICE



1. If the energy difference between two electronic states is 214·68 kJ mol^{-1}, calculate the frequency of light emitted when an electron drops from the higher to the lower state. Planck's constant, h=39·79 × 10^{-14} kJ sec mol^{-1}.
[Ans. 5·395 × 10^{14} sec^{-1}]

2. In hydrogen atom, an electron jumps from 3rd orbit to the 2nd orbit. Calculate the wavelength of the radiation emitted. (h = 6·63 × 10^{-34} J sec).
[Ans. 6564 Å]

3. The energy associated with the first orbit in the hydrogen atom is – 2·17 × 10^{-18} J atom^{-1}. What is the energy associated with the fifth orbit ?
(N.C.E.R.T.) [Ans. –8·72 × 10^{-20} J]

4. Calculate the wave number for the longest wavelength transition in the Balmer series of atomic hydrogen. *(N.C.E.R.T.)* [Ans. 1·523 × 10^6 m^{-1}]

5. The electron energy in hydrogen atom is given by $E_n = (-2\cdot18 \times 10^{-18})/n^2$ J. Calculate the energy required to remove the electron completely from n = 2 orbit. What is the longest wavelength of light in cm that can be used to cause this transition ?
(N.C.E.R.T.) Ans. 5·45 × 10^{-19} J, 3·647 × 10^{-5} cm]

6. What is the energy in joules required to shift the electron of the hydrogen atom from the first Bohr orbit to the fifth Bohr orbit and what is the wavelength of the light emitted when the electron returns to the ground state ? The ground state electron energy is – 2·18 × 10^{-11} ergs.
(N.C.E.R.T.) [Ans. 2·09 × 10^{-11} ergs, 951 Å]

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*1 J = work done = Force × Distance

= (Mass × Acceleration) × Distance = (kg ms^{-2}) × m = kg $m^2 s^{-2}$

HINTS FOR DIFFICULT PROBLEMS

1. $\Delta E = h\nu$ *i.e.* $(214 \cdot 68 \text{ kJ mol}^{-1})$

$$= (39 \cdot 79 \times 10^{-14} \text{ kJ sec mol}^{-1})\,\nu$$

or $\nu = 5 \cdot 395 \times 10^{14}\, s^{-1}$

2. $E_n = -\dfrac{21 \cdot 8 \times 10^{-19}}{n^2}$ J atom^{-1}

$$\Delta E = E_3 - E_2 = 21 \cdot 8 \times 10^{-19}\left(\frac{1}{2^2} - \frac{1}{3^2}\right)$$

$$= 3 \cdot 03 \times 10^{-19} \text{ J}$$

$$\Delta E = h\nu = h\frac{c}{\lambda}$$

$$\lambda = \frac{hc}{\Delta E} = \frac{(6 \cdot 63 \times 10^{-34} \text{ Js})(3 \times 10^8\, ms^{-1})}{(3 \cdot 03 \times 10^{-19} \text{ J})}$$

$$= 6 \cdot 564 \times 10^{-7}\, m = 6564 \times 10^{-10}\, m = 6564 \text{ Å}$$

3. $E_n = -\dfrac{2 \cdot 17 \times 10^{-18}}{n^2}$ J

$$\therefore\ E_5 = -\frac{2 \cdot 17 \times 10^{-18}}{5^2} = -8 \cdot 72 \times 10^{-20} \text{ J.}$$

4. For Balmer series,

$$\bar{\nu} = 109,677\left(\frac{1}{2^2} - \frac{1}{n^2}\right) \text{ cm}$$

λ will be maximum or $\bar{\nu}$ is minimum $\left(\bar{\nu} = \dfrac{1}{\lambda}\right)$

for $n = 3$. The value will be

$$\bar{\nu} = 109,677 \text{ cm}^{-1}\left(\frac{1}{2^2} - \frac{1}{3^2}\right)$$

$$= 109,677 \times \frac{5}{36} \text{ cm}^{-1}$$

$$= 15232 \cdot 9 \text{ cm}^{-1} = 1 \cdot 523 \times 10^6\, m^{-1}.$$

5. $\Delta E = E_\infty - E_2$

$$= 0 - \left(\frac{2 \cdot 18 \times 10^{-18} \text{ J atom}^{-1}}{2^2}\right)$$

$$= 5 \cdot 45 \times 10^{-19} \text{ J atom}^{-1}$$

$$\Delta E = h\nu = h\frac{c}{\lambda}$$

$$\text{or } \lambda = \frac{hc}{\Delta E}$$

$$= \frac{(6 \cdot 626 \times 10^{-34} \text{ Js}) \times (3 \times 10^8 \text{ ms}^{-1})}{5 \cdot 45 \times 10^{-19} \text{ J}}$$

$$= 3 \cdot 647 \times 10^{-7}\, m$$

$$= 3 \cdot 647 \times 10^{-5} \text{ cm.}$$

6. $\Delta E = E_5 - E_1 = 2 \cdot 18 \times 10^{-11}\left(\dfrac{1}{1^2} - \dfrac{1}{5^2}\right)$

$$= 2 \cdot 18 \times 10^{-11}\left(\frac{24}{25}\right) = 2 \cdot 09 \times 10^{-11} \text{ ergs}$$

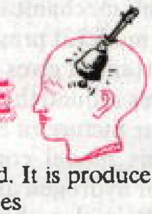
When electron returns to ground state (*i.e.* to $n=1$), energy emitted $= 2 \cdot 09 \times 10^{-11}$ ergs.

As $E = h\nu = h\dfrac{c}{\lambda}$ or $\lambda = \dfrac{hc}{E}$

$$= \frac{(6 \cdot 626 \times 10^{-27} \text{ erg sec})(3 \times 10^{10} \text{ cm } s^{-1})}{2 \cdot 09 \times 10^{-11} \text{ ergs}}$$

$$= 9 \cdot 51 \times 10^{-6} \text{ cm} = 951 \times 10^{-8} \text{ cm} = 951 \text{ Å}$$

ADD TO YOUR KNOWLEDGE



1. **Humphrey series.** This is another series of spectral lines which has been reported. It is produced when the electron in the hydrogen atom jumps from outer shells to 6th shell *i.e.* for these lines

$$\bar{\nu} = R\left(\frac{1}{6^2} - \frac{1}{n_2^2}\right) \text{ where } n_2 = 7, 8, 9 \ldots$$

These lines lie in the far infrared region.

2. The number of spectral lines produced when the electron from the nth shell jumps to the ground state (due to all possible jumps) $= \dfrac{n(n-1)}{2}$. When an electron returns from n_2 to n_1 energy level, number of spectral lines produced $= \dfrac{(n_2 - n_1)(n_2 - n_1 + 1)}{2}$.

3. Bohr's model of circular orbits was extended by Sommerfeld by introducing the concept of elliptical orbits. This helped to explain the fine lines of the atomic spectra.

4. In any spectral series of the hydrogen spectrum, the intensity of line decreases as n_2 increases.

ADD TO YOUR KNOWLEDGE CONTD.

5. The radius of the first Bohr's orbit is 0·529 Å (52·9 pm).

The radius of *n*th orbit of H-atom *i.e.* $r_n = 0\cdot529 \times n^2$ (Å). Putting $n = 1, 2, 3, 4$ and 5 the radii of the first five orbits of H-atom are given below :

Orbit (n)	1	2	3	4	5
Radius (Å)	0·529	2·116	4·761	8·464	13·225

Similarly, for H-like particles (*e.g.* He^+, Li^{2+} etc.), $r_n = \dfrac{0\cdot529 \times n^2}{Z}$ Å.

6. Velocity of an electron in any orbit of the H-like particle is related to the radius of the orbit as

$$v = \sqrt{\frac{Ze^2}{m\,r}} \quad i.e.\ v \propto \frac{1}{\sqrt{r}}$$

[From eqn. (*i*), page 3/61]

7. Balmer series contains four important lines whose wavelengths are 6563 Å, 4862 Å, 4341 Å and 4102 Å. These are respectively called H_α, H_β, H_γ and H_δ lines. They are obtained as a result of jump from $n = 3, 4, 5$ and 6 respectively to $n = 2$.

8. Bohr was awarded Nobel prize in Physics in 1922.

SECTION—III

MODERN CONCEPT OF STRUCTURE OF ATOM

3.16. Introduction

Though Bohr's model could explain the line spectra of hydrogen and hydrogen like particles and also the drawback of Rutherford's model, it suffered a serious blow with the advent of de Broglie concept of dual character of electrons and Heisenberg's uncertainty principle. Hence a new model of atom, called the 'Wave mechanical model' or 'Quantum mechanical model' has been put forward. This model at present is considered to be the most important. It gives a detailed arrangement of the electrons around the nucleus. In other words, it gives a clear picture of the 'electronic structure of atoms'. This model could explain fully the line spectrum of hydrogen as well as those of the other elements. It is also able to explain the chemical behaviour or characteristics of the atoms.

Just as Bohr model of atom was developed on the basis of Planck's quantum theory, the wave-mechanical model of atom has been developed on the basis of a new branch of science called **Quantum mechanics.*** It takes into account the *de Broglie concept of dual character of electron* (put forward in 1924) and *Heisenberg's uncertainty principle* (put forward in 1927) which are briefly described below :

(1) de Broglie concept of dual nature of matter. Einstein in 1905 suggested that light has wave character as well particle character *i.e.* it has dual nature. de Broglie in 1924 extended this idea to all material particles (electrons, protons, atoms etc.) and suggested that *all material particles in motion have dual character.* He derived that if any particle of mass '*m*' is moving with a velocity *v*, the wavelength associated with the moving particle is given by

$$\lambda = \frac{h}{mv} = \frac{h}{p}$$

where *h* is Planck's constant and $mv = p$ is the momentum of the particle. This relation is known as *de Broglie relation.*

(2) Heisenberg uncertainty principle. As a consequence of the dual nature of matter and radiation, Werner Heisenberg in 1927 stated that *it is impossible to determine simultaneously the exact position and exact velocity of a microscopic particle.* This is due to the fact that to locate the position of the electron, we have to use light so that photon of light hits the electron and the reflected photon is seen in the microscope. However, as a result of hitting, the position as well as velocity of the electron are disturbed. If we attempt to measure position with greater accuracy (by using light of shorter wavelength), the uncertainty in velocity (or momentum) increases and vice-versa. If Δx is the

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* For more details, read matter given in the shaded background on page 3/34 and 3/35.

uncertainty in position and Δp is the uncertainty in momentum, their product is always constant and equal to $h/4\pi$. Thus $\Delta x \times \Delta p = h/4\pi$

In the light of uncertainty principle, Bohr model of atom postulating that electrons move along definite circular paths and hence their position and momentum could be determined with absolute accuracy became unacceptable. Now we can speak of only in terms of '*probability*' of finding the electron at any particular position about the nucleus at any instant of time.

Keeping in view the wave nature of electron and the uncertainty principle, the movement of the electron around the nucleus is like that of a bee around the hive. Sometimes it may come close to the nucleus and sometimes it may move away from it. Further it does not move in one plane (as wrongly postulated by Bohr) but moves in all directions and in all planes around the nucleus.

The concept of '*probability*' may be understood with the help of the following simple examples :

(*i*) Suppose on a particular day, there are clouds in the sky. We predict that there is a *chance* that it may rain. However, there is no certainty that it would definitely rain because the clouds may disappear. This is expressed by saying that there is a probability of rainfall.

(*ii*) In a game of chess, a better player has a *chance* to win but one cannot say with certainty that he will definitely win. Thus a better player has a probability to win.

(*iii*) A brilliant student has a chance to qualify any entrance test but one cannot say with certainty that he/she will definitely qualify. Thus a brilliant student has a probability to qualify the entrance test.

Probability provides the best possible description of a situation which cannot be described with certainty.

To clarify the concept of electron probability, it is helpful to do a hypothetical experiment in which we take a set of pictures of a particular electron, say the only electron of hydrogen atom, at very very short intervals of time (say almost instantaneously). If the electron in each picture is represented by a small dot and if all the pictures are super-imposed then the final picture looks like the one given in Fig. 3.24.

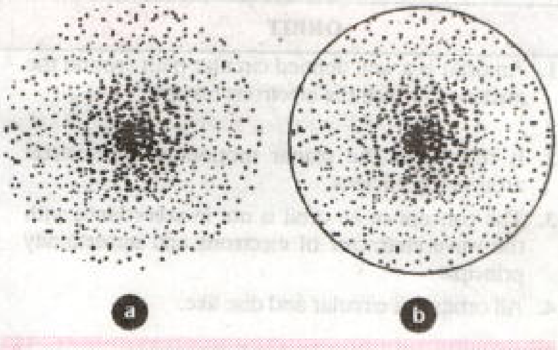

FIGURE 3.24. (a) Electron cloud for the only electron of the hydrogen atom (b) Boundary surface for maximum probability density.

It is clear from the picture that most of the dots lie at a certain distance from the nucleus on all sides. Since the probability of finding an electron is directly proportional to the intensity of dots, therefore, the electron spends most of its time in the volume of sphere bounded by that distance and for rest of the time, the electron can be found outside the volume of this sphere.

The region of space around the nucleus which describes the probability of finding an electron of given energy in terms of dots is called an electron cloud.

Nowhere is the probability of finding an electron equal to zero. Even at very large distance from the nucleus, there is a finite, though small, probability of finding an electron of a given energy. This means that electron clouds do not have sharp boundaries. However, for sake of pictorical clarity and for convenience of representation, a boundary surface may be drawn which connects points of equal probability and encloses a certain volume of the space around nucleus within which the probability of finding an electron of given energy is maximum, say upto 90%. This is called an atomic orbital.

An atomic orbital may be defined as the three dimensional space around the nucleus within which the probability of finding an electron of given energy is maximum (say upto 90%).

Difference between Orbit and Orbital. Some important points of difference between orbit and orbital are given below :

ORBIT	ORBITAL
1. An orbit is a well defined circular path around the nucleus in which the electrons revolve.	1. An orbital is the three dimensional space around the nucleus within which the probability of finding an electron is maximum (upto 90%).
2. It represents the planar motion of an electron around the nucleus.	2. It represents the three dimensional motion of an electron around the nucleus.
3. The concept of an orbit is not in accordance with the wave character of electrons and uncertainity principle.	3. The concept of an orbital is in accordance with the wave character of electrons and uncertainty principle.
4. All orbits are circular and disc like.	4. Different orbitals have different shapes. i.e. s-orbitals are spherically symmetrical, p-orbitals are dumbell shaped and so on.
5. Orbits do not have any directional characteristics.	5. All orbitals except s-orbitals have directional characteristics.
6. The maximum number of electrons in any orbit is given by $2n^2$ where n is the number of the orbit.	6. The maximum number of electrons present in any orbital is two.

Quantum Mechanics. Classical mechanics, based on Newton's laws of motion, was successful in explaining the motion of macroscopic bodies like falling stones or motion of planets around the sun etc. but it failed when applied to microscopic particles like electrons, atoms, molecules etc. This was mainly because it did not take into account the concept of dual nature of matter and Heisenberg's uncertainty principle. Hence a new branch of science which takes dual nature of matter into consideration has been put forward. This is known as 'Quantum mechanics'.

Quantum mechanics, as developed by Erwin Schrodinger in 1926, is based on the wave motion associated with the particles. For the wave motion of the electron in the three dimensional space around the nucleus, he put forward the following equation, known after his name as Schrodinger wave equation, which is considered as the heart of quantum mechanics :

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} + \frac{8\pi^2 m}{h^2}(E - V)\psi = 0$$

where ψ is the amplitude of the wave where the co- ordinates of the electron are (x, y, z), E is the total energy of the electron, V is its potential energy, m is the mass of the electron and h is Planck's constant. $\partial^2 \psi / dx^2$ represents second derivative of ψ w.r.t. x and so on.

In short, Schrodinger wave equation is written as $\hat{H}\psi = E\psi$ where $\hat{H}$ is a mathematical operator, called Hamiltonian operator.

The solution of Schrodinger wave equation for an electron in an atom gives the values of E and ψ. The values of E represent the quantized values of energy which the electrons in the atom can have. The corresponding values of ψ are called wave functions*. The wave function ψ for an electron in an atom has no physical significance as such. However, just as in case of light or sound, the square of the amplitude of the wave at any point gives the intensity of the sound or light at that point, similarly the square of the amplitude of the electron wave *i.e.* ψ^2 at any point gives the intensity of the electron wave at that point which in view of Heisenberg's uncertainty principle means **probability** of finding the electron at that point. Thus *ψ^2 at any point gives the probability of finding the electron at that point, i.e. electron density at that point.* Since the region around the nucleus which represents the electron density at different points is called an orbital, that is why the wave functon for an electron in an atom is called **orbital wave function** or simply **atomic orbital.** Since an electron can have many wave functions, therefore there are many atomic orbitals in an atom.

Important Features of the Quantum Mechanical Model of Atom. The basis of this model of atom is Quantum mechanics which in turn is

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*The values of E and ψ are called **eigen values and eigen functions.**

based on Schrodinger wave equation. The important features of this model are as follows :

1. The electrons in an atom have only quantized values of energy.

2. These quantized values of energy are obtained from the solution of Schrodinger wave equation. The corresponding values of the wave function ψ are also obtained from the solution of Schrodinger wave equation.

3. The wave function ψ is simply a function of coordinates of the electron and has no physical significance as such. However, ψ^2 gives the probability of finding the electron at that point *i.e.* electron density at that point. The concept of probability is justified in view of Heisenberg's uncertainty principle.

4. By finding ψ^2 at different points around the nucleus in an atom, we can predict the region of space around the nucleus within which the probability of finding the electron with a definite value of energy is maximum. This space around the nucleus is called **orbital.** That is wave function ψ is called *orbital wave function* or simply *atomic orbital.*

5. Since an electron can have many wave functions, therefore, there are many atomic orbitals in an atom.

6. The orbital wave function ψ contains all the information about an electron in an atom and quantum mechanics helps to extract this information.

PROBLEMS ON DE BROGLIE EQUATION

EXAMPLE 1. *Calculate the wavelength of an electron moving with velocity of 2·05 × 10⁷ ms⁻¹.* **(N.C.E.R.T.)**

Solution. By de Broglie equation

$$\lambda = \frac{h}{mv}$$

$$= \frac{6\cdot626 \times 10^{-34}\ \text{Js}}{(9\cdot11 \times 10^{-31}\ \text{kg})\ (2\cdot05 \times 10^{7}\ \text{ms}^{-1})}$$

$$= 3\cdot55 \times 10^{-11}\ m$$

$$(\text{J} = \text{kg}\ m^2\ s^{-2})$$

EXAMPLE 2. *The mass of an electron is $9\cdot1 \times 10^{-31}$ kg. If its K.E. is $3\cdot0 \times 10^{-25}$ J, calculate its wavelength.* **(N.C.E.R.T.)**

Solution. K.E. $= \frac{1}{2}mv^2$

$$\therefore\ v = \sqrt{\frac{2\,\text{K.E.}}{m}} = \sqrt{\frac{2 \times 3\cdot0 \times 10^{-25}\ \text{J}}{9\cdot1 \times 10^{-31}\ \text{kg}}}$$

$$= 812\ \text{ms}^{-1}$$

By de Broglie equation

$$\lambda = \frac{h}{mv} = \frac{6\cdot626 \times 10^{-34}\ \text{Js}}{(9\cdot1 \times 10^{-31}\ \text{kg})\ (812\ \text{ms}^{-1})}$$

$$= 8\cdot967 \times 10^{-7}\ \text{m} = \mathbf{8967\ Å.}$$

EXAMPLE 3. *Calculate the mass of a photon with wavelength 3·6 Å.* **(N.C.E.R.T.)**

Solution. Here, $\lambda = 3\cdot6\ \text{Å} = 3\cdot6 \times 10^{-10}\ m.$

As photon travels with the velocity of light, $v = 3\cdot0 \times 10^{8}\ \text{ms}^{-1}$

By de Broglie equation, $\lambda = \frac{h}{mv}$

or $m = \frac{h}{\lambda v}$

$$= \frac{6\cdot626 \times 10^{-34}\ \text{Js}}{(3\cdot6 \times 10^{-10}\ m)\ (3\cdot0 \times 10^{8}\ \text{ms}^{-1})}$$

$$= 6\cdot135 \times 10^{-29}\ \textbf{kg.}$$

PROBLEMS FOR PRACTICE

1. What will be the wavelength of a ball of mass 0·1 kg moving with a velocity of 10 ms⁻¹ ?

[Ans. $6\cdot626 \times 10^{-34}\ m$]

2. A moving electron has $4\cdot55 \times 10^{-25}$ Joules of kinetic energy. Calculate its wavelength (mass of electron = $9\cdot1 \times 10^{-31}$ kg and Planck's constant $h = 6\cdot6 \times 10^{-34}$ Js).

[Ans. $7\cdot25 \times 10^{-7}\ m$]

3. Calculate de Broglie wavelength of an electron that has been accelerated from rest through a potential difference of 1 kV.

[Ans. $3\cdot87 \times 10^{-11}\ m$]

HINTS FOR DIFFICULT PROBLEMS

3. K.E. of electron = 1000 eV = 1000 × ($1 \cdot 602 \times 10^{-19}$) J. Further proceed as in solved example 2 above.

3.17. Quantum Numbers

An atom contains a large number of orbitals. These are distinguished from each other on the basis of their *size, shape* and *orientation* (direction) in space. These parameters of an orbital are expressed in terms of three numbers, called *principal, azimuthal* and *magnetic quantum numbers*.* Further, to represent the spin (rotation) of the electron about its own axis, a fourth quantum number, called *spin quantum number* is introduced. Thus

Quantum numbers may be defined as a set of four numbers which give complete information about the electron in an atom i.e., energy, orbital occupied, size, shape and orientation of that orbital and the direction of electron spin.

These numbers are like the postal address of a person. To know about a particular person, Mr X, we should know about his country, his town, his lane and house number.

The various quantum numbers are briefly described below :

1. Principal Quantum Number. It is represented by 'n'. It gives the following information :–

(*i*) Approximate distance of the electron from the nucleus i.e. the size of the electron cloud.

(*ii*) Energy of the electron present in any shell**, *e.g.* for hydrogen atom,

$$E_n = \frac{-21 \cdot 8 \times 10^{-19}}{n^2} \text{ J atom}^{-1} = -\frac{1312}{n^2} \text{ kJ mol}^{-1},$$

(*iii*) Maximum number of electrons present in any shell (given by the formula $2n^2$).

This number helps to explain the main lines of the spectrum.

It can have values $n = 1, 2, 3, 4$........etc. which are called K, L, M, N.......etc. shells respectively.

2. Azimuthal (or Subsidiary or Angular momentum) Quantum Number. This number is represented by 'l'. It is found that the energy of an electron calculated from the value of n includes in itself some contribution due to angular momentum of the electron. As different electrons may have different angular momenta, the electrons within the same shell occupy different energy levels called sub-levels or sub-shells. The azimuthal quantum number gives the following information :

(*i*) Number of sub-shells present within any main shell

(*ii*) Contribution of energy due to angular momentum towards the total energy of the electron.

(*iii*) Relative energies of the sub-shells belonging to the same shell.

(*iv*) Shapes of the subshells.

(*v*) Orbital angular momentum which is equal to $\frac{h}{2\pi}\sqrt{l(l+1)}$

Note that orbital angular momentum depends only on the value of 'l' and not 'n'. Thus all s-orbitals ($l = 0$) *i.e.* 1s, 2s, 3s etc. have orbital angular momentum $= \sqrt{0(0+1)}\, h/2\pi = 0$. Similarly, all p-orbitals ($l = 1$) *i.e.* 2p, 3p, 4p etc. have orbital angular momentum $= \sqrt{1(1+1)}\, h/2\pi = \sqrt{2}\, h/\pi$ and so on.

This number helps to explain the fine lines of the spectrum because due to the presence of a large number of sub-levels, the number of probable transitions (jumps) of electrons becomes very large.

For a given value of n, l can have values from 0 to $n-1$. For example,

For $n = 1$, $l = 0$ i.e. only one value
For $n = 2$, $l = 0, 1$ i.e. two values
For $n = 3$, $l = 0, 1, 2$, i.e. three values
For $n = 4$, $l = 0, 1, 2, 3$, i.e. four values

Thus 1st, 2nd, 3rd, 4th shells have 1, 2, 3, and 4 sub-shells respectively. In general, nth shell has n sub-shells.

Further, these sub-shells are designated by the letters s, p, d and f for $l = 0, 1, 2$, and 3 respectively (derived from the first letter of the words *sharp, principal, diffused* and *fundamental* lines of the spectra)

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*These three quantum numbers follow from the solution of Schrodinger wave equation.

**As the electron clouds are three dimensional, the word 'shell' is now preferred over orbit or level.

Shell	Sub-shells present
1st (K)	1s
2nd (L)	2s, 2p
3rd (M)	3s, 3p, 3d
4th (N)	4s, 4p, 4d, 4f

(The prefix before the symbol of sub-shell represents value of *n*)

The number of sub-shells within the various main shells are shown in Fig. 3.25.

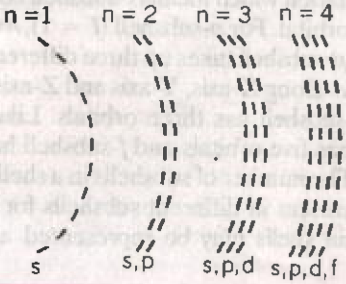


FIGURE 3.25. Sub-shells present in the main shells.

The energies of the different sub-shells present within the same main shell are found to be in the order s < p < d < f

Further, the electron cloud of 's' is found to be spherical while that of 'p' is found to be dumb-bell shaped. d and f have complex shapes.

3. Magnetic Quantum Number. This number is represented by '*m*' or 'm_l'. This number is required to explain the fact that when the source giving the line spectrum is placed in a magnetic field, each spectral line splits into a number of lines (Zeeman effect). This was obviously due to the fact that each subshell contains a number of orbitals which take up different orientations under the influence of the external magnetic field. The magnetic quantum number tells the number of orientations which the orbitals present within the same sub- shell can take up. In other words, *it tells the number of orbitals present within the same sub-shell* (as each orientation represents an orbital).

For a given value of *l*, *m* can have values from $-l$ to $+l$ including '0'. Thus

For s-sub-shell, $l = 0$. Hence $m = 0$ (only one value) i.e. s-sub-shell has only one orientation or has only one orbital.

For p-sub-shell, $l = 1$. Hence $m = -1, 0, +1$ (three values) i.e. p-sub-shell has three orbitals oriented along X-axis, Y-axis and Z-axis and represented by p_x, p_y and p_z respectively.

Similarly, for d-sub-shell, $l = 2$ so that $m = -2, -1, 0, +1, +2$ i.e. d-sub-shell contains five orbitals. For f- sub-shell, $l = 3$ so that $m = -3, -2, -1, 0, +1, +2, +3$ i.e. f-sub-shell has seven orbitals.

REMEMBER

Usually $m=0$ is taken for p_z orbial and $m = \pm 1$ for p_x and p_y orbitals. Similarly, $m = 0$ for d_{z^2} and -2 or $+2$ for $d_{x^2-y^2}$ and d_{xy} and -1 or $+1$ for d_{xz} and d_{yz}

4. Spin Quantum Number. It is represented by '*s*' or m_s. This number was introduced to account for the fact that the electron in an atom not only moves around the nucleus but also spins about its own axis (like the earth which not only revolves around the sun but also spins around its own axis) (Fig. 3.26). This number gives the information about the direction of spinning of the electron present in any orbital. Since the electron in an orbital can spin either in the clockwise direction or in the anti-clockwise direction, hence for a given value of *m*, *s* can have only two values i.e. + 1/2 and − 1/2 or these are very often represented by two arrows pointing in the opposite direction i.e. ↑ and ↓.

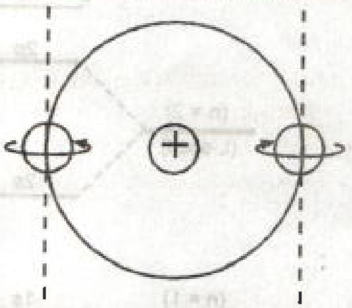


FIGURE 3.26. Spinning of electrons.

This quantum number helps to explain the magnetic properties of the substances. A spinning electron behaves like a micromagnet with a definite magnetic moment. If an orbital contains two electrons, the two magnetic moments oppose and cancel each other.

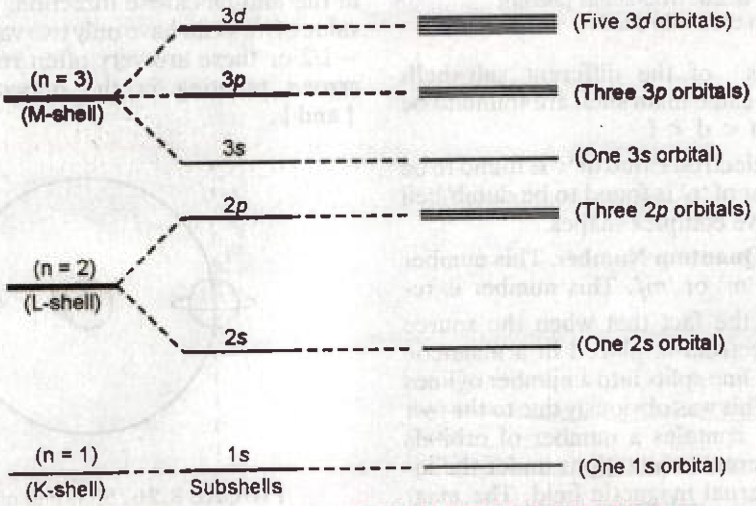
Thus in an atom, if all the orbitals are fully filled, net magnetic moment is zero ,and the substance is *diamagnetic* (i.e. repelled by the external magnetic field). However, if some half- filled orbitals are present, the substance has a net magnetic moment and is *paramagnetic* (i.e. attracted by the external magnetic field).

Idea of shells, subshells and orbitals. To sum up

Shell represents the main energy level occupied by the electron. It is given by the principal quantum number (n). For example, if $n = 1$, the electron is present in the first main shell, called K-shell. If $n = 2$, the electron is present in the second main shell, called L-shell and so on.

Subshell represents the sub-energy level occupied by the electron (as main energy level is considered to consist of a number of sublevels of energy). It is given by azimuthal quantum number (l). For a given value of n, $l = 0$ to $n - 1$. Thus for $n = 1$, $l = 0$ *i.e.* l has only one value which means that it does not have subshells. For $n = 2$, $l = 0, 1$ *i.e.* l has two values which means that it has two subshells. Similarly, 3rd shell has three subshells, 4th has four and so on. The subshells corresponding to $l = 0$, 1, 2 and 3 are represented by *s, p, d* and *f* respectively. Hence 1st main shell ($n = 1$) has only one subshell (1*s*), 2nd main shell ($n = 2$) has two subshells (2 *s*, 2 *p*), 3rd main shell ($n = 3$) has three subshells (3 *s*, 3 *p*, 3 *d*), 4th main shell has four subshells (4 *s*, 4 *p*, 4 *d*, 4 *f*).

Orbital represents the orientation which a subshell takes place under the influence of an external magnetic field. It is given by magnetic quantum number (m). For a given value of l, $m = -l$ to $+l$ including '0'. Thus for *s*-subshell ($l = 0$), $m = 0$ *i.e.* it has only one orientation which means *s*-subshell consists of only one orbital. For *p*-subshell ($l = 1$), $m = -1$, 0, $+1$ *i.e.* *p*-subshell takes up three different orientations (*i.e.* along X-axis, Y-axis and Z-axis) which means *p*-subshell has three orbitals. Likewise *d*-subshell has five orbitals and *f*-subshell has seven orbitals. The number of subshells in a shell and the orbitals present in different subshells for the first three main shells may be represented as shown below :



PROBLEMS ON QUANTUM NUMBERS

EXAMPLE 1. *An electron is in a 4f orbital. What possible values for the quantum numbers, n, l, m and s can it have ?*

Solution. Since the electron is in a 4f orbital, the value of the principal quantum number, $n = 4$.

For the f-orbital, the secondary quantum number, $l = 3$.

The values of the magnetic quantum (m) are $-l$ to $+l$ including zero. Therefore, when $l = 3$, m has seven values *i.e.* $-3, -2, -1, 0, +1, +2$ and 3.

For each value of m, the spin quantum number, s has two values, i.e., s = + 1/2 and s = − 1/2.

EXAMPLE 2. ● *Write down the quantum numbers n, l and m for the following orbitals :*

(*i*) $3\,d_{x^2-y^2}$ (*ii*) $4\,d_{z^2}$ (*iii*) $3\,d_{xy}$ (*iv*) $4\,d_{xz}$ (*v*) $2\,p_z$ (*vi*) $3\,p_x$

Solution. (*i*) $n = 3, l = 2, m = -2$ or $+2$

(*ii*) $n = 4, l = 2, m = 0$

(*iii*) $n = 3, l = 2, m = -2$ or $+2$

(*iv*) $n = 4, l = 2, m = -1$ or $+1$

(*v*) $n = 2, l = 1, m = 0$

(*vi*) $n = 3, l = 1, m = -1$ or $+1$

EXAMPLE 3. *What designation is given to an orbital having (i) $n = 2, l = 1$, (ii) $n = 3, l = 0$, (iii) $n = 5, l = 3$ and (iv) $n = 4, l = 2$?*

Solution. (*i*) $n = 2, l = 1$ means 2p-orbital

(*ii*) $n = 3, l = 0$ means 3s-orbital

(*iii*) $n = 5, l = 3$ means 5f-orbital

(*iv*) $n = 4, l = 2$ means 4d orbital.

EXAMPLE 4. *Which of the following sets of quantum numbers are not permitted ?*

(*i*) $n = 2, l = 2, m = -1, s = +1/2$

(*ii*) $n = 2, l = 1, m = -1, s = -1/2$

(*iii*) $n = 2, l = 0, m = 0, s = 0$

(*iv*) $n = 2, l = 1, m = 2, s = +1/2$

Solution. (*i*) This set of quantum numbers is not permitted since the value of l cannot be equal to n.

(*ii*) This set of quantum numbers is permitted.

(*iii*) This set of quantum numbers is not permitted because the value of spin quantum number cannot be zero.

(*iv*) This set of quantum numbers is also not permitted since the value of 'm' cannot be greater than 1.

EXAMPLE 5. *Which of the following orbitals are not possible ?*

1p, 2s, 3f and 4d.

Solution. (*i*) The first shell has only one subshell, i.e. 1s which has only one orbital, i.e, 1s orbital. Therefore 1p orbital is not possible.

(*ii*) The second sub-shell has two subshells, i.e. 2s and 2p. Therefore 2s orbitals are possible.

(*iii*) The third subshell has three subshells, i.e. 3s, 3p and 3d. Therefore, 3f-orbitals are not possible.

(*iv*) The fourth shell has four subshells, i.e. 4s, 4p, 4d and 4f. Therefore, 4d-orbitals are possible.

PROBLEMS FOR PRACTICE

1. If n is equal to 3, what are the values of quantum numbers l and m ?

   [**Ans.** $l = 0, 1, 2$ $m = -2, -1, 0, +1, +2$ **and** $s = +1/2$ **and** $-1/2$ **for each value of** m]

2. If the quantum number 'l' has a value of 2, what are the permitted values of the quantum number 'm. ?

   [**Ans.** $-2, -1, 0, +1, +2$]

3. List the quantum numbers (l and m_l) of electrons for 3d orbital ? (*N.C.E.R.T.*)

   [**Ans.** $n = 3, l = 2, m = -2, -1, 0, +1, +2$ **and** $s = +1/2$ **and** $-1/2$ **for each value of** m]

4. What are the values of n, l and m for 2p-orbitals ?

   [**Ans. For all 2p-electrons,** $n = 2$ **and** $l = 1$**, but** m **can have any one of three values** ***i.e.*** -1**, 0 and** $+1$]

5. Write the correct orbital notations for each of the following sets of quantum numbers :

   (*i*) $n = 1, l = 0, m = 0$; (*ii*) $n = 2, l = 1, m = -1$; and (*iii*) $n = 3, l = 2, m = +1$

   [**Ans.** (*i*) **1s** (*ii*) **2p** ($2p_x$ **or** $2p_y$) (*iii*) **3d**]

6. Give the values of the quantum numbers for the electron with the highest energy in sodium atom.

   [**Ans.** $n = 3, l = 0, m = 0$ **and** $s = +1/2$ **or** $-1/2$]

7. Which of the following orbitals are not possible?

   1p, 2s, 2p and 3f.

   [**Ans. 1p and 3f**]

8. Which of the following sets of quantum numbers are not possible ?

   (*i*) $n = 3, l = 2, m = 0, s = -1/2$

   (*ii*) $n = 3, l = 2, m = -2, s = -1/2$

   (*iii*) $n = 3, l = 3, m = -3, s = +1/2$

   (*iv*) $n = 3, l = 1, m = 0, s = +1/2$

   [**Ans.** (*iii*)]

$n = 3$
$l = 2$

HINTS FOR DIFFICULT PROBLEMS

6. Electronic configuration of $_{11}Na = 1s^2\ 2s^2\ 2p^6\ 3s^1$.

   The electron with highest energy is $3s^1$ for which $n = 3, l = 0$.

8. (*iii*) is not possible because if

   $n = 3, l = 0, 1, 2.$

0 1 2 3
s p d f

0 1

-2 -1 0 1 2

3.18. Pauli Exclusion Principle

From a study of the quantum numbers, *Wolfgang Pauli*, a German physicist in 1925 put forward a principle known after his name as Pauli exclusion principle. It states that :

No two electrons in an atom can have the same set of four quantum numbers.

If one electron in an atom has some particular values for the four quantum numbers, then all the other electrons in that atom are excluded from having the same set of values. It is because of this reason that this principle is called exclusion principle. Thus, it follows from the above discussion that in an atom, any two electrons may have the same values for any of the three quantum numbers but the fourth must be different.

Now, any particular orbital is described by three quantum numbers *i.e.*, n, l and m. For example, 3s-orbital has $n = 3, l = 0$ and $m = 0$. Since for each value of m, there are two values of the spin quantum number, i.e., + 1/2 and − 1/2, therefore, 3s-orbital can have two electrons; one with quantum numbers, $n = 3, l = 0, m = 0$ and $s = +1/2$ and the other with quantum numbers, $n = 3, l = 0$, $m = 0$ and $s = -1/2$. Similarly, any given orbital can have two and not more than two electrons. This gives us another definition of Pauli's exclusion principle which states that

An orbital can have a maximum two electrons and these must have opposite spins.

On the basis of a study of quantum numbers and Pauli exclusion principle, the maximum number of electrons that can be accommodated in any subshell or shell can be calculated. This is illustrated in Table 3.3. for the first four shells, namely, K, L, M and N i.e. for $n = 1, 2, 3, 4$.

TABLE 3.3. Calculation of maximum number of electrons that can be accommodated in a shell, its sub-shells and orbitals

Shell	Principal Quantum No. (n)	Azimuthal Quantum No. (subshell and its designation) (l)	Magnetic Quantum No. (Orbitals) (m)	Spin Quantum No. (s)	Electrons present	Total No. of electrons
K	1	0 (1s)	0	$+\frac{1}{2}, -\frac{1}{2}$	2	2
L	2	0 (2s)	0	$+\frac{1}{2}, -\frac{1}{2}$	2	8
		1 (2p)	−1	$+\frac{1}{2}, -\frac{1}{2}$	6	
			0	$+\frac{1}{2}, -\frac{1}{2}$		
			+1	$+\frac{1}{2}, -\frac{1}{2}$		
M	3	0 (3s)	0	$+\frac{1}{2}, -\frac{1}{2}$	2	
		1 (3p)	−1	$+\frac{1}{2}, -\frac{1}{2}$	6	
			0	$+\frac{1}{2}, -\frac{1}{2}$		
			+ 1	$+\frac{1}{2}, -\frac{1}{2}$		

Contd. on next page...

		2 (3*d*)	−2	$+\frac{1}{2}, -\frac{1}{2}$	10	18
			−1	$+\frac{1}{2}, -\frac{1}{2}$		
			0	$+\frac{1}{2}, -\frac{1}{2}$		
			+ 1	$+\frac{1}{2}, -\frac{1}{2}$		
			+ 2	$+\frac{1}{2}, -\frac{1}{2}$		
N	4	0 (4*s*)	0	$+\frac{1}{2}, -\frac{1}{2}$	2	32
		1 (4*p*)	−1	$+\frac{1}{2}, -\frac{1}{2}$	6	
			0	$+\frac{1}{2}, -\frac{1}{2}$		
			+ 1	$+\frac{1}{2}, -\frac{1}{2}$		
		2 (4*d*)	−2	$+\frac{1}{2}, -\frac{1}{2}$	10	
			−1	$+\frac{1}{2}, -\frac{1}{2}$		
			0	$+\frac{1}{2}, -\frac{1}{2}$		
			+ 1	$+\frac{1}{2}, -\frac{1}{2}$		
			+ 2	$+\frac{1}{2}, -\frac{1}{2}$		
		3 (4*f*)	−3	$+\frac{1}{2}, \frac{1}{2}$	14	
			−2	$+\frac{1}{2}, -\frac{1}{2}$		
			−1	$+\frac{1}{2}, -\frac{1}{2}$		
			0	$+\frac{1}{2}, -\frac{1}{2}$		
			+1	$+\frac{1}{2}, -\frac{1}{2}$		
			+2	$+\frac{1}{2}, -\frac{1}{2}$		
			+3	$+\frac{1}{2}, -\frac{1}{2}$		

This it may be concluded that

No. of subshells in *n*th shell = *n*

No. of orbitals in a subshell = $2l + 1$,

Maximum no. of electrons in a subshell = $2(2l + 1)$.

No. of orbitals in *n*th shell = n^2

Maximum no. of electrons in *n*th shell = $2n^2$.

ADD TO YOUR KNOWLEDGE

1. Quantum numbers were discovered by different scientists as follows :
   Principal by Bohr, Azimuthal by Sommerfeld, Magnetic by Lande and Spin by Uhlenbeck and Goudsmith.
2. *Principal* quantum number tells about the *size* of the orbital, *azimuthal* quantum number tells about the *shape* of the orbital while *magnetic* quantum number tells about the number of *orientations* which the orbital takes up in the magnetic field or *the number of orbitals* present in a subshell.
3. Principal quantum number, *n* used by Bohr and azimuthal quantum number, *k* used by Sommerfeld (by introducing the concept of elliptical orbits) are related to each other as

$$\frac{n}{k} = \frac{\text{Length of the major axis of the elliptical orbit}}{\text{Length of the minor axis of the elliptical orbit}}$$

   When $k = n$, the orbit becomes circular. Further *k* cannot be zero because that means minor axis is zero which in turn implies linear motion of the electron passing through the nucleus.
4. The shape of an orbital is the boundary or contour surface diagram obtained by joining the points of equal probability (ψ^2) of the electron around the nucleus. In other words, it is the surface on which the probability density (ψ^2) is constant. Many such surfaces are possible but the one that encloses the region within which the probability of finding the electron is very high, say upto 90%, gives the shape and size of the orbital.
5. The surface on which ψ^2 is constant, ψ is also constant on that surface. Hence boundary surfaces for ψ^2 and ψ are identical.

3.19. Shapes of Orbitals

As already defined, an orbital is the region of space around the nucleus within which the probability of finding an electron of given energy is maximum (say 90%). The shape of the electron cloud thus obtained gives the shape of the orbital. The shapes of s and p-orbitals are briefly described below :

Shapes of s-orbitals. The probability of finding the electron belonging to s-orbital of any main shell is found to be identical in all directions at a given distance from the nucleus. Hence s- orbital is spherical in shape which is symmetrical around the nucleus (Fig. 3.27).

Alternatively, the shape of s-orbitals follows from the concept of quantum numbers as follows :

For s-orbital, azimuthal quantum number $l = 0$. Hence magnetic quantum number *m* is also equal to '0' (i.e. has only one value). Thus s-orbital has only one orientation. The only shape having one orientation is a sphere. Hence s-orbital is spherical in shape.

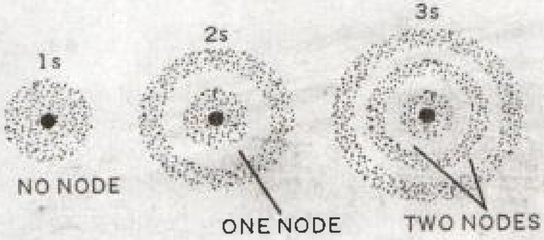


FIGURE 3.27. Shapes of 1s, 2s and 3s orbitals.

Although the s-orbitals belonging to different shells are spherically symmetrical, yet they differ in certain respects as explained below :

(*i*) The probability of 1s electron is found to be maximum near the nucleus and decreases as the distance from the nucleus increases. In case of 2s electrons, the probability is again maximum near the nucleus and then decreases to zero and increases again and then decreases as the distance from the nucleus increases. The intermediate region (a spherical shell) where the probability is zero is called a **nodal surface** or simply **node**. Thus 2s orbital differs from 1s orbital in having one node within it. Similarly, 3s has two nodes. In general, any ns orbital has $(n-1)$ nodes.

(ii) The size and energy of the s-orbital increases as the **principal quantum number** n increases *i.e.* the size and energy of s-orbital increases in the order $1s < 2s < 3s$....

Shapes of p-orbitals. On the basis of probability calculations, it is found that the probability of finding the p-electrons is maximum in two lobes on the opposite sides of the nucleus. This gives rise to a dumb-bell shape for the p-orbital (Fig. 3.28).

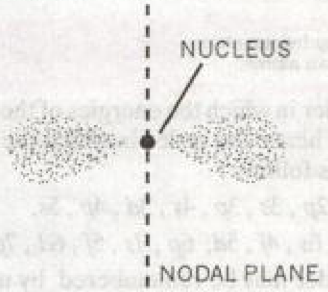


FIGURE 3.28. Shapes of p-orbital.

However, it may be noted that the probability of finding a particular p-electron is equal in both the lobes. Further, there is a plane passing through the nucleus on which the probability of finding the electron is almost zero. This is called a **nodal plane.**

Further, for p-orbital, $l = 1$. Hence $m = -1, 0, +1$. Thus p-orbitals have three different orientations. These are designated as p_x, p_y and p_z depending upon whether the electron density is maximum along the X-axis, Y-axis and Z-axis respectively (Fig. 3.29).

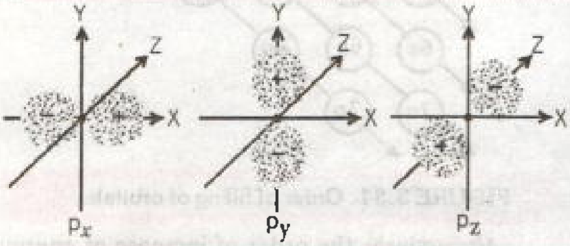


FIGURE 3.29. Different orientations of p–orbitals.

Thus unlike s-orbitals, p-orbitals have directional characteristics and hence are helpful in predicting the shapes of molecules. Further it may be mentioned that every energy level with n greater than 1 has three p-orbitals. As n increases, these p-orbitals become larger in size and have higher energies. However, the three p-orbitals belonging to a particular energy level have equal energies and are called *degenerate orbitals*. Further whereas $2p$ orbital has no node, $3p$ has one node, $4p$ has two nodes and so on. Thus, we may conclude that

Number of nodes in any orbital $= (n - l - 1)$.

Note. 1. The formula given above is for finding the number of **spherical/radial** nodes only. It is interesting to point out that whereas s-orbitals have spherical nodes only, p and d-orbitals have spherical as well as **planar nodes.** For example, $2p$ orbital has one nodal plane passing through the nucleus at the origin. Similarly d-orbitals have two nodal planes. The number of spherical nodes depends upon the value of n.

Thus the above results may be generalized as follows :

Number of spherical/radial nodes in any orbital $= n - l - 1$

Number of planar nodes in any orbital $= l$

$\therefore$ ***Total number of nodes in any orbital*** $= n - 1$.

2. Positive and negative signs shown inside the lobes of p-orbitals are for the wave function ψ and have nothing to do with the positive or negative charge. However, the probability density, ψ^2, is always positive.

3.20. Energy Level Diagrams of Hydrogen Atom and Multielectron Atoms

It has already been discussed that the different subshells of the same main shell have different energies. However this is true only in case of *multi-electron atoms* as shown in Fig. 3.30(b). In case of hydrogen or hydrogen-like particles (containing one electron only), they have the same energy as shown in Fig. 3.30(a). In other words, it may be concluded that *whereas energies of different orbitals of hydrogen and hydrogen like particles depend upon the value of principal quantum number (n) only, those of multielectron atoms depend both upon principal quantum number (n) as well as azimuthal quantum number (l).*

Such diagrams representing the arrangement of orbitals in order of their increasing energies are called Energy Level Diagrams.

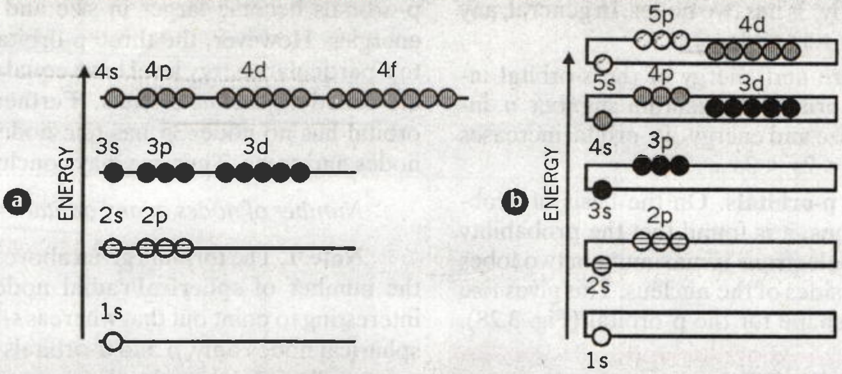


FIGURE 3.30. (a) Enegy level diagram for hydrogen atom.
(b) Energy level diagram for multielectron atoms.

Some important observations from energy level diagram of multielectron atoms may be made as follows :

(*i*) The subshells of a particular shell do not have equal energies *e.g.* 2*s* and 2*p* have different energies.

(*ii*) In a particular shell, subshell with lower value of *l* has lower energy. Thus in the second shell 2*s* ($l = 0$) has lower energy than 2*p* ($l = 1$). Similarly in the 3rd shell, energies are in the order $3s < 3p < 3d$ and in the 4th shell they are in the order $4s < 4p < 4d < 4f$.

(*iii*) For the same value of *n*, the difference between energies of *s* and *p*-subshells is small whereas between *p* and *d*-subshells, it is large and so on.

(*iv*) As the value of *n* increases, the subshell of lower shell may have higher energy than that of the higher shell *e.g.* 3 *d* has higher energy than 4 *s*.

Note. In case of H-atom, the energies of the orbitals are in the order $1s < 2s = 2p < 3s = 3p = 3d < 4s = 4p = 4d = 4f < ...$

3.21. Filling of Orbitals in Atoms

The filling of electrons into the orbitals of different atoms takes place according to the following three rules :

(1) **Aufbau Principle.** The word 'aufbau' in German means 'building up'. The building up of orbitals means the filling up of orbials with electrons. The principle states as follows :—

In the ground state of the atoms, the orbitals are filled in order of their increasing energies. In other words, electrons first occupy the lowest-energy orbital available to them and enter into higher energy orbitals only when the lower energy orbitals are filled.

The order in which the energies of the orbitals increase and hence the order in which the orbitals are filled is as follows :

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

This order may be remembered by using the method given in Fig. 3.31. Starting from the top, the direction of the arrows gives the order of filling of orbitals.

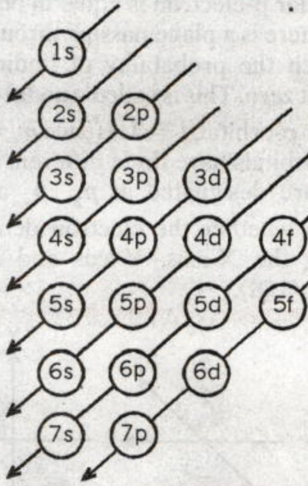


FIGURE 3.31. Order of filling of orbitals.

Alternatively, the order of increase of energy of orbitals can be calculated from **(*n* + *l*) rule.**

The energy of an orbital depends upon the values of principal quantum number, *n* and the azimuthal quantum number *l* (in the absence of an external magnetic field). The (*n* + *l*) rule states as follows :

Lower the value of (n+l) for an orbital, the lower is its energy. Hence orbitals are filled in order of increasing (n+l) values. If two orbitals have the same (n + l) value, the orbital with lower value of n has lower energy and hence is filled first.

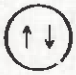
The following table illustrates the (n + *l*) rule:

Orbital	Value of n	Value of *l*	Value of (n + *l*)
1*s*	1	0	1 + 0 = 1
2*s*	2	0	2 + 0 = 2
2*p*	2	1	2 + 1 = 3 } 2*p* (*n*=2) has lower energy than 3*s* (*n* = 3)
3*s*	3	0	3 +0 = 3
3*p*	3	1	3 + 1 = 4 } 3*p* (n = 3) has lower energy than 4*s* (*n* = 4)
4*s*	4	0	4 +0 = 4
3*d*	3	2	3 + 2 = 5 } 3*d* (n = 3) has lower energy than 4*p*(*n* = 4).
4*p*	4	1	4 + 1 = 5

(2) Pauli Exclusion Principle. As already explained, Pauli exclusion principle states as follows:

An orbital can have maximum two electrons and these must have opposite spins.

If an orbital is represented by a circle and it contains two electrons, it is represented as



or

i.e. the two arrows must point in the opposite direction. The electrons are said to be paired or the orbital is said to be fully filled. It will be wrong to represent it as

or

If an orbital contains only one electron, it is represented as

or

and is said to be half-filled. The electron is said to be in an unpaired state.

(3) Hund's Rule of Maximum Multiplicity. This rule deals with the filling of electrons into the orbitals belonging to the same sub- shell (i.e. orbitals of equal energy, called *degenerate* orbitals). It states as under :—

The pairing of electrons in the orbitals belonging to the same sub-shell (p, d or f) does not take place until each orbital belonging to that sub-shell has got one electron each i.e. is singly occupied.

Since there are three p, five d and seven f orbitals, therefore the pairing of electrons will start in the p, d and f orbitals with the entry of 4th, 6th and 8th electron respectively.

The reason for such a tendency is quite obvious. The electrons are negatively charged and repel each other. Hence they spread out and occupy the identical orbitals singly before they begin to pair. As a result, the repulsions are minimum. Hence the energy is minimum and the stability is maximum. Pairing occurs because less energy is needed to do so than the energy required to place the electron in the next higher empty orbital.

Further, it is important to note that whenever orbitals are singly occupied as above, the electrons present in them have the spin in the same direction i.e. either all clockwise or all anticlockwise. This is because of the fact that such a state has lower energy and hence is more stable.

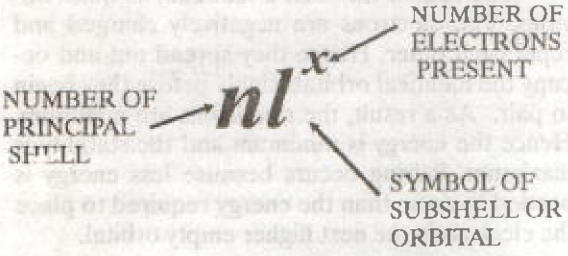
3.22. Electronic Configuration of Atoms

The distribution of electrons into different levels, sublevels and orbitals of an atom is called its electronic configuration.

Keeping in view the above rules, and representing an orbital by a circle and an electron and the direction of its spin by an arrow, the electronic configurations of the first 12 elements may be represented as follows :

Element	Atomic No. = No. of electrons	Electronic configuration 1s	2s	2p	3s
Hydrogen	1	(↑)			
Helium	2	(↑↓)			
Lithium	3	(↑↓)	(↑)		
Beryllium	4	(↑↓)	(↑↓)		
Boron	5	(↑↓)	(↑↓)	(↑) ( ) ( )	
Carbon	6	(↑↓)	(↑↓)	(↑) (↑) ( )	
Nitrogen	7	(↑↓)	(↑↓)	(↑) (↑) (↑)	
Oxygen	8	(↑↓)	(↑↓)	(↑↓) (↑) (↑)	
Fluorine	9	(↑↓)	(↑↓)	(↑↓) (↑↓) (↑)	
Neon	10	(↑↓)	(↑↓)	(↑↓) (↑↓) (↑↓)	
Sodium	11	(↑↓)	(↑↓)	(↑↓) (↑↓) (↑↓)	(↑)
Magnesium	12	(↑↓)	(↑↓)	(↑↓) (↑↓) (↑↓)	(↑↓)

The above method of writing the electronic configurations is quite cumbersome. Hence, usually the electronic configuration of the atom of any element is simply represented by the notation.



e.g. $1s^2$ means 2 electrons are present in the s-subshell of the 1st main shell.

To get the complete configuration of an atom, a number of such notations are written one after the other in order of increasing energies of the orbitals, starting always with the orbital of lowest energy *i.e.* 1s.

Using the above method of representation, the electronic configurations of the various elements are listed in Table 3.4 on page 3/48 to 3/49.

Some exceptional electronic configurations. Some elements such as chromium (At. No. 24), copper (At. No. 29) etc. possess electronic configurations different from those expected from the aufbau order. This is because of the *tendency of the sub-shells to be exactly half-filled or completely filled* .

To illustrate this point, a few examples are given below :–

Chromium (Atomic number = 24) :

Expected configuration :

$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^4\ 4s^2$

Actual configuration :

$1s^2\ 2s^2\ 2p^6\ 3p^6\ 3d^5\ 4s^1$

Copper (Atomic number = 29) :

Expected configuration :

$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^9\ 4s^2$

Actual configuration :

$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^1$

Molybdenum (Atomic number = 42)

Expected configuration :

$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^6\ 4d^4\ 5s^2$

Actual configuration :

$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^6\ 4d^5\ 5s^1$

Palladium (Atomic number = 46)

Expected configuration :

$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^6\ 4d^8\ 5s^2$

Actual configuration :

$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^6\ 4d^{10}\ 5s^0$

Thus generally only one electron jumps from lower orbital to higher energy orbital e.g. from 4s to 3d. However in case of palladium, two electrons are involved (the only case with a difference).

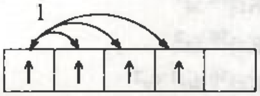
The reason for the tendency of the subshells to be completely filled or exactly half-filled is that it leads to **greater stability**.

Cause of greater stability of exactly half-filled and completely filled configurations. The greater stability of these configurations is due to the following two reasons :

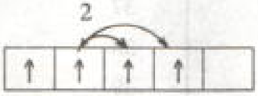
(*i*) **Symmetry.** The half-filled and completely filled configurations are more symmetrical and symmetry leads to greater stability.

(*ii*) **Exchange energy.** The electrons present in the different orbitals of the same subshell can exchange their positions. Each such exchange results in release of energy, called exchange energy and hence leads to a greater stability. As the number of exchanges that can take place is maximum in the exactly half-filled and completely filled arrangements (i.e. more in d^5 than in d^4 and more in d^{10} than in d^9), therefore exchange energy is maximum and hence the stability is maximum.

The number of exchanges that can take place in d^4 configuration are as follows :–



3 EXCHANGES BY
ELECTRON 1

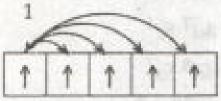


2 EXCHANGES BY
ELECTRON 2

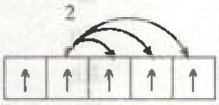
1 EXCHANGE BY
ELECTRON 3

Total number of exchanges = 3 + 2 + 1 = 6

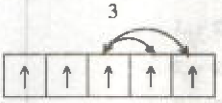
The number of exchanges that can take place in d^5 configuration are as follows :–



4 EXCHANGES BY
ELECTRON 1



3 EXCHANGES BY
ELECTRON 2



2 EXCHAGES BY
ELECTRON 3

1 EXCHANGE BY
ELECTRON 4

Total number of exchanges =4+3+2+1=10

Some important points in writing electronic configurations. While writing the electronic configurations, the following points may also be noted:

(*i*) To avoid the writing of electronic configurations in a lengthy way, usually the symbols $[He]^2$, $[Ne]^{10}$, $[Ar]^{18}$ etc. are used as the first part of the configuration. Such a symbol stands for the electronic configuration of that inert gas and is usually called the core of the inert gas.

(*ii*) Although the orbitals of lower energy are filled first but the electronic configuration are written not in the order in which the orbitals were filled but in the order of principal quantum numbers.

(*iii*) Unless otherwise mentioned, electronic configuration always means the electronic configuration in the ground state.

For elements with very high atomic numbers, some deviations are observed other than on account of half-filled and fully filled subshells. However, for our purposes, such exceptions are not important.

Utility/Importance of studying electronic configuration. In the end, a student may be curious to know as to why we study electronic configurations. It is important to know that according to modern approach, the chemical behaviour of all elements and compounds is explained on the basis of their electronic configuration *e.g.* why atoms combine to form molecules, why some elements are metals whereas others are non-metals or why some elements like alkali metals and halogens are highly reactive whereas noble gases like helium, neon, argon etc. are not etc.

TABLE 3.4. Electronic configurations of elements in the ground state

Atomic number	Element	Electronic Configuration
1	H	$1s^1$
2	He	$1s^2$
3	Li	$[He]^2\ 2s^1$
4	Be	$[He]^2\ 2s^2$
5	B	$[He]^2\ 2s^2\ 2p^1$
6	C	$[He]^2\ 2s^2\ 2p^2$
7	N	$[He]^2\ 2s^2\ 2p^3$
8	O	$[He]^2\ 2s^2\ 2p^4$
9	F	$[He]^2\ 2s^2\ 2p^5$
10	Ne	$[He]^2\ 2s^2\ 2p^6$ or $1s^2,\ 2s^2,\ 2p^6$
11	Na	$[Ne]^{10}\ 3s^1$
12	Mg	$[Ne]^{10}\ 3s^2$
13	Al	$[Ne]^{10}\ 3s^2\ 3p^1$
14	Si	$[Ne]^{10}\ 3s^2\ 3p^2$
15	P	$[Ne]^{10}\ 3s^2\ 3p^3$
16	S	$[Ne]^{10}\ 3s^2\ 3p^4$
17	Cl	$[Ne]^{10}\ 3s^2\ 3p^5$
18	Ar	$[Ne]^{10}\ 3s^2\ 3p^6$ or $1s^2\ 2s^2,\ 2p^6,\ 3s^2,\ 3p^6$
19	K	$[Ar]^{18}\ 4s^1$
20	Ca	$[Ar]^{18}\ 4s^2$
21	Sc	$[Ar]^{18}\ 3d^1\ 4s^2$
22	Ti	$[Ar]^{18}\ 3d^2\ 4s^2$
23	V	$[Ar]^{18}\ 3d^3\ 4s^2$
*24	Cr	$[Ar]^{18}\ 3d^5\ 4s^1$
25	Mn	$[Ar]^{18}\ 3d^5\ 4s^2$
26	Fe	$[Ar]^{18}\ 3d^6\ 4s^2$
27	Co	$[Ar]^{18}\ 3d^7\ 4s^2$
28	Ni	$[Ar]^{18}\ 3d^8\ 4s^2$
*29	Cu	$[Ar]^{18}\ 3d^{10}\ 4s^1$
30	Zn	$[Ar]^{18}\ 3d^{10}\ 4s^2$
31	Ga	$[Ar]^{18}\ 3d^{10}\ 4s^2\ 4p^1$
32	Ge	$[Ar]^{18}\ 3d^{10}\ 4s^2\ 4p^2$
33	As	$[Ar]^{18}\ 3d^{10}\ 4s^2\ 4p^3$
34	Se	$[Ar]^{18}\ 3d^{10}\ 4s^2\ 4p^4$
35	Br	$[Ar]^{18}\ 3d^{10}\ 4s^2\ 4p^5$
36	Kr	$[Ar]^{18}\ 3d^{10}\ 4s^2\ 4p^6$ or $1s^2,\ 2s^2 2p^6\ 3s^2\ 3p^6\ 3d^{10}$ $4s^2\ 4p^6$
37	Rb	$[Kr]^{36}\ 5s^1$
38	Sr	$[Kr]^{36}\ 5s^2$
39	Y	$[Kr]^{36}\ 4d^1\ 5s^2$
40	Zr	$[Kr]^{36}\ 4d^2\ 5s^2$
*41	Nb	$[Kr]^{36}\ 4d^4\ 5s^1$
*42	Mo	$[Kr]^{36}\ 4d^5\ 5s^1$
43	Tc	$[Kr]^{36}\ 4d^6\ 5s^2$
*44	Ru	$[Kr]^{36}\ 4d^7\ 5s^1$
*45	Rh	$[Kr]^{36}\ 4d^8\ 5s^1$
*46	Pd	$[Kr]^{36}\ 4d^{10}\ 5s^0$
*47	Ag	$[Kr]^{34}\ 4d^{10}\ 5s^1$
48	Cd	$[Kr]^{36}\ 4d^{10}\ 5s^2$
49	In	$[Kr]^{36}\ 4d^{10}\ 5s^2\ 5p^1$
50	Sn	$[Kr]^{36}\ 4d^{10}\ 5s^2\ 5p^2$
51	Sb	$[Kr]^{36}\ 4d^{10}\ 5s^2\ 5p^3$
52	Te	$[Kr]^{36}\ 4d^{10}\ 5s^2\ 5p^4$
53	I	$[Kr]^{36}\ 4d^{10}\ 5s^2\ 5p^5$
54	Xe	$[Kr]^{36}\ 4d^{10}\ 5s^2\ 5p^6$ or $1s^2,\ 2s^2 2p^6,\ 3s^2\ 3p^6\ 3d^{10},$ $4s^2\ 4p^6\ 4d^{10},\ 5s^2\ 5p^6$
55	Cs	$[Xe]^{54}\ 6s^1$
56	Ba	$[Xe]^{54}\ 6s^2$
*57	La	$[Xe]^{54}\ 5d^1\ 6s^2$
*58	Ce	$[Xe]^{54}\ 4f^1\ 5d^1\ 6s^2$
59	Pr	$[Xe]^{54}\ 4f^3\ 5d^0\ 6s^2$
60	Nd	$[Xe]^{54}\ 4f^4\ 6s^2$
61	Pm	$[Xe]^{54}\ 4f^5\ 6s^2$
62	Sm	$[Xe]^{54}\ 4f^6\ 6s^2$

*Elements with exceptional electronic configurations.

Atomic number	Element	Electronic Configuration
63	Eu	$[Xe]^{54}\, 4f^{7}\, 6s^{2}$
*64	Gd	$[Xe]^{54}\, 4f^{7}\, 5d^{1}\, 6s^{2}$
65	Tb	$[Xe]^{54}\, 4f^{9}\, 6s^{2}$
66	Dy	$[Xe]^{54}\, 4f^{10}\, 6s^{2}$
67	Ho	$[Xe]^{54}\, 4f^{11}\, 6s^{2}$
68	Er	$[Xe]^{54}\, 4f^{12}\, 6s$
69	Tm	$[Xe]^{54}\, 4f^{13}\, 6s^{2}$
70	Yb	$[Xe]^{54}\, 4f^{14}\, 6s^{2}$
71	Lu	$[Xe]^{54}\, 4f^{14}\, 5d^{1}\, 6s^{2}$
72	Hf	$[Xe]^{54}\, 4f^{14}\, 5d^{2}\, 6s^{2}$
73	Ta	$[Xe]^{54}\, 4f^{14}\, 5d^{3}\, 6s^{2}$
74	W	$[Xe]^{54}\, 4f^{14}\, 5d^{4}\, 6s^{2}$
75	Re	$[He]^{54}\, 4f^{14}\, 5d^{5}\, 6s^{2}$
76	Os	$[Xe]^{54}\, 4f^{14}\, 5d^{6}\, 6s^{2}$
77	Ir	$[Xe]^{54}\, 4f^{14}\, 5d^{7}\, 6s^{2}$
*78	Pt	$[Xe]^{54}\, 4f^{14}\, 5d^{9}\, 6s^{1}$
✓*79	Au	$[Xe]^{54}\, 4f^{14}\, 5d^{10}\, 6s^{1}$
80	Hg	$[Xe]^{54}\, 4f^{14}\, 5d^{10}\, 6s^{2}$
81	Tl	$[Xe]^{54}\, 4f^{14}\, 5d^{10}\, 6s^{2}\, 6p^{1}$
82	Pb	$[Xe]^{54}\, 4f^{14}\, 5d^{10}\, 6s^{2}\, 6p^{2}$
83	Bi	$[Xe]^{54}\, 4f^{14}\, 5d^{10}\, 6s^{2}\, 6p^{3}$
84	Po	$[Xe]^{54}\, 4f^{14}\, 5d^{10}\, 6s^{2}\, 6p^{4}$
85	At	$[Xe]^{54}\, 4f^{14}\, 5d^{10}\, 6s^{2}\, 6p^{5}$
86	Rn	$[Xe]^{54}\, 4f^{14}\, 5d^{10}\, 6s^{2}\, 6p^{6}$, or $1s^{2}, 2s^{2}\, 2p^{6}, 3s^{2}\, 3p^{6}\, 3d^{10}$ $4s^{2}\, 4p^{6}\, 4d^{10}\, 4f^{14}, 5s^{2}$ $5p^{6}\, 5d^{10}, 6s^{2}\, 6p^{6}$
87	Fr	$[Rn]^{86}\, 7s^{1}$
88	Ra	$[Rn]^{86}\, 7s^{2}$
*89	Ac	$[Rn]^{86}\, 6d^{1}\, 7s^{2}$
90	Th	$[Rn]^{86}\, 5f^{2}\, 6d^{0}\, 7s^{2}$
*91	Pa	$[Rn]^{86}\, 5f^{2}\, 6d^{1}\, 7s^{2}$
*92	U	$[Rn]^{86}\, 5f^{3}\, 6d^{1}\, 7s^{2}$
*93	Np	$[Rn]^{86}\, 5f^{4}\, 6d^{1}\, 7s^{2}$
94	Pu	$[Rn]^{86}\, 5f^{6}\, 7s^{2}$

Atomic Number	Element	Electronic Configuration
95	Am	$[Rn]^{86}\, 5f^{7}\, 7s^{2}$
*96	Cm	$[Rn]s\ 5f^{7}\, 6d^{1}\, 7s^{2}$
97	Bk	$[Rn]^{86}\, 5f^{9}\, 7s^{2}$
98	Cf	$[Rn]^{86}\, 5f^{10}\, 7s^{2}$
99	Es	$[Rn]^{86}\, 5f^{11}\, 7s^{2}$
100	Fm	$[Rn]^{86}\, 5f^{12}\, 7s^{2}$
101	Md	$[Rn]^{86}\, 5f^{13}\, 7s^{2}$
102	No	$[Rn]^{86}\, 5f^{14}\, 7s^{2}$
103	Lr	$[Rn]^{86}\, 5f^{14}\, 6d^{1}\, 7s^{2}$
104	Rf or Ku or Unq Rutherfordium or Kurchatovium (Unnilquadium)	$[Rn]^{86}\, 5f^{14}\, 6d^{2}\, 7s^{2}$
105	Ha or Db or Unp Hahnium or Dubnium (Unnilpentium)	$[Rn]^{86}\, 5f^{14}\, 6d^{3} 7s^{2}$
106	Sg or Unh Seaborgium (Unnilhexium)	$[Rn]^{86}\, 5f^{14}\, 6d^{4}\, 7s^{2}$
107	Ns or Bh or Uns Neilsbohrium or Bohrium (Unnilseptium)	$[Rn]^{86}\, 5f^{14}\, 6d^{5}\, 7s^{2}$
108	Hs or Uno Hassnium (Unniloctium)	$[Rn]^{86}\, 5f^{14}\, 6d^{6}\, 7s^{2}$
109	Mt or Une Meitnerium (Unnilennium)	$[Rn]^{86}\, 5f^{14}\, 6d^{7}\, 7s^{2}$
110	Uun (Ununnilium) or Ekaplatinum	$[Rn]^{86}\, 5f^{14}\, 6d^{8}\, 7s^{2}$
111	Uuu (Unununium) or Ekagold	$[Rn]^{86}\, 5f^{14}\, 6d^{9}\, 7s^{2}$
112	Uub (Ununbium) or Ekamercury	$[Rn]^{86}\, 5f^{14}\, 6d^{10}\, 7s^{2}$
113	Uuq (Ununquadium)	$[Rn]^{86}\, 5f^{14}\, 6d^{10}\, 7s^{2}\, 7p^{2}$
114	Uup (Ununpentium)	$[Rn]^{86}\, 5f^{14}\, 6d^{10}\, 7s^{2}\, p^{3}$

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*Elements with exceptional electronic configurations.

*The names given in brackets are IUPAC names. Rules for naming them are described in Unit 4.

PROBLEMS ON ELECTRONIC CONFIGURATION

EXAMPLE 1. *Find the number of unpaired electrons present in phosphorus (atomic No. 15) chromium (atomic No. 24) and copper (atomic No. 29) after writing their orbital electronic configuration.*

Solution.

Element	At. No.	Electronic configuration	No. of unpaired electrons
P	15	$1s^2, 2s^2 2p^6, 3s^2 3p_x^1 3p_y^1 3p_z^1$	3
Cr	24	$1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^5, 4s^1$	5 + 1 = 6
Cu	29	$1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^{10}, 4s^1$	1

EXAMPLE 2. *Write the electronic configurations of the elements with the following atomic numbers :*

3, 8, 10, 14, 17, 25, 29, and 38.

Also mention the groups of the periodic table to which they belong.

Solution.

Atomic No.	Electronic configuration	Group of periodic Table
3	$1s^2 2s^1$	1
8	$1s^2 2s^2 2p_x^2 2p_y^1 2p_z^1$	16
10	$1s^2 2s^2 2p_x^2 2p_y^2 2p_z^2$	18
14	$1s^2 2s^2 2p^6 3s^2 3p_x^1 3p_y^1$	14
17	$1s^2 2s^2 2p^6 3s^2 3p_x^2 3p_y^2 3p_z^1$	17
25	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^5 4s^2$	7
29	$1s^2, 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^1$	11
38	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 5s^2$	2

Rules for finding the Group No.

(*i*) If the last shell contains 1 or 2 electrons, then the group number is 1 and 2 respectively.

(*ii*) If the last shell contains more than 2 electrons then the group number is the total number of electrons in the last shell plus 10.

(*iii*) If electrons are present in $(n-1)$ *d* orbital in addition to those in the *ns* orbital, then the group number is equal to the total number of electrons present in the $(n-1)$ *d* orbital and *ns* orbital.

EXAMPLE 3. *What atoms are indicated by the following electronic configurations ?*

(*i*) $1s^2 2s^2 2p^1$ (*ii*) $[Ar]\, 4s^2 3d^1$

Solution. (*i*) Total number of electrons in

$$1s^2 2s^2 2p^1 = 2 + 2 + 1 = 5$$

∴ Atomic number of the element = 5

Hence the element is *Boron* (B)

(*ii*) Total number of electrons in

$$[\text{Ar}]\, 4s^2 3d^1 = 18 + 2 + 1 = 21$$

∴ Atomic number of the element = 21

Hence the element is *Scandium* (Sc)

EXAMPLE 4. *A neutral atom of element has 2K, 8L and 5M electrons. Find out the following from the data : (a) Atomic No. (b) Total No. of s electrons (c) Total No. of p-electrons (d) No. of protons in the nucleus and (e) Valency of the element.*

Solution. The electronic configuration of the element with 2K, 8L and 5M electrons will be

$$1s^2 2s^2 2p_x^2 2p_y^2 2p_z^2 3s^2 3p_x^1 3p_y^1 3p_z^1$$

(*a*) Total no. of electrons = 2 + 8 + 5 = 15

∴ Atomic No. of the element = 15

(*b*) Total no. of s-electrons = 2 + 2 + 2 = 6

(*c*) Total no. of p-electrons = 6 + 3 = 9

(*d*) Since the atom is neutral,

∴ No. of protons = No. of electrons

= Atomic No. = 15

(*e*) Since the element has only three half-filled atomic orbitals, therefore, valency of the element = 3.

EXAMPLE 5. *Give the electronic configuration of the following ions :*

(i) Cu^{2+} *(ii)* Cr^{3+} *(iii)* Fe^{2+} *and* Fe^{3+}

(iv) H^- *(v)* S^{2-}

Solution. During the formation of cations, electrons are lost while in the formation of anions, electrons are added to the valence shell. The number of electrons added or lost is equal to the numerical value of the charge present on the ion. Following this general concept, we can write the electronic configurations of all the ions given in the question.

(i) $Cu^{2+} = {}_{29}Cu - 2e^-$

$= 1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,3d^{10}\,4s^1 - 2e^-$

$= 1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,3d^9$

(ii) $Cr^{3+} = {}_{24}Cr - 3e^-$

$= 1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,3d^5\,4s^1 - 3e^-$

$= 1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,3d^3$

(iii) $Fe^{2+} = {}_{26}Fe - 2e^-$

$= 1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,3d^6\,4s^2 - 2e^-$

$= 1s^2\,2s^2\,2p^6\,3s^2\,3d^6\,3d^6$

$Fe^{3+} = {}_{26}Fe - 3e^-$

$= 1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,3d^5$

(iv) $H^- = {}_1H + 1e^- = 1s^1 + 1e^1 = 1s^2$

(v) $S^{2-} = {}_{16}S + 2e^-$

$= 1s^2\,2s^2\,2p^6\,3s^2\,3p_x^2\,3p_y^1\,3p_z^1 + 2e^-$

$= 1s^2\,2s^2\,2p^6\,3s^2\,3p_x^2\,3p_y^2\,3p_z^2$

Method to write the electronic configuration of ions. For writing the electric configuration of cations, first write the electronic configuration of neutral atom and then remove number of electrons equal to the units of positive charge, ***starting from the outermost shell irrespective of the order in which they were filled***. Similarly, the electronic configurations of anions are written.

EXAMPLE 6. *Discuss the possibility of the atom for existing in the following electronic configurations:*

(i) $1s^2\,2s^2\,2p_x^1$ *(ii)* $1s^2\,2s^1\,2p_x^2\,2p_y^1\,2p_z^1$

(iii) $1s^2\,2s^2\,2p_x^2\,2p_y^1$ *(iv)* $1s^2\,2s^2\,3s^2$

Solution. *(i)* This electronic configuration is correct since it is in accordance with the rules for filling up of various orbitals.

(ii) This electronic configuration is wrong because it violates aufbau principle which states that an orbital with lower energy i.e. 2s in the present case should be completely filled before the electrons go to higher energy subshell, i.e. 2p in the present case.

(iv) This electronic configuration is not correct since it violates Hund's rule. According to this rule all the three 2p orbitals must have one electron each before the pairing occurs. But in the present case $2p_x$ orbital has two electrons while $2p_z$ orbital is empty.

(iv) This electronic configuration is wrong since after filling 2s-orbtial, the electrons should go to 2p-orbital rather than 3s-orbital.

EXAMPLE 7. *Consider the following electronic configurations :*

(i) $1s^2\,2s^1$ *(ii)* $1s^2\,3s^1$

(a) Name the element corresponding to (i)

(b) Does (ii) correspond to the same or different element ?

(c) How can (ii) be obtained from (i) ?

(d) Is it easier to remove one electron from (ii) or (i) ? Explain.

Solution. *(a)* The element corresponding to *(i)* is Lithium (Li).

(b) This electronic configuration represents the same element in the excited state.

(c) By supplying energy to the element when the electron jumps from the lower energy 2s-orbital to the higher energy 3s-orbital.

(d) It is easier to remove an electron from (ii) than from (i) since in the former case the electron is present in a 3s-orbital which is away from the nucleus and hence is less strongly attracted by the nucleus than an electron in the 2s-orbital.

EXAMPLE 8. *An atom of an element contains 29 electrons and 35 neutrons. Deduce (i) the number of protons and (ii) the electronic configuration of the element.* 29 P **(N.C.E.R.T.)**

Solution. For neutral atom, number of protons = number of electrons = 29

Thus atomic number of the element = 29

Electronic configuration of element with Z = 29 will be

$$1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,3d^{10}\,4s^1$$

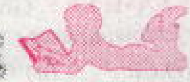
or $[Ar]^{18}\,3d^{10}\,4s^1$ *i.e.* ${}_{29}Cu$.

Note. No. of neutrons are needed only to find mass number.

Mass number = No. of protons + No. of neutrons

= 29 + 35 = 64

PROBLEMS FOR PRACTICE



1. Give the electronic configurations of :
   (*i*) Scandium (At. No. 21), and
   (*ii*) Chromium (At. No. 24).

[Ans. (*i*) $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^1\ 4s^2$
(*ii*) $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^5\ 4s^1$]

2. Write the electronic configgrations and the names of the elements having the atomic numbers 5, 9, 10, 19 and 20.

[*Atomic No.*	*Electronic configurations*	*Name*
5	$1s^2\ 2s^2\ 2p_x^1$	**Boron**
9	$1s^2\ 2s^2\ 2p_x^2\ 2p_y^2\ 2p_z^1$	**Flourine**
10	$1s^2\ 2s^2\ 2p_x^2\ 2p_y^2\ 2p_z^2$	**Neon**
19	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^1$	**Potassium**
20	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2$	**Calcium]**

3. Give the electronic configurations of the following elements : $_{19}K$, $_{25}Mn$, $_{20}Ca$

[Ans. $_{19}K = 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^1$:
$_{25}Mn = 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^5\ 4s^2$,
$_{20}Ca = 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2$]

4. Write the electronic configurations of the elements: Chlorine and Phosphorus.

[Ans. **Chlorine** ($_{17}Cl$) $= 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p_x^2\ 3p_y^2\ 3p_z^1$:
Phosphorus ($_{15}P$) $= 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p_x^1\ 3p_y^1\ 3p_z^1$]

5. Give the electronic configurations of the following ions : (*i*) H^- (*ii*) Na^+ (*iv*) N^- (*iv*) N^{2+}

[Ans. (*i*) $1s^2$ (*ii*) $1s^2\ 2s^2\ 2p^6$ (*iv*) $1s^2\ 2s^2\ 2p^4$
(*iv*) $1s^2\ 2s^2\ 2p^1$]

6. Write down the electronic configuration of an element with atomic number 14. Which group in the periodic table does this element belong to ?

[Ans. **Group 14**]

7. Name the elements that correspond to each of the following electronic configurations. Write down their atomic numbers also.
   (*i*) $1s^2\ 2s^2\ 2p^2$ (*ii*) $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^1$
   (*iii*) $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$

[Ans. (*i*) $_6C$ (*ii*) $_{13}Al$ (*iv*) $_{18}Ar$]

8. Correct the following electronic configurations of the elements in the ground state :
   (*i*) $1s^2\ 2s^1\ 2p_x^2\ 2p_y^2\ 2p_z^2\ 3s^2\ 3p_x^1$
   (*ii*) $1s^2\ 2s^2\ 2p_y^2\ 2p_z^1$
   (*iii*) $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^5$
   (*iv*) $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^4\ 4s^2$

[Ans. (*i*) $1s^2\ 2s^2\ 2p_x^2\ 2p_y^2\ 2p_z^2\ 3s^2$
(*ii*) $1s^2\ 2s^2\ 2p_x^1\ 2p_y^1\ 2p_z^1$
(*iii*) $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^3$
(*iv*) $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^5\ 4s^1$]

9. The atomic mass of an element is double its atomic number. If there are four electrons in the 2*p*-orbital, then draw the model of the atom showing the arrangement of protons, neutrons and electrons. Give its valency and name the element.

[Ans. $1s^2\ 2s^2\ 2p_x^2\ 2p_y^1\ 2p_z^1$, **two, Oxygen**]

10. Write the electronic configuration of $_9F^{19}$, $_{16}S^{32}$ and $_{18}Ar^{38}$ and then point out the element with :
    (*i*) Maximum nuclear charge (*ii*) minimum number of neutrons (*iii*) highest mass number (*iv*) maximum number of unpaired electrons.

[Ans. $_9F^{19} = 1s^2\ 2s^2\ 2p_x^2\ 2p_y^2\ 2p_z^1$:
$_{16}S^{32} = 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p_x^2\ 3p_y^1\ 3p_z^1$,
$_{18}Ar^{38} = 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$

(*i*) Max. nuclear charge = 18 in $_{18}Ar^{38}$

(*ii*) Minimum no. of neutrons = 10 in $_9F^{19}$

(*iii*) Maximum no. of unpaired electrons = 2 in $_{16}S^{32}$]

11. What are the atomic numbers of elements whose outermost electrons are represented by
    (*i*) $3s^1$ (*ii*) $2p^3$ and
    (*iii*) $3d^6$?

[Ans. **(*i*) 11 (*ii*) 7 (*iii*) 26**]

12. What atoms are indicated by the following configurations ?
    (*i*) [He] $2s^1$ (*ii*) [Ne] $3s^2\ 3p^3$
    (*iii*) [Ar] $4s^2\ 3d^1$

[Ans. **(*i*) Li (*ii*) P (*iii*) Sc**]

13. Which of the following configurations represent the element in the ground and which in the excited state ? Name the element in each case :
    (*i*) $1s^2\ 2s^1\ 2p^1$ (*ii*) $1s^2\ 2s^2\ 2p^1$
    (*iii*) $1s^2\ 2s^1\ 2p_x^1\ 2p_y^1\ 2p_z^1$
    (*iv*) $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p_x^1\ 3p_y^1\ 3p_z^1\ 3d^1$

[Ans. **(*i*) Be (*ii*) B (*iii*) C (*iv*) S**
(All are in excited state except (*ii*))]

PRACTICE PROBLEMS CONTD.

14. A p-subshell which consists of p_x, p_y and p_z orbitals contains only one electron. In which one of these three orbitals should the electron be located? Justify your answer.

[Ans. In any one because they are degenerate]

15. Which of the following quantum numbers for orbitals in hydrogen atom has a greater energy for electrons ?

(*i*) $n = 3$, $l = 2$ and $m = +1$

(*ii*) $n = 3$, $l = 2$ and $m = -1$

[Ans. Same energy but different orientations]

16. Write the electronic configurations of the following ions :

(*a*) H^+ (*b*) Na^+ (*c*) O^{2-} (*d*) F^- *(N.C.E.R.T.)*

[Ans. (a) $1s^0$ (b) $1s^2\, 2s^2\, 2p^6$ (c) $1s^2\, 2s^2\, 2p^6$ (d) $1s^2\, 2s^2\, 2p^6$]

17. What atoms are indicated by the following configurations ?

(*a*) [He] $2s^1$ (*b*) [Ne] $3s^2\, 3p^3$ (*c*) [Ar] $4s^2\, 3d^1$ *(N.C.E.R.T.)*

[Ans. (a) $_3Li$ (b) $_{15}P$ (c) $_{21}Sc$]

18. Give the number of electrons in the species H_2^+, H_2 and O_2^+. *(N.C.E.R.T.)*

[Ans. $H_2^+ = 2 - 1 = 1\, e^-$, $H_2 = 1 + 1 = 2\, e^-$, $O_2^+ = 8 + 8 - 1 = 15\, e$]

HINTS FOR DIFFICULT PROBLEMS

6. E.C. of $_{14}X = 1s^2\, 2s^2\, 2p^6\, 3s^2\, 3p^2$. As the last shell contains 4 electrons, group number = 10 + 4 = 14.

7. (*i*) Z = 6, Element is C (*ii*) Z = 13, Element is Al (*iii*) Z = 18, Element is Ar.

9. Valency = Number of half-filled orbitals.

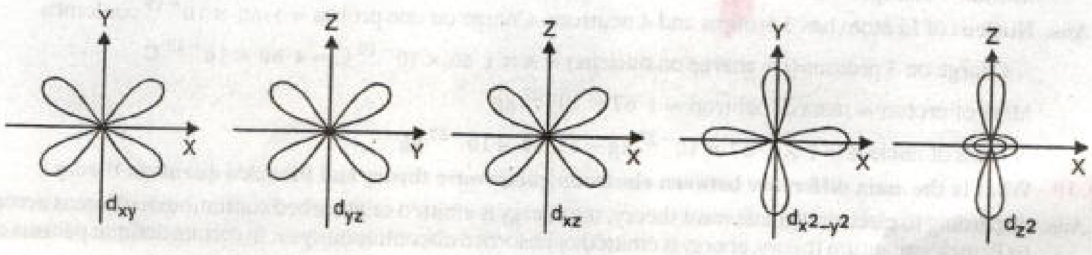
11. (*i*) When last shell is $3s^1$, complete E.C. $= 1s^2\, 2s^2\, 2p^6\, 3s^1$

(*ii*) When last shell is $2p^3$, complete E.C. $= 1s^2\, 2s^2\, 2p^3$

(*iii*) When last shell is $3d^6$, complete E.C. $= 1s^2\, 2s^2\, 2p^6\, 3s^2\, 3p^6\, 4s^2\, 3d^6$.

ADD TO YOUR KNOWLEDGE

1. The shapes of five d-orbitals and their designations are as follows :



The shape of the first four orbitals is called **clover-leaf** while that of the last one is called **dough-nut** shape.

2. The shapes of seven f-orbitals are complicated but their designations are as follows :

$$f_x^3,\ f_y^3,\ f_z^3,\ f_{x(z^2-y^2)},\ f_{y(x^2-z^2)},\ f_{z(y^2-x^2)},\ f_{xyz}.$$

3. For La (Z = 57), the expected electronic configuration is $[Xe]^{54}\, 4f^1\, 6s^2$. But actual electronic configuration is $[Xe]^{54}\, 5d^1\, 6s^2$ *i.e.* it belongs to d-block and not f-block elements.

Conceptual Questions

Q. 1. Why cathode rays are produced only when the pressure of the gas inside the discharge tube is very low ?

Ans. At higher pressure (*e.g.* at 1 atmospheric pressure), no electric current flows through the tube because gases are poor conductor of electricity.

Q. 2. Give two examples from everyday life where cathode ray tubes are used.

Ans. (*i*) Television picture tube (*ii*) fluorescent light tubes.

Q. 3. What is the difference in the origin of cathode rays and anode rays ?

Ans. Cathode rays originate from the cathode whereas anode rays are not produced from the anode. They are produced from the gaseous atoms by knock out of the electrons by high speed cathode rays.

Q. 4. In one discharge tube, H_2 gas is taken and in the other O_2 gas is taken. Will the electrons and positive ions in the cathode rays and in the anode rays be same or different ?

Ans. Electrons will be same but positive ions will not be same.

Q. 5. When α-rays hit a thin foil of gold, very few α-particles are deflected back. What does it prove ?

Ans. There is a very small heavy body present within the atom, called nucleus.

Q. 6. What is the difference between atomic mass and mass number ?

Ans. Mass number is a whole number because it is the sum of number of protons and number of neutrons whereas atomic mass is fractional because it is the average relative mass of its atoms as compared with mass an atom of C — 12 isotope taken as 12.

Q. 7. Give one example of each of the following :

(*i*) Isotope of $^{35}_{17}Cl$ (*ii*) Isobar of $^{40}_{18}Ar$ (*iii*) Isotone of $^{14}_{6}C$

Ans. (*i*) $^{37}_{17}Cl$ (*ii*) $^{40}_{19}K$ (*iii*) $^{16}_{8}O$

Q. 8. Name the element in each of the following cases :

(*i*) A bivalent anion of the element having 10 electrons

(*ii*) A trivalent cation of the element having 10 electrons.

What is the relationship between the two ions called?

Ans. (*i*) Oxygen

(*ii*) Aluminium.

The two ions are called isoelectronic.

Q. 9. Calculate the approximate charge in coulombs and approximate mass in kilograms of the nucleus of lithium-7 isotope.

Ans. Nucleus of Li atom has 3 protons and 4 neutrons. Charge on one proton = $1 \cdot 60 \times 10^{-19}$ coulombs

$\therefore$ Charge on 3 protons (*i.e.* charge on nucleus) = $3 \times 1 \cdot 60 \times 10^{-19}$ C = $\mathbf{4 \cdot 80 \times 10^{-19}}$ **C**

Mass of proton ≈ mass of neutron ≈ $1 \cdot 67 \times 10^{-27}$ kg

$\therefore$ Mass of nucleus = $7 \times 1 \cdot 67 \times 10^{-27}$ kg = $\mathbf{11 \cdot 69 \times 10^{-27}}$ **kg**

Q. 10. What is the main difference between electromagnetic wave theory and Planck's quantum theory ?

Ans. According to electromagnetic wave theory, the energy is emitted or absorbed continuously whereas according to Planck's quantum theory, energy is emitted or absorbed discontinuously *i.e.* in certain definite packets called 'quanta'.

Q. 11. What is the difference between a quantum and a photon ?

Ans. The smallest packet of energy of any radiation is called a quantum whereas that of light is called photon.

Q. 12. How are frequency and wave number related to each other ?

Ans. $c = \nu \lambda = \nu \frac{1}{\bar{\nu}}$ or $\nu = c\,\bar{\nu}$, where c is velocity of light, ν is frequency and $\bar{\nu}$ is wave number.

Q. 13. Arrange X-rays, cosmic rays and radiowaves according to frequency.

Ans. Cosmic rays > X-rays > Radiowaves

Q. 14. What do you observe in the spectrum of NaCl ?

Ans. Two yellow lines with wavelengths 5890 Å and 5896 Å.

Q. 15. Which series of lines of the hydrogen spectrum lie in the visible region ?

Ans. Balmer series.

Q. 16. Why are Bohr's orbits called stationary states ?

Ans. This is because the energies of the orbits in which the electrons revolve are fixed.

Q. 17. What is the difference between ground state and excited state ?

Ans. Ground state means the lowest energy state. When the electrons absorb energy and jump to outer orbits, this state is called excited state.

Q. 18. Why electronic energy is negative ? Comment on the spacing between the energy levels.

Ans. Refer to text (page 3/27). The spacing between the energy levels decreases as we move outwards from the nucleus.

Q. 19. What do you mean by saying that energy of the electron is quantized ?

Ans. This means that the electrons in an atom have only definite values of energies.

Q. 20. Why the number of lines observed in the hydrogen spectrum is very large ?

Ans. Refer to the text (page 3/28).

Q. 21. How much energy is required for the removal of the only electron present in the hydrogen atom ?

Ans. $\Delta E = E_{\infty} - E_1 = 0 - (-21{\cdot}8 \times 10^{-19}\ \text{J})$

$$= 21{\cdot}8 \times 10^{-19}\ \text{J.}$$

Q. 22. What is the maximum number of lines obtained when the excited electron of a H atom in $n = 6$ drops to the ground state ? *(N.C.E.R.T.)*

Ans. No. of lines produced when electron from nth shell drops to ground state $= \dfrac{n\,(n-1)}{2} = \dfrac{6\,(6-1)}{2} = 15$

[These are produced due to following transitions

6 ⟶ 5	5 ⟶ 4	4 ⟶ 3	3 ⟶ 2	2 ⟶ 1
6 ⟶ 4	5 ⟶ 3	4 ⟶ 2	3 ⟶ 1	
6 ⟶ 3	5 ⟶ 2	4 ⟶ 1		
6 ⟶ 2	5 ⟶ 1			
6 ⟶ 1				
(5 lines)	(4 lines)	(3 lines)	(2 lines)	(1 line)]

Q. 23. Which transition between Bohr orbits corresponds to third line in the Balmer series of the hydrogen spectrum.

Ans. 5th orbit to 2nd orbit.

Q. 24. Which of the following relate to wave nature of light or particle nature or both ?

(a) Interference (b) Diffraction (c) Photoelectric effect

(d) Black body radiation (e) Planck's equation $E = h\nu$

(f) Einstein equation $E = mc^2$.

Ans. (*a*) Wave nature (*b*) Wave nature (*c*) Particle nature (*d*) Particle nature (*e*) Both particle and wave nature (*f*) Particle nature.

Q. 25. Which quantum number does not follow from the solution of Schrodinger wave equation ?

Ans. Spin quantum number.

Q. 26. What shell would be the first to have a *g*-subshell ? How many orbitals will be possible in a *g*-subshell ? *(N.C.E.R.T.)*

Ans. For *g*-subshell, $l = 4$. As $l = 0$ to $n-1$, hence $n = 5$ *i.e.* 5th shell.

For $l = 4, m = -4, -3, -2, -1, 0, +1, +2, +3, +4$ *i.e.* 9 values which means 9 orbitals.

Q. 27. How many electrons are present in all subshells (fully-filled) with $n + l = 5$?

Ans. Subshells with $n + l = 5$ are $5s$, $4p$, $3d$. Hence electrons present $= 2 + 6 + 10 = 18$.

Q. 28. How many electrons in an atom have the following quantum numbers ?

(*i*) $n = 4, m_s = -\frac{1}{2}$ (*ii*) $n = 3, l = 0$. (*N.C.E.R.T.*)

Ans. (*i*) Total electrons in $n=4$ are $2n^2$ *i.e.* $2 \times 4^2 = 32$. Half of them *i.e.* 16 electrons have $m_s = -\frac{1}{2}$.

(*ii*) $n = 3, l = 0$ means $3s$ orbital which can have 2 electrons.

Q. 29. What is the angular momentum of an electron in (i) 2 s orbital (ii) 4 f orbital ?

Ans. Angular momentum of electron in any orbital $= \sqrt{l\,(l+1)}\,\frac{h}{2\pi}$

$\therefore$ For $2\,s$ orbital, $l = 0$, $\therefore$ angular momentum $= \sqrt{0\,(0+1)}\,\frac{h}{2\pi} = 0$.

For $4f$ orbital, $l = 3$, $\therefore$ angular momentum $= \sqrt{3\,(3+1)}\,\frac{h}{2\pi} = \sqrt{3}\,\frac{h}{\pi}$

Q. 30. What is the difference between the notations *l* and L ?

Ans. '*l*' represents azimuthal quantum number which can have values 0, 1, 2 etc. L represents second Bohr orbit for which $n = 2$ always.

Q. 31. Do atomic orbitals have sharp boundaries ? Explain why or why not ?

or Why don't we draw a boundary surface diagram within which the probability of finding the electron is 100% ?

Ans. No, atomic orbitals do not have sharp boundaries because the probability of finding the electron even at large distances may be very small but not equal to zero.

Q. 32. What is the difference in the angular momentum of an electron present in 3*p* and that present in 4*p* orbital ?

Ans. No difference because angular momentum $= \frac{h}{2\pi}\sqrt{l\,(l+1)}$ *i.e.* it depends only on the value of *l* and not *n*.

Q. 33. Why spliting of spectral lines takes place when the source giving the spectrum is placed in a magnetic field ?

Ans. In the presence of magnetic field, the orbitals present in a sub-shell (which were degenerate) take up different orientations.

Q. 34. How many electrons in sulphur (Z = 16) can have $n + l = 3$?

Ans. ${}_{16}S = 1s^2\,2s^2\,2p^6\,3s^2\,3p^4$

For $1s^2$, $n + l = 1 + 0 = 1$

For $2s^2$, $n + l = 2 + 0 = 2$

For $2p^6$, $n + l = 2 + 1 = 3$

For $3s^2$, $n + l = 3 + 0 = 3$

For $3p^4$, $n + l = 3 + 1 = 4$

Thus $n + l = 3$ for $2p^6$ and $3s^2$ electrons *i.e.* for 8 electrons.

Q. 35. The 4*f* subshell of an atom contains 10 electrons. What is the maximum number of electrons having spin in the same direction ?

Ans. Seven.

Q. 36. Why Pauli exclusion principle is called exclusion principle ?

Ans. This is because according to this principle, if one electron in an atom has some particular values for the four quantum numbers, then all the other electrons in that atom are excluded from having the same set of values.

Q. 37. How many orbitals are present in the M-shell ?

Ans.

Shell (n)	Sub-shells (l)	Orbitals (m)	
3	0 ($3s$)	0	= 1
	1 ($3p$)	−1, 0, +1	= 3
	2 ($3d$)	−2, −1, 0, +1, +2	= 5
			Total = 9

Alternatively, no. of orbitals $= n^2 = 3^2 = 9$.

Q. 38. How many spherical nodes are present in 3 p orbital ?

Ans. No. of nodes = $(n - l - 1) = (3 - 1 - 1) = 1$.

Q. 39. Why Hund's rule is called rule of maximum multiplicity ?

Ans. This is because out of the various possible electronic configurations, only that configuration is correct for which the total spin value is maximum.

Q. 40. Which out of Cu^{2+}, Fe^{2+} and Ci^{3+} has highest paramagnetism and why ?

Ans. Cu^{2+} has one, Fe^{2+} has four and Cr^{3+} has three unpaired electrons. Hence Fe^{2+} has highest paramagnetism.

Q. 41. Which of the following are isoelectronic species ?

Na^+, K^+, Mg^{2+}, Ca^{2+}, S^{2-}, Ar. *(N.C.E.R.T.)*

Ans. No. of electrons are : $Na^+ = 11 - 1 = 10$, $K^+ = 19 - 1 = 18$, $Mg^{2+} = 12 - 2 = 10$,

$Ca^{2+} = 20 - 2 = 18$, $S^{2-} = 16 + 2 = 18$, $Ar = 18$.

Hence isoelectronic species are Na^+ and Mg^{2+} ; K^+, Ca^{2+}, S^{2-} and Ar.

Q. 42. What are the atomic numbers of elements whose outermost electrons are represented by

(*a*) $3s^1$ (*b*) $2p^3$ and $3d^6$? *(N.C.E.R.T.)*

Ans. (*a*) $1s^2\,2s^2\,2p^6\,3s^1$ (Z = 11) (*b*) $1s^2\,2s^2\,2p^3$ (Z = 7) (*c*) $1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,4s^2\,3d^6$ (Z = 26).

Q. 43. What is the maximum number of electrons that can be present in an atom in which the highest principal quantum number is 4.

Ans. Keeping in view aufbau principle, the electronic configuration of atom having highest value of $n = 4$ will be $1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,4s^2\,3d^{10}\,4p^6$ (After 4p, filling of 5s starts)

Hence maximum number of electrons present = 36 (Kr).

Very Short Answer Questions CARRYING 1 MARK

Q. 1. What are the different isotopes of hydrogen ?

Ans. Protium ($_1H^1$), Deuterium ($_1H^2$), Tritium ($_1H^3$)

Q. 2. How many neutrons are present in $_{92}U^{238}$?

Ans. 238 − 92 = 146

Q. 3. What happens when a mica wheel is placed in the path of cathode rays ?

Ans. It begins to rotate

Q. 4. Write down the actual value of charge and mass of an electron ?

Ans. Charge = $1 \cdot 60 \times 10^{-19}$ coulombs,

mass = $9 \cdot 11 \times 10^{-31}$ kg

Q. 5. What type of cathode was used by Goldstein in his experiments on the study of anode rays ?

Ans. Perforated cathode

Q. 6. Which element does not have any neutron in it ?

Ans. Hydrogen

Q. 7. What is the value of Planck's constant in S.I. units?

Ans. $6 \cdot 62 \times 10^{-34}$ Js

Q. 8. What is Ritz combination principle ?

Ans. $\bar{v} = R\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$ where R is called Rydberg constant.

Q. 9. Write the expression for the energy of electron of hydrogen atom in the nth level.

Ans. $E_n = -\frac{1312}{n^2}$ kJ mol^{-1}.

Q. 10. What is Bohr's postulate of angular momentum ?

Ans. Angular momentum, $mvr = n\frac{h}{2\pi}$.

Q. 11. Which orbital does not have directional characteristic ?

Ans. *s*-orbital.

Q. 12. Which quantum number determines the

(*a*) shape (*b*) orientation and (*c*) size of the orbital ?

Ans. (*a*) Azimuthal (*b*) magnetic (*c*) principal

Q. 13. Which energy level does not have a *p*-orbital ?

Ans. 1st energy level.

Q. 14. Which is the first energy level containing *f*-orbitals?

Ans. 4th

Q. 15. What is the maximum number of electrons that can be accommodated in the *d*-sub-shell ?

Ans. Ten

Q. 16. Which element has only one electron in the *d*-orbital ?

Ans. Scandium (Z = 21).

Q. 17. What is the physical significance of ψ and ψ^2 ?

Ans. ψ as such has no physical significance. ψ^2 gives the probability of finding the electron at any point around the nucleus.

Q. 18. Write Schrodinger wave equation in the briefest possible form.

Ans. $\hat{H}\psi = E\psi$ where $\hat{H}$ is called Hamiltonian operator.

Q. 19. Which quantum number tends to specify the orientation in space for an orbital ?

Ans. Magnetic quantum number.

Short Answer Questions CARRYING 2 or 3 MARKS

Sec. 3.1. to 3.2.

1. How are cathode rays originated ?
2. How can you say that electron is a universal constituent of all atoms ?
3. Give experiments to show that

   (*i*) Cathode rays carry negative charge (*ii*) Cathode rays consist of material particles.

Sec. 3.3.

4. How was proton discovered ?

Sec. 3.4. to 3.5.

5. What was Thomson model of atom ?
6. How can you say that nucleus is small in size but heavy in mass ?

Sec. 3.6.

7. Who discovered neutron and how ?

Sec. 3.7. to 3.8.

8. Define 'Atomic number' and 'Mass number'.
9. What are isotopes ? How are they represened ?

Sec. 3.9. to 3.10.

10. Define wavelength, frequency, wave number and velocity of a wave. How are they inter-related ?

Sec. 3.11.

11. What is Planck's Quantum Theory ?

Sec. 3.12.

12. How is the atomic spectra of hydrogen obtained ? What are the different series of lines present in it ? In which regions do they lie ?
13. What is Rydberg formula ? How does it help to calculate the wave numbers of different series of lines of the hydrogen spectra ?
14. What is the difference between Rydberg formula and Balmer formula ?

Sec. 3.13.

15. What was the drawback of Rutherford's model of atom ?

Sec.3.14. to 3.15.

16. What do you understand by stationary states ?

17. What do you mean by quantisation of electronic energy and angular momentum ?

18. How does Bohr model explain the line spectrum of hydrogen ?

19. How does Bohr model explain the simultaneous appearance of a large number of lines in the hydrogen spectrum ?

20. Outline the weaknesses of Bohr's model of atom.

Sec. 3.16. 21. What happened to Bohr's model of atom in the light of uncertainty principle ? Explain the concept of 'probability'. Define 'atomic orbital'.

Sec. 3.17. 22. How are the quantum numbers related to each other ?

Sec. 3.18. 23. Define Pauli exclusion principle. Why is it called exclusion principle ?

Sec. 3.19. 24. How do 1*s*, 2*s* and 3*s*-orbitals differ from each other ?

Sec. 3.20. to 3.21. 25. State and explain 'aufbau principle.'

26. State and explain 'Hund's rule of maximum multiplicity'.

27. Why do some atoms possess exceptional electronic configuration ? Explain with suitable examples.

Long Answer Questions CARRYING 5 or more MARKS

Sec. 3.1. to 3.2. 1. How was electron discovered ?

2. How are cathode rays produced ? Briefly explain their important properties.

Sec. 3.3. 3. What are Anode Rays ? How do they originate ? List their important properties.

Sec. 3.5. 4. Briefly describe Rutherford's scattering experiment about the discovery of nucleus.

5. How was the nuclear model of atom discovered ?

Sec. 3.6. 6. How was neutron discovered ? Describe briefly.

Sec. 3.7. to 3.8. 7. (*a*) Define the terms Atomic Number and Mass Number. (*b*) How does mass number differ from atomic mass? How do atomic number (Z) and mass number (A) help to calculate the number of electrons, protons and neutrons in an atom ?

Sec. 3.9. to 3.11. 8. What were the main points of Electromagnetic wave theory ? What were its limitations ? How have these been overcome by Planck's quantum theory ?

9. Briefly explain what do you understand by black body radiation and photoelectric effect ? What is work function ? How they led to the concept of particle nature of electromagnetic waves ?

Sec. 3.12. 10. Write short notes on the following :

(*i*) Solar spectrum or continuous spectrum

(*ii*) Atomic spectra or line spectra

Sec. 3.13. to 3.16. 11. What was the drawback of Rutherford's model of atom ? Describe Bohr's model of atom and explain its usefulness over Rutherford's model.

12. What were the weaknesses or limitations of Bohr's model of atom? Briefly describe the quantum mechanical model of atom.

13. List the main points of difference between orbit and orbital.

14. List the main features of the "quantum mechanical model of atom".

Sec. 3.17. to 3.18. 15. What are 'quantum numbers' ?

16. Briefly describe each of them.

(*a*) How the study of quantum numbers led to Pauli exclusion principle ?

(*b*) Using the concept of quantum numbers, calculate the distribution of electrons as well as maximum number of electrons in the N-shell (4th shell).

Sec. 3.19. 17. Describe the shapes of *s* and *p*-orbitals.

Sec. 3.20. to 3.21. 18. State and explain the following :

(*i*) Aufbau principle (*ii*) Pauli exclusion principle

(*iii*) Hund's rule of maximum multiplicity.

COMPETITION FOCUS

ADDITIONAL USEFUL INFORMATION

1. Can we see the atoms ? For the last nearly 200 years, the atoms were believed to exist but there was no direct proof to show their existence. It is only recently that the direct photographs of the atoms have been taken using a technique called **Scanning Tunneling Microscopy (STM).**

2. Moseley's work on Atomic Number. Roentgen in 1895 observed that when cathode rays hit the anode (made of a harder metal like tungsten, molybdenum etc.), some new radiations are emitted from the anode, called X-rays (so named because their nature was not known at that time). Moseley found that the frequency of the X-rays emitted depended upon the atomic number (Z) of the element (being hit by cathode rays) according to the equation $\sqrt{\nu} = a\,(Z - b)$ where a and b are constants. Thus a plot of $\sqrt{\nu}$ *vs* atomic no. Z is a straight line. A straight line plot is not obtained when $\sqrt{\nu}$ is plotted against atomic mass (A). This had led Moseley to modify the periodic law as discussed in the next unit.

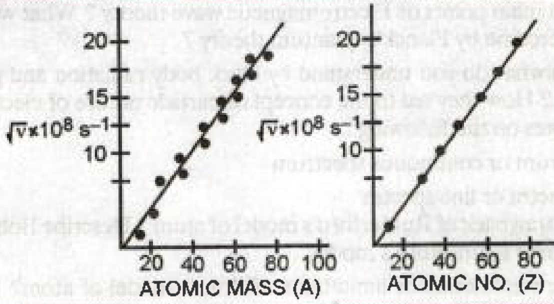


FIGURE 3.32. Plot of $\sqrt{\nu}$ vs A and $\sqrt{\nu}$ vs Z.

3. Bohr Bury Scheme of distribution of electrons. To describe the distribution of electrons in different orbits around the nucleus, Bohr and Bury in 1926 put forward the following scheme :

(*i*) The maximum number of electrons in the nth orbit is given by the formula $2n^2$.

(*ii*) The outermost orbit cannot have more than 8 electrons and next to the outermost not more than 18 electrons.

(*iii*) It is not necessary for an orbit to be complete before another starts to be formed. In fact, a new orbit starts as soon as the outermost orbit has got 8 electrons.

4. Calculation of radius of the orbit. In a H-like particle, for the electron to continue to move along the orbit of radius r,

Force of attraction on the electron by the nucleus = Centripetal force acting on the electron

ADDITIONAL USEFUL INFORMATION contd.

i.e. $$\frac{Ze^2}{r^2} = \frac{m\,v^2}{r} \qquad ...(i)$$

where m is the mass and e is the charge on the electron, Z is atomic no. of the H-like particle (*e.g.* for He^+, Z=2, for Li^{2+}, Z=3 etc.) and v is the tangential velocity. Also according to Bohr's postulate of angular momentum.

$$m\,v\,r = n\frac{h}{2\pi} \qquad ...(ii)$$

Eliminating v from eqns. (*i*) and (*ii*) (by substituting value of v from (*ii*) in (*i*) and rearranging), we get

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

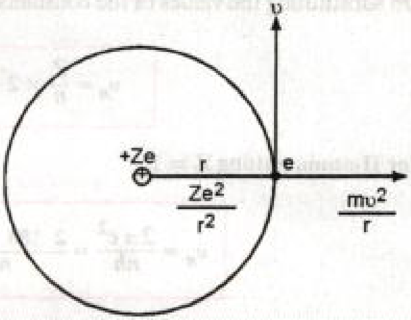


FIGURE 3.33. Bohr's H-like atom.

For H-atom, Z = 1 and for 1st orbit, $n = 1$ so that

$$r_0 = \frac{h^2}{4\pi^2 m\,e^2} = 0{\cdot}529\ \text{Å} \quad \text{(called Bohr's radius)}$$

Thus $$\boxed{r_n = n^2 \times r_0 = n^2 \times 0{\cdot}529\ \text{Å for H-atom}}$$

For H-like atoms, $$r_0 = \frac{0{\cdot}529}{Z}\ \text{Å}$$

and $$\boxed{r_n(\text{H-like atom}) = \frac{r_n\,(\text{H}-\text{atom})}{Z} = \frac{0{\cdot}529\,n^2}{Z}\ \text{Å}}$$

5. Calculation of energy of the electron.

Total energy of the electron (E) = Kinetic energy + Potential energy*

$$= \frac{1}{2}mv^2 + \left(-\frac{Ze^2}{r}\right)$$

But from eqn. (*i*), $$mv^2 = \frac{Ze^2}{r}$$

$$\therefore \quad E = \frac{Ze^2}{2r} - \frac{Ze^2}{r} = -\frac{Ze^2}{2r}$$

Substituting the value of r from eqn. (*iii*), we get

$$E = -\frac{Ze^2}{2} \times \frac{4\pi^2 m\,Ze^2}{n^2 h^2} = -\frac{2\pi^2 m\,Z^2 e^4}{n^2 h^2}$$

Note that K.E. $= \frac{Ze^2}{2r}$, P.E. $= -\frac{Ze^2}{r}$, Total energy (E_{total}) $= -\frac{Ze^2}{2r}$

$$\therefore \quad E_{total}/\text{K.E.} = (-Ze^2/2r)/(Ze^2/2r) = -1$$

$$E_{total}/\text{P.E.} = (-Ze^2/2r)/(-Ze^2/r) = 1/2$$

$$\text{K.E.}/\text{P.E.} = (Ze^2/2r)/(-Ze^2/r) = -1/2$$

6. Calculation of the velocity of the electron in any orbit. Eliminating r from (*i*) and (*ii*) (by substituting the value of r from (*ii*) in (*i*) and rearranging), we get

For H-like atoms $$v_n = \frac{2\pi Ze^2}{nh}$$

---

*Potential energy of the electron at distance r from the nucleus is the work done when the electron moves from distance ∞ to distance r. Hence P.E. $= \int_{\infty}^{r} -\frac{Ze^2}{r^2}\,dr = -\frac{Ze^2}{r}$.

ADDITIONAL USEFUL INFORMATION contd.

On substituting the values of the constants π, e and h, we get

$$\boxed{v_n = \frac{Z}{n} \times 2{\cdot}188 \times 10^8 \text{ cm } s^{-1}}$$

For H-atom, putting Z = 1

$$\boxed{v_n = \frac{2\pi e^2}{nh} = \frac{2{\cdot}188 \times 10^8}{n} \text{ cm } s^{-1}}$$

Further putting $n = 1$, the velocity of electron in the first orbit of H-atom will be $= 2{\cdot}188 \times 10^8 \text{ cm } s^{-1}$ which is nearly 1/137th of the velocity of light.

Also, from eqn. (*i*), it may be seen that $v^2 = \frac{Ze^2}{mr}$ which shows that $v \propto \frac{1}{\sqrt{r}}$

7. Calculation of the number of revolutions of the electron in an orbit per sec

By Bohr postulate, $mvr = n\frac{h}{2\pi}$ or $v = \frac{nh}{2\pi mr}$

$$\text{Number of revolutions per sec} = \frac{\text{Velocity of the electron}}{\text{Circumference of the orbit}}$$

$$= \frac{v}{2\pi r}$$

$$= \frac{nh}{2\pi mr} \times \frac{1}{2\pi r} \text{ (On substituting the value of } v\text{)}$$

$$= \frac{nh}{4\pi^2 mr^2} \quad \text{...}(iv)$$

$$\therefore \text{Time taken for one revolution} = \frac{4\pi^2 mr^2}{nh}$$

$$\text{No. of revolutions per sec} = \frac{nh}{4\pi^2 m} \times \left(\frac{4\pi^2 m Ze^2}{n^2 h^2}\right)^2$$

$$= \frac{4\pi^2 m Z^2 e^4}{n^3 h^3}$$

$$= -\frac{E_1}{h}\left(\frac{2}{n^3}\right)$$

where $E_1 = -\frac{2\pi^2 m Z^2 e^4}{h^2}$ is the energy of the first shell.

8. Calculation of number of waves in any orbit

$$\text{No. of waves in any orbit} = \frac{\text{Circumference of that orbit}}{\text{Wavelength}} = \frac{2\pi r}{\lambda} = \frac{2\pi r}{h/mv}$$

($\lambda = \frac{h}{mv}$ by de Broglie relation)

$$= \frac{2\pi rmv}{h} = \frac{2\pi}{h}(mvr) = \frac{2\pi}{h}\frac{nh}{2\pi} = n$$

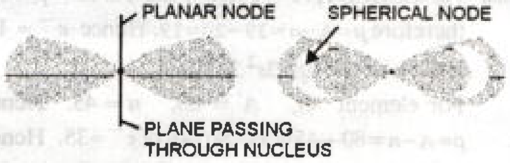
C.B.S.E.-P.M.T. (MAINS) SPECIAL

A. SUBJECTIVE QUESTIONS

Q. 1. **How many nodes are present in 3*p*-orbital. Represent diagrammatically.**

Ans. Number of planar nodes = 1 (because for *p*-orbital, $l = 1$ and number of planar nodes = value of l for that orbital)

Number of radial/spherical nodes $= n - l - 1$ $= 3 - 1 - 1 = 1$



$\therefore$ Total number of nodes in 3*p*-orbital $= n - 1 = 3 - 1 = 2$.

Q. 2. **If the energy of an electron in 3rd Bohr orbit is –E, what is the energy of the electron in (*i*) 1st Bohr orbit (*ii*) 2nd Bohr orbit ?**

Ans. $E_n \propto \frac{1}{n^2} \therefore E_3 \propto \frac{1}{3^2}$ *i.e.* $E_3 \propto \frac{1}{9}, E_2 \propto \frac{1}{2^2}$

i.e. $E_2 \propto \frac{1}{4}, E_1 \propto \frac{1}{1^2}$.

$$\therefore \frac{E_3}{E_1} = \frac{1}{9} \therefore E_1 = 9\,E_3 = -9\,E\ (\because E_3 = -E)$$

$$\frac{E_3}{E_2} = \frac{4}{9}$$

$$\therefore E_2 = \frac{9}{4}E_3 = -\frac{9}{4}E = -2{\cdot}25\ E.$$

Q. 3. **Calculate the total number of electrons, protons and neutrons in (*i*) NH_4^+ ion (*ii*) PO_4^{3-} ion.**

Ans. (*i*) Electrons in NH_4^+ ion = 7 (from N atom) + 4 × 1 (from H atoms) – 1 (due to presence of +1 charge) = 7 + 4 – 1 = 10

Protons in NH_4^+ ion = 7 (in N) + 4 × 1 (in H) = 7 + 4 = 11

Neutrons in NH_4^+ ion $= \underset{\text{(in N)}}{(14 - 7)} + \underset{\text{in H}}{4\,(1 - 1)}$ = 7 + 0 = 7

(*ii*) Electrons in PO_4^{3-} ion = 15 (from P atom) + 4 × 8 (from O atom) + 3 (due to presence of – 3 charge)

= 15 + 32 + 3 = 50

Protons in PO_4^{3-} ion = 15 (in P) + 4 × 8 (in O) = 15 + 32 = 47

Neutrons in PO_4^{3-} ion

$$= \underset{\text{(in P)}}{(31 - 15)} + \underset{\text{(in O)}}{4\,(16 - 8)} = 16 + 32 = 48$$

Q. 4. **Show that the circumference of the Bohr orbit for hydrogen atom is an integral multiple of the de Broglie wavelength associated with the electron moving around the orbit. (*N.C.E.R.T.*)**

Ans. According to Bohr postulate of angular momentum

$$mvr = n\,\frac{h}{2\pi}$$

or $$2\pi r = n\,\frac{h}{mv} \qquad ...(i)$$

According to de Broglie equation

$$\lambda = \frac{h}{mv} \qquad ...(ii)$$

Substituting this value in eqn. (*i*), we get

$$2\pi r = n\lambda$$

Thus, the circumference ($2\pi r$) of the Bohr orbit for hydrogen atom is an integral multiple of de Broglie wavelength.

Q. 5. **(*i*) An atomic orbital has n = 3. What are the possible values of *l* and m_l ?**

(*ii*) List the quantum numbers (m_l and *l*) of electrons for 3d-orbital.

(*iii*) Which of the following orbitals are possible ?

1*p*, 2*s* and 3*f*. (*N.C.E.R.T.*)

Ans. (*i*) When $n = 3, l = 0, 1, 2$.

When $l = 0, m_l = 0$. When $l = 1, m_l = -1, 0, +1$.

When $l = 2, m = -2, -1, 0, +1, +2$

(*ii*) For 3*d*-orbital, $n = 3, l = 2$,

For $l = 2, m_l = -2, -1, 0, +1, +2$.

(*iii*) 1*p* is not possible because when $n = 1, l = 0$ only (for *p*, $l = 1$)

2*s* is possible because when $n = 2, l = 0, 1$ (for *s*, $l = 0$)

2*p* is possible because when $n = 2, l = 0, 1$ (for *p*, $l = 1$)

3*f* is not possible because when $n = 3, l = 0, 1, 2$ (for *f*, $l = 3$).

Q. 6. **Show that ground state energy of electron in hydrogen atom is equal to the first excited state energy of electron in He^+ ion, assuming that their Rydberg constants are equal.**

Ans. $E_n = -R_n \frac{Z^2}{n^2}$.

For H-atom, Z = 1 and for the ground state, $n = 1$

$\therefore E_1 = -R_H$

For He^+ ion, Z = 2 and for the first excited state, $n = 2$

$$\therefore E_2 = -R_H \frac{2^2}{2^2} = -R_H$$

Hence the required result is proved.

Q. 7. **(*b*) Derive the relationship between the wavelength associated with a moving particle and its kinetic energy.**

or Derive the relationship $\lambda = \frac{h}{\sqrt{2\,m\,(\text{K.E.})}}$

$= -2{\cdot}4 \times 10^{-19}$ J

(*b*) How is the frequency of the matter wave related to the kinetic energy of the particle ?

Ans. (*a*) According to de Broglie equation, $\lambda = \frac{h}{mv}$ ...(*i*)

Further, $\text{K.E.} = \frac{1}{2}mv^2$ or $v = \sqrt{\frac{2\,\text{K.E.}}{m}}$ ...(*ii*)

Substituting in eqn. (*i*), we get

$$\lambda = \frac{h}{m}\sqrt{\frac{m}{2\,\text{K.E.}}} = \frac{h}{\sqrt{2\,m\,(\text{K.E.})}}$$

(*b*) Frequency of the matter wave,

$$\nu = \frac{v}{\lambda} = \frac{v}{h/mv} = \frac{mv^2}{h} = \frac{2\,\text{K.E.}}{h}$$

Thus frequency of the matter wave is directly proportional to the kinetic energy of the material particle.

Q. 8. **For a hydrogen-like particle, derive the following expression**

where v_n is the velocity of the electron at distance r_n from the nucleus, Z is the atomic number of the H-like particle, *m* and *e* are the charge and mass of the electron.

Ans. For H-like particle, force of attraction between the electron and the nucleus = centrifugal force

i.e. $\frac{Ze^2}{r_n^2} = \frac{mv_n^2}{r_n}$

or $v_n^2 = \frac{Ze^2}{mr_n}$ or $v_n = \left(\frac{Ze^2}{mr_n}\right)^{1/2}$

Q. 9. **Calculate the ratio of kinetic energy to potential energy of any hydrogen-like particle.**

Ans. Refer to page 3/61.

Q. 10. **The two extra-nuclear electrons in the 1s orbital of helium have antiparallel spins (↑ ↓). Why not they have parallel spins (↑ ↑) ?** ***(B.I.T. Ranchi 1991)***

Ans. If they had parallel spins, the repulsion will increase. As a result, energy will increase and the stability will decrease.

Q. 11. **The elements P (Atomic weight 39) and Q (Atomic weight 80) contain 20 and 45 neutrons respectively in their nucleus. Give their electronic arrangements separately.** ***(I.S.M. Dhanbad 1991)***

Ans. For element P, A = 39, n = 20. As A = $p + n$, therefore $p = A - n = 39 - 20 = 19$. Hence $e^- = 19$

E.C. = $1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,4s^1$

For element Q, A = 80, n = 45. Hence $p = A - n = 80 - 45 = 35$. So no. of $e^- = 35$. Hence

E.C. = $1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,3d^{10}\,4s^2\,4p_x^2\,4p_y^2\,4p_z^1$

Q. 12. **Give the name and atomic number of the inert gas atom in which the total number of *d*-electrons is equal to the difference between the numbers of total *p* and total *s* electrons.** ***(West Bengal J.E.E. 2003)***

Ans. Electronic configuration of Krypton (Z = 36) is

$_{36}Kr = 1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,3d^{10}\,4s^2\,4p^6$

Total number of *s* electrons = 8,

Total number of *p*-electrons = 18

Difference = 10. Number of *d*-electrons is also = 10.

Q. 13. **What are the total number of orbitals associated with the principal quantum number, *n* = 3 ? Briefly explain.** ***(Bihar C.E.E. 2003)***

Ans. Number of orbitals in *n*th shell = n^2. Hence for $n = 3$, number of orbitals = $3^2 = 9$ (For explanation, see Table 3.3, page 3/40).

Q. 14. **A monoatomic anion of unit charge contains 45 neutrons and 36 electrons. Find the atomic number, mass number of the ion with its identification.** ***(West Bengal J.E.E. 2004)***

Ans. No. of electrons in the monoatomic anion $(X^{-1}) = 36$

$\therefore$ No. of electrons in the monoatomic atom (X) = 35

Atomic No. = No. of protons = No. of electrons in neutral atom = 35

Mass No. = No. of protons + No. of neutrons = 35 + 45 = 80

Hence the ion must be Br^- (bromide ion)

B. PROBLEMS

Problem 1. **Calculate the distance of separation between the second and third orbits of hydrogen atom.**

Solution. For H-atom, the radius of nth orbit is given by $r_n = 0\cdot529 \times n^2$ Å

$$\therefore \quad r_3 - r_2 = 0\cdot529\,(3^2 - 2^2)\ \text{Å}$$

$$= 0\cdot529 \times 5 = \mathbf{2\cdot645\ Å}.$$

Problem 2. **To which orbit the electron in the hydrogen atom will jump after absorbing $1\cdot94 \times 10^{-18}$ J of energy ?**

Solution. Energy of electron in the nth orbit of H-atom is given by $\text{E}_n = -\dfrac{21\cdot8 \times 10^{-19}}{n^2}$ J

$\therefore$ $\text{E}_1 = -21\cdot8 \times 10^{-19}$ J ($\because n = 1$ for ground state of H-atom)

After absorbing $1\cdot94 \times 10^{-8}$ J of energy, the energy of the electron will be

$$= -21\cdot8 \times 10^{-19} + 1\cdot94 \times 10^{-18}\ \text{J}$$

$$= -2\cdot4 \times 10^{-19}\ \text{J}$$

$$\text{Thus } -\frac{21\cdot8 \times 10^{-19}}{n^2} = -2\cdot4 \times 10^{-19}$$

$$\text{or } n^2 = \frac{21\cdot8}{2\cdot4} = 9 \text{ or } n = 3$$

Thus the electron will jump to the **third orbit.**

Problem 3. **An electron in a hydrogen atom in the ground state absorbs energy equal to 1·5 time the minimum energy required to remove the electron from the hydrogen atom. Calculate the wavelength of the electron emitted.**

Solution. Energy required to remove electron from ground state of H-atom = 13·6 eV

$\therefore$ Energy absorbed by the electron

$= 1\cdot5 \times 13\cdot6$ eV $= 20\cdot4$ eV

After the removal of electron from the atom, extra energy which is converted into kinetic energy $= 20\cdot4 - 13\cdot6 = 6\cdot8$ eV

$$\text{Thus } \frac{1}{2}mv^2 = 6\cdot8 \times 1\cdot602 \times 10^{-19}\ \text{J}$$

$$\text{or } v = \sqrt{\frac{2 \times 6\cdot8 \times 1\cdot602 \times 10^{-19}}{9\cdot11 \times 10^{-31}}}$$

$$= \sqrt{2\cdot4 \times 10^{12}} = 1\cdot55 \times 10^6\ \text{ms}^{-1}$$

$$\lambda = \frac{h}{mv}$$

$$= \frac{6\cdot63 \times 10^{-34}\ \text{kg}\,m^2\,s^{-1}}{(9\cdot11 \times 10^{-31}\ \text{kg})\,(1\cdot55 \times 10^6\ \text{ms}^{-1})}$$

$$= \mathbf{4\cdot70 \times 10^{-10}\ m}$$

Problem 4. **When a certain metal was irradiated with a light of frequency $3\cdot2 \times 10^{16}$ Hz, the photoelectrons had twice the kinetic energy as emitted when the same metal was irradiated with light of frequency $2\cdot0 \times 10^{16}$ Hz. Calculate the threshold frequency (ν_0) of the metal.**

Solution. Kinetic energy of photoelectrons emitted $= h\nu - h\nu_0 = h\,(\nu - \nu_0)$

In 1st case, $(\text{K.E.})_1 = h\,(3\cdot2 \times 10^{16} - \nu_0)$

In 2nd case, $(\text{K.E.})_2 = h\,(2\cdot0 \times 10^{16} - \nu_0)$

But $(\text{K.E.})_1 = 2\,(\text{K.E.})_2$ (Given)

$$\therefore \quad h\,(3\cdot2 \times 10^{16} - \nu_0) = 2\,h\,(2\cdot0 \times 10^{16} - \nu_0)$$

$$\text{or} \quad \nu_0 = 4 \times 10^{16} - 3\cdot2 \times 10^{16}$$

$$= 0\cdot8 \times 10^{16} = \mathbf{8 \times 10^{15}\ Hz.}$$

Problem 5. **The wavelength of H_α line of Balmer series is 6500 Å. What is the wavelength of H_β line of Balmer series ?**

Solution. H_α line of Balmer series is obtained when $n_1 = 2, n_2 = 3$

H_β line of Balmer series is obtained when $n_1 = 2$, $n_2 = 4$

$$\text{Thus } \bar{\nu}_{\text{H}_\alpha} = \frac{1}{\lambda_{\text{H}_\alpha}} = \text{R}_\text{H}\left(\frac{1}{2^2} - \frac{1}{3^2}\right) = \text{R}_\text{H}\left(\frac{1}{4} - \frac{1}{9}\right)$$

$$= \text{R}_\text{H} \times \frac{5}{36} \qquad ...(i)$$

$$\bar{\nu}_{\text{H}_\beta} = \frac{1}{\lambda_{H_\beta}} = \text{R}_\text{H}\left(\frac{1}{2^2} - \frac{1}{4^2}\right) = \text{R}_\text{H}\left(\frac{1}{4} - \frac{1}{16}\right)$$

$$= \text{R}_\text{H} \times \frac{3}{16} \qquad ...(ii)$$

Dividing eqn. (*i*) by eqn. (*iii*), we get

$$\frac{\lambda_{\text{H}_\beta}}{\lambda_{\text{H}_\alpha}} = \frac{5}{36} \times \frac{16}{3} = \frac{20}{27}$$

$$\therefore \lambda_{\text{H}_\beta} = \frac{20}{27} \times \lambda_{\text{H}_\alpha} = \frac{20}{27} \times 6500\ \text{Å} = \mathbf{4814\cdot8\ Å.}$$

Problem 6. **The atomic spectrum of hydrogen is found to contain a series of lines at wavelengths 656·46, 486·27, 434·17 and 410·29 nm. What will be the wavelength of the next line in the series ?**

Solution. The given wavelengths lie in the visible region. Hence they are expected to belong to Balmer series. Thus, $n_1 = 2$. Let us calculate n_2 for the shortest wavelength viz. 410·29 nm

$$\frac{1}{\lambda} = \text{R}_\text{H}\left(\frac{1}{2^2} - \frac{1}{n_2^2}\right)$$

$$\frac{1}{410\cdot29 \times 10^{-7}\ \text{cm}} = 109{,}677\ \text{cm}^{-1}\left(\frac{1}{4} - \frac{1}{n_2^2}\right)$$

This on solving gives $n_2 = 6$

Thus the next line will be obtained for jump from $n_2 = 7$ to $n_1 = 2$, so that

$$\frac{1}{\lambda} = 109{,}677 \text{ cm}^{-1}\left(\frac{1}{2^2} - \frac{1}{7^2}\right)$$

$$= 109{,}677 \times \left(\frac{1}{4} - \frac{1}{49}\right) \text{ cm}^{-1}$$

$$= 109{,}677 \times \frac{45}{196} \text{ cm}^{-1} = 25180 \cdot 9 \text{ cm}^{-1}$$

$$\text{or } \lambda = \frac{1}{25180 \cdot 9 \text{ cm}^{-1}} = 397 \cdot 1 \times 10^{-7} \text{ cm}$$

$$= \mathbf{397 \cdot 1 \text{ nm.}}$$

Problem 7. **Calculate the radius of the first orbit of electron in an atom of hydrogen.** ***(I.S.M. Dhanbad 1985)***

Solution. As derived on page 3/61, from eqn. (*iii*)

$$\text{Radius } r = \frac{n^2 h^2}{4\pi^2 m Ze^2}$$

$$= \frac{1^2 \times (6 \cdot 63 \times 10^{-27} \text{ erg sec})^2}{4 \times \left(\frac{22}{7}\right)^2 \times (9 \cdot 11 \times 10^{-28} g) \times (4 \cdot 8 \times 10^{-10} \text{ esu})^2}$$

$$= 0 \cdot 53 \times 10^{-8} \text{ cm} = 0 \cdot 53 \text{Å}$$

Problem 8. **Calculate the energy required for the process**

$$\text{He}^+ (g) \longrightarrow \text{He}^{2+} (g) + e^-$$

The ionization energy for the H-atom in the ground state is $2 \cdot 18 \times 10^{-18}$ J atom^{-1}. (*N.C.E.R.T.*)

Solution. The energy of the electron in the *n*th orbit of H- like particles is

$$E_n = -\frac{2\pi^2 me^4 Z^2}{n^2 h^2} = -K \times \frac{Z^2}{n^2} \quad (K = \text{constant})$$

$$\text{I.E.}_H = E_\infty - E_1 = 0 - \left(-\frac{K \times 1^2}{1^2}\right) = +K \quad ...(i)$$

The energy required for the given process is I.E. of He^+ for which Z = 2.

As He^+ is hydrogen-like particle

$$\therefore \text{I.E.}_{He^+} = E_\infty - E_1$$

$$= 0 - \left(-\frac{K \times 2^2}{1^2}\right) = +4K \quad ...(ii)$$

From eqns. (*i*) and (*ii*), $\frac{\text{I.E.}_{He^+}}{\text{I.E.}_H} = 4$

i.e. $\text{I.E.}_{He^+} = 4 \times \text{I.E.}_H$

$$= 4 \times 2 \cdot 18 \times 10^{-18} \text{ J}$$

$$= \mathbf{8 \cdot 72 \times 10^{-18} \text{ J.}}$$

Problem 9. **Sodium street lamp gives off a characteristic yellow light of wavelength 588 nm. Calculate the energy per mole (in kJ/mol) of these photons.** ***(Bihar C.E.E. 2003)***

Solution. $\lambda = 588 \text{ nm} = 588 \times 10^{-9}\ m$, $c = 3 \times 10^8 \text{ ms}^{-1}$

$$E = N_0 h\nu = N_0 h \frac{c}{\lambda}$$

$$= \frac{(6 \cdot 02 \times 10^{23}) \times (6 \cdot 63 \times 10^{-34}) \times (3 \times 10^8)}{588 \times 10^{-9}} \text{ J mol}^{-1}$$

$$= 2 \cdot 036 \times 10^6 \text{ J mol}^{-1}$$

$$= 2 \cdot 036 \times 10^3 \text{ kJ mol}^{-1}.$$

Problem 10. **Calculate the radius of Bohr's fifth orbit for hydrogen atom.** (*N.C.E.R.T.*)

Solution. For H-atom, $r_n = 0 \cdot 529 \times n^2$ Å

$$\therefore r_5 = 0 \cdot 529 \times 5^2 = 13 \cdot 225 \text{ Å} = \mathbf{1 \cdot 3225 \text{ nm.}}$$

Problem 11. **The angular momentum of an electron in Bohr's orbit of hydrogen atom is $4 \cdot 22 \times 10^{-34}$ kg m^2 s^{-1}. Calculate the wavelength of the spectral line when the electron falls from this level to the next lower level.**

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

$$= 4 \cdot 22 \times 10^{-34} \text{ kg } m^2 s^{-1} \quad \text{(Given)}$$

$$\therefore n = 4 \cdot 22 \times 10^{-34} \times \frac{2\pi}{h}$$

$$= \frac{2 \times 4 \cdot 22 \times 10^{-34} \times 3 \cdot 14}{6 \cdot 626 \times 10^{-34}} = 4$$

When the electron jumps from $n = 4$ to $n = 3$, the wavelength of the spectral line can be calculated as follows :

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

$$= 109{,}677 \text{ cm}^{-1}\left(\frac{1}{3^2} - \frac{1}{4^2}\right)$$

$$= 109677 \times \left(\frac{1}{9} - \frac{1}{16}\right) = 109677 \times \frac{7}{144} \text{ cm}^{-1}$$

$$\text{or } \lambda = \frac{144}{109677 \times 7} \text{ cm} = 1 \cdot 88 \times 10^{-4} \text{ cm.}$$

I.I.T. (MAINS) SPECIAL

Problem 1. **Find the quantum number 'n' corresponding to the excited state of He$^+$ ion if on transition to the ground state that ion emits two photons in succession with wavelengths 108·5 and 30·4 nm respectively.**

Solution. Suppose the electron in the excited state is present in the shell n_2. First it falls from n_2 to n_1 and then from n_1 to ground state (for which $n = 1$). Thus the two transitions involved and the corresponding wavelengths emitted are

$$(i)\ n_2 \longrightarrow n_1, \lambda_1 = 108{\cdot}5 \text{ nm} = 108{\cdot}5 \times 10^{-7} \text{ cm}$$

$$(ii)\ n_1 \longrightarrow 1, \lambda_2 = 30{\cdot}4 \text{ nm} = 30{\cdot}4 \times 10^{-7} \text{ cm}$$

Applying Rydberg's formula first to case (*ii*), we get

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

$$\text{i.e.}\quad \frac{1}{30{\cdot}4 \times 10^{-7}} = 109677 \times 2^2 \times \left(\frac{1}{1^2} - \frac{1}{n_1^2}\right)$$

$$\text{or}\quad \frac{1}{n_1^2} = 1 - \frac{1}{30{\cdot}4 \times 10^{-7} \times 4 \times 109677}$$

$$= 1 - 0{\cdot}75 = 0{\cdot}25$$

$$\text{or}\quad n_1^2 = \frac{1}{0{\cdot}25} = 4 \quad \text{or} \quad n_1 = 2$$

Applying Rydberg's formula now to case (*i*), we get

$$\frac{1}{108{\cdot}5 \times 10^{-7}} = RZ^2 \left(\frac{1}{2^2} - \frac{1}{n_2^2}\right)$$

$$= 109677 \times 2^2 \times \left(\frac{1}{4} - \frac{1}{n_2^2}\right)$$

$$\text{or}\quad \frac{1}{n_2^2} = \frac{1}{4} - \frac{1}{108{\cdot}5 \times 10^{-7} \times 4 \times 109677}$$

$$= 0{\cdot}25 - 0{\cdot}21 = 0{\cdot}04$$

$$\text{or}\quad n_2^2 = \frac{1}{0{\cdot}04} = 25 \quad \text{or} \quad n_2 = 5.$$

Problem 2. **1 *g* hydrogen atoms are excited by radiations. The study of spectrum indicates that 27% of the atoms are in 3rd energy level and 15% of atoms are in 2nd energy level and the rest in the ground state. Ionization potential of hydrogen is 13·6 *eV*. Calculate**

(*a*) number of atoms present in energy level 1st, 2nd and 3rd.

(*b*) total energy released in joules when all atoms return to ground state.

Solution. By mole concept, 1 *g* of hydrogen atoms contain = $6{\cdot}02 \times 10^{23}$ atoms

∴ 1·8 *g* of hydrogen atoms contain H-atoms

$$= 6{\cdot}02 \times 10^{23} \times 1{\cdot}8$$

$$= 10{\cdot}84 \times 10^{23}$$

Atoms present in 3rd energy level

$$= \frac{27}{100} \times 10{\cdot}84 \times 10^{23} = \mathbf{292{\cdot}68 \times 10^{21}}$$

Atoms present in 2nd energy level

$$= \frac{15}{100} \times 10{\cdot}84 \times 10^{23} = \mathbf{162{\cdot}6 \times 10^{21}}$$

Atoms present in 1st energy level

$$= \frac{58}{100} \times 10{\cdot}84 \times 10^{23} = \mathbf{628{\cdot}72 \times 10^{21}}$$

Ionization potential of H = 13·6 *eV* means that

$$E_1 = -13{\cdot}6\, eV,\ E_2 = -\frac{13{\cdot}6}{2^2}\, eV,$$

$$E_3 = -\frac{13{\cdot}3}{3^2}\, eV$$

Energy released from all atoms when electrons return from 3rd level to 1st level

$$= (E_3 - E_1) \times 292{\cdot}68 \times 10^{21}$$

$$= \left(-\frac{13{\cdot}6}{9} + 13{\cdot}6\right) \times 292{\cdot}68 \times 10^{21}\, eV$$

$$= 3{\cdot}537 \times 10^{24}\, eV$$

Energy released from all atoms when electrons return from 2nd level to 1st level

$$= (E_2 - E_1) \times 162{\cdot}6 \times 10^{21}$$

$$= \left(\frac{-13{\cdot}6}{4} + 13{\cdot}6\right) \times 162{\cdot}6 \times 10^{21}\, eV$$

$$= 1{\cdot}659 \times 10^{24}\, eV$$

∴ Total energy released

$$= (3{\cdot}537 + 1{\cdot}659) \times 10^{24}\, eV = 5{\cdot}196 \times 10^{24}\, eV$$

$$= (5{\cdot}196 \times 10^{24}) \times (1{\cdot}602 \times 10^{-19})\text{ J}$$

$$= 8{\cdot}3239 \times 10^{5}\text{ J} = \mathbf{832{\cdot}4\ kJ}.$$

Problem 3. **Which state of triply ionized beryllium (Be^{3+}) has the same orbital radius as that of the ground state of hydrogen atom ?**

Solution. For H-like particles, $r_n = 0{\cdot}529 \times \dfrac{n^2}{Z}$

For ground state of H-atom, Z = 1, n = 1, $r_1 = 0{\cdot}529$ Å

For Be^{3+} (Z = 4), if nth orbit has the same radius, then

$$0\cdot529 \times \frac{n^2}{4} = 0\cdot529 \text{ or } n^2 = 4 \text{ i.e. } n = 2$$

Thus, second orbit of Be^{3+} ion has same radius as that of ground state (1st orbit) of H-atom.

Problem 4. **An electron in a certain Bohr orbit has velocity 1/275 of the velocity of light. In which orbit the electron is revolving ?**

Solution. Velocity of electron

$$= \frac{1}{275} \times 3 \times 10^{10} \text{ cm } s^{-1}$$

$$= 1\cdot09 \times 10^{8} \text{ cm } s^{-1}$$

Velocity of electron in nth orbit of H-like particles in C.G.S. units is given by

$$v_n = \frac{2\,\pi\,Ze^2}{nh}$$

Putting Z = 1 for H and $e = 4\cdot80 \times 10^{-10}$ *esu* (in C.G.S. units) and $h = 6\cdot626 \times 10^{-27}$ erg sec, we get

$$v_n = \frac{2 \times 3\cdot14 \times (4\cdot80 \times 10^{-10})^2}{n \times (6\cdot626 \times 10^{-27})} = \frac{2\cdot18 \times 10^{8}}{n}$$

$$\therefore \quad \frac{2\cdot18 \times 10^{8}}{n} = 1\cdot09 \times 10^{8} \quad \textit{(calculated above)}$$

$$\therefore \quad n = 2$$

Problem 5. **A laser emits monochromatic radiation of wavelength 663 nm. If it emits 10^{15} quanta per second per square metre, calculate the power output of the laser in joule per square metre per second.**

Solution. Energy of one quantum $= h\nu = h\,\frac{c}{\lambda}$

$$= \frac{(6\cdot63 \times 10^{-34} \text{ Js})\,(3 \times 10^{8} \text{ ms}^{-1})}{(663 \times 10^{-9}\,m)}$$

$$= 3 \times 10^{-19} \text{ J}$$

Energy emitted per sec per square metre = No. of quanta emitted per sq. metre per sec × Energy of one quantum

$$= 10^{15} \times 3 \times 10^{-19} \text{ J m}^{-2} \text{ s}^{-1}$$

$$= \mathbf{3 \times 10^{-4}\ J\ m^{-2}\ s^{-1}}$$

Problem 6. **Calculate the frequency of the spectral line emitted when the electron in $n = 3$ in hydrogen atom de-excites to the ground state (Rydberg constant = 109,737 cm^{-1})** ***(Roorkee 1985)***

Solution. $\bar{\nu} = R\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) = 109737\left(\frac{1}{1^2} - \frac{1}{3^2}\right)$

$$= 97544 \text{ cm}^{-1}$$

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

$$= (3 \times 10^{10} \text{ cm s}^{-1})\,(97544 \text{ cm}^{-1})$$

$$= \mathbf{2\cdot9263 \times 10^{15}\ s^{-1}}$$

Problem 7. **The ionization energy of hydrogen atom is 13·6 eV. What will be the ionization energy of He^+ and Li^{2+} ions ?** ***(Roorkee 1986)***

Solution. $E_n = -\frac{2\pi^2\,m\,Z^2e^4}{n^2h^2}$ for hydrogen like particles

$$\text{I.E.} = E_\infty - E_1$$

$$= 0 - \left(-\frac{2\pi^2\,m\,Z^2\,e^4}{h^2}\right) = \frac{2\pi^2\,m\,Z^2\,e^4}{h^2}$$

$$\text{For H, } Z = 1.\ \text{I.E.} = \frac{2\pi^2\,m\,e^4}{h^2} = 13\cdot6 \text{ eV}$$

...(Given)

$$\text{For } He^+,\ Z = 2, \text{I.E.} = 13\cdot6 \times Z^2$$

$$= 13\cdot6 \times 2^2 = \mathbf{54\cdot4\ eV}$$

$$\text{For } Li^{2+},\ Z = 3, \text{I.E.} = 13\cdot6 \times 3^2 = \mathbf{122\cdot4\ eV}$$

Problem 8. **Calculate the velocity (cm/sec) of an electron placed in the third orbit of hydrogen atom. Also calculate the number of revolutions per second that this electron makes around the nucleus.** ***(Roorkee 1987)***

Solution. As derived on page 3/61

$$v = \frac{2\pi\,Ze^2}{nh} = \frac{2 \times 3\cdot14 \times 1 \times (4\cdot8 \times 10^{-10})^2}{3 \times 6\cdot63 \times 10^{-27}}$$

$$= \mathbf{7\cdot27 \times 10^{7}\ cm/sec}$$

$$\text{No. of revolutions per sec.} = \frac{v}{2\pi r}$$

$$= \frac{v}{2\pi\left(\frac{n^2\,h^2}{4\,\pi^2\,m\,Ze^2}\right)} \quad \text{(Eqn. (\textit{iii}), page 3/61)}$$

$$= \frac{4\,\pi^2\,mv\,Ze^2}{2\pi\,n^2\,h^2} = \frac{2\,\pi\,mv\,Ze^2}{n^2\,h^2}$$

$$= \frac{2 \times 3\cdot14 \times 9\cdot11 \times 10^{-28} \times 7\cdot27 \times 10^{7} \times 1 \times (4\cdot8 \times 10^{-10})^2}{(3)^2 \times (6\cdot63 \times 10^{-27})^2}$$

$$= \mathbf{2\cdot42 \times 10^{14}}$$

Problem 9. **Calculate the wavelength and energy of radiation emitted for the electronic transition from infinity (∞) to stationary state one of the hydrogen atom (Rydberg constant = $1\cdot09678 \times 10^{7}$ m^{-1}, $h = 6\cdot6256 \times 10^{-34}$ Js).** ***(Roorkee 1988)***

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

$$= 1\cdot009678 \times 10^{7}\left(\frac{1}{1^2} - \frac{1}{\infty^2}\right) \text{ m}^{-1}$$

$$= 1\cdot09678 \times 10^{7} \text{ m}^{-1}$$

$$\lambda = \frac{1}{\bar{\nu}} = \frac{1}{1\cdot09678 \times 10^{7}} = \mathbf{9\cdot11 \times 10^{-8}\ m}$$

$$E = h\nu = h \cdot \frac{c}{\lambda} = 6 \cdot 6256 \times 10^{-34} \times \frac{3 \times 10^{8}}{9 \cdot 11 \times 10^{-8}}$$

$$= 2 \cdot 179 \times 10^{-18}\ \text{J}$$

$$= \frac{2 \cdot 179 \times 10^{-18}}{1 \cdot 6 \times 10^{-19}}\ \text{eV}$$

$$= 13 \cdot 6\ \text{eV} \quad (\because 1\ \text{eV} = 1 \cdot 6 \times 10^{-19}\ \text{J})$$

Problem 10. **(*a*) Electromagnetic radiation of wavelength 242 nm is just sufficient to ionize the sodium atom. Calculate the ionization energy of sodium in kJ mol^{-1}.**

(*b*) The ionization energy of He^{+} is 19·6 × 10^{-18} J atom^{-1}. Calculate the energy of the first stationary state of Li^{2+}. ***(Roorkee 1989, 92)***

Solution. (*a*) We have to calculate energy of radiation with λ = 242 nm = 242 × 10^{-9} m.

$$E = h\nu = h\frac{c}{\lambda} = \frac{(6 \cdot 6256 \times 10^{-34}\ \text{Js})(3 \times 10^{8}\ \text{m s}^{-1})}{(242 \times 10^{-9}\ \text{m})}$$

$$= 0 \cdot 0821 \times 10^{-17}\ \text{J/atom}$$

$$= (0 \cdot 0821 \times 10^{-17}) \times (6 \cdot 023 \times 10^{23})\ \text{J mol}^{-1}$$

$$= 0 \cdot 494 \times 10^{6}\ \text{J mol}^{-1} = \mathbf{494\ kJ\ mol^{-1}}$$

(*b*) As discussed on page 3/29

$$\text{I.E. of H-like particle} = \text{I.E. of H} \times Z^2$$

$$= E \times Z^2$$

$$\therefore \quad \text{I.E. (He}^{+}) = E \times 2^2 \quad (Z \text{ for He} = 2)$$

$$\text{I.E. (Li}^{2+}) = E \times 3^2 \quad (Z \text{ for Li} = 3)$$

$$\therefore \quad \frac{\text{I.E.(He}^{+})}{\text{I.E.(Li}^{2+})} = \frac{4}{9}$$

$$\text{or I.E. (Li}^{2+}) = \frac{9}{4} \times \text{I.E. (He}^{+})$$

$$= \frac{9}{4} \times 19 \cdot 6 \times 10^{-18}\ \text{J atom}^{-1}$$

$$= \mathbf{4 \cdot 41 \times 10^{-17}\ J\ atom^{-1}}$$

Problem 11. **According to Bohr's theory, the electronic energy of hydrogen atom in the Bohr's orbit is given by**

$$E_n = -\frac{21 \cdot 79 \times 10^{-19}}{n^2}\ \text{J}$$

Calculate the lowest wavelength of light that will be needed to remove an electron from the third Bohr orbit of He^{+} ions. ***(I.I.T. 1990)***

Solution. Energy of the *n*th orbit of H-like particle

$$= -\frac{21 \cdot 79 \times 10^{-19}}{n^2} \times Z^2\ \text{J}$$

∴ Energy of the 3rd orbit of He^{+} ion

$$= -\frac{21 \cdot 79 \times 10^{-19} \times 2^2}{3^2}\ \text{J} = -9 \cdot 68 \times 10^{-19}\ \text{J}$$

Energy required to remove the electron

$$= 9 \cdot 68 \times 10^{-19}\ \text{J}$$

$$\text{Now} \quad E = h\nu = h\frac{c}{\lambda}$$

$$\text{or} \quad \lambda = \frac{hc}{E} = \frac{6 \cdot 62 \times 10^{-34} \times 3 \times 10^{8}}{9 \cdot 68 \times 10^{-19}}$$

$$= \mathbf{2 \cdot 052 \times 10^{-7}\ m.}$$

Problem 12. **Calculate the frequency, energy and wavelength of the radiation corresponding to the spectral line of lowest frequency in Lyman series in the spectra of hydrogen atom. Also calculate the frequency for the corresponding line in the spectra of Li^{2+} ion.**

($R_H = 1 \cdot 09678 \times 10^{7}\ \text{m}^{-1}$, $c = 3 \times 10^{8}\ \text{m s}^{-1}$,

$h = 6 \cdot 625 \times 10^{-24}$ Js) ***(Roorkee 1991)***

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

For lowest frequency in Lyman series,

$$n_1 = 1, n_2 = 2$$

$$\therefore \quad \bar{\nu} = 1 \cdot 09677 \times 10^{7}\left(\frac{1}{1^2} - \frac{1}{2^2}\right)$$

$$= 0 \cdot 82258 \times 10^{7}\ \text{m}^{-1}$$

$$\therefore \quad \lambda = \frac{1}{\bar{\nu}} = \frac{1}{0 \cdot 82258 \times 10^{7}}\ m$$

$$= \mathbf{1 \cdot 216 \times 10^{-7}\ m}$$

$$\nu = \frac{c}{\lambda} = c \times \bar{\nu} = 3 \times 10^{8} \times 0 \cdot 82258 \times 10^{7}$$

$$= \mathbf{2 \cdot 47 \times 10^{15}\ s^{-1}}$$

$$E = h\nu = 6 \cdot 625 \times 10^{-34} \times 2 \cdot 47 \times 10^{15}\ \text{J}$$

$$= \mathbf{16 \cdot 36 \times 10^{-19}\ J}$$

Problem 13. **Estimate the difference in energy between the 1st and 2nd Bohr orbit for a hydrogen atom. At what minimum atomic number, a transition from *n* = 2 to *n* = 1 energy level would result in the emission**

of X-rays with $\lambda = 3\cdot0 \times 10^{-8}$ m ? Which hydrogen atom-like species does this atomic number correspond to ? *(I.I.T. 1993)*

Solution. $E_n = -\dfrac{21\cdot79 \times 10^{-19}}{n^2}$ J

$$\therefore \; E_2 - E_1 = -\,21\cdot79 \times 10^{-19}\left(\frac{1}{2^2} - \frac{1}{1^2}\right)$$

$$= 16\cdot34 \times 10^{-19}\text{ J.}$$

For H-like particles, $E_n = -\dfrac{21\cdot79 \times 10^{-19} \times Z^2}{n^2}$ J

For a transition from $n = 2$ to $n = 1$,

$$\Delta E = 21\cdot79 \times 10^{-19} \times Z^2\left(\frac{1}{1^2} - \frac{1}{2^2}\right)$$

$$= 16\cdot34 \times 10^{-19}\, Z^2 \text{ J}$$

$$\Delta E = h\nu = h\frac{c}{\lambda}$$

$$\therefore \; 16\cdot34 \times 10^{-19} Z^2 = 6\cdot626 \times 10^{-34} \times \frac{3 \times 10^8}{3 \times 10^{-8}}$$

or $\quad Z^2 = \dfrac{6\cdot626 \times 10^{-18}}{16\cdot34 \times 10^{-19}} = 4\cdot06$ or $Z = 2$.

H-atom like species that corresponds to $Z = 2$ is He^+.

Problem 14. **What transition in the hydrogen spectrum would have the same wavelength as the Balmer transition, $n = 4$ to $n = 2$ of He^+ spectrum ?** *(I.I.T. 1993, N.C.E.R.T.)*

Solution. For H-like particles in general

$$\bar{\nu} = \frac{2\pi^2 m Z^2 e^4}{ch^3}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) = RZ^2\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

∴ For He^+ spectrum, for Balmer transition, $n = 4$ to $n = 2$.

$$\bar{\nu} = \frac{1}{\lambda} = RZ^2\left(\frac{1}{2^2} - \frac{1}{4^2}\right)$$

$$= R \times 4 \times \frac{3}{16} = \frac{3R}{4}$$

For hydrogen spectrum

$$\bar{\nu} = \frac{1}{\lambda} = R\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) = \frac{3}{4}R$$

or $\quad \dfrac{1}{n_1^2} - \dfrac{1}{n_2^2} = \dfrac{3}{4}$

which can be so for $n_1 = 1$ and $n_2 = 2$

i.e. the transition is from $n = 2$ to $n = 1$

Problem 15. **Calculate the energy emitted when electrons of 1·0 g atom of hydrogen undergo transition giving the spectral line of lowest energy in the visible region of its atomic spectrum ($R_H = 1\cdot1 \times 10^7$ m^{-1}, $c = 3 \times 10^8$ ms^{-1}, $h = 6\cdot62 \times 10^{-34}$ Js)** *(Roorkee 1993)*

Solution. For lowest energy in the visible region of atomic spectrum (Balmer series), $n_1 = 2$, $n_2 = 3$.

$$\bar{\nu} = R\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) = 1\cdot1 \times 10^7\left(\frac{1}{2^2} - \frac{1}{3^2}\right)$$

$$= 1\cdot1 \times 10^7\left(\frac{1}{4} - \frac{1}{9}\right) = 1\cdot1 \times 10^7 \times \frac{5}{36}$$

$$= 0\cdot1528 \times 10^7\,\text{m}^{-1}$$

$$E = h\nu = h\frac{c}{\lambda} = hc\,\bar{\nu}$$

$$= 6\cdot62 \times 10^{-34} \times 3 \times 10^8 \times 0\cdot01528 \times 10^7$$

$$= 3\cdot0346 \times 10^{-19}\text{ J/g atom}$$

$$= (3\cdot046 \times 10^{-19}) \times (6\cdot02 \times 10^{23})\text{ J/atom}$$

$$= 18\cdot268 \times 10^4\text{ J/g atom}$$

$$= \mathbf{182\cdot68\ kJ/g\ atom.}$$

Problem 16. **Find out the number of waves made by a Bohr electron in its 3rd orbit.** *(I.I.T. 1994)*

Solution. No. of waves in any orbit

$$= \frac{\text{Circumference of that orbit}}{\text{Wavelength}}$$

$$= \frac{2\pi r}{\lambda} = \frac{2\pi r}{(h/mv)} = \frac{2\pi}{h}(mvr) = \frac{2\pi}{h}\frac{nh}{2\pi} = n$$

Thus, the number of waved in 3rd orbit = 3.

Problem 17. **A bulb emits light of wavelength 4500 Å. The bulb is rated as 150 watt and 8% of the eergy is emitted as light. How many photons are emitted by the bulb per second.** *(I.I.T. 1995)*

Solution. Electrical energy in joules = Power in watts × Time in seconds

Thus 150 watt = 150 joules of energy emitted per second.

∴ Energy emitted as light

$$= \frac{8}{100} \times 150 = 12\text{ J}$$

$$E = nh\nu = nh\frac{c}{\lambda}$$

$$\therefore \; n = \frac{E \times \lambda}{h \times c}$$

$$= \frac{(12\text{ J}) \times (4500 \times 10^{-10}\, m)}{(6\cdot626 \times 10^{-34}\text{ Js}) \times (3 \times 10^{8}\text{ ms}^{-1})}$$

$$= 2\cdot717 \times 10^{19}.$$

Problem 18. **Calculate the wavelength of the radiation emitted producing a line in the Lyman series when an electron falls from fourth stationary state in hydrogen atom. ($R_H = 1\cdot1 \times 10^7\text{ m}^{-1}$)** ***(Roorkee 1995)***

Solution. For Lyman series, $n_1 = 1, n_2 = 4$ (Given)

Applying Rydberg's formula, $\bar{\nu} = R\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$

$$\therefore \quad \bar{\nu} = 1\cdot1 \times 10^7 \left(\frac{1}{1^2} - \frac{1}{4^2}\right)$$

$$= 1\cdot1 \times 10^7 \times \frac{15}{16}\text{ m}^{-1}$$

$$\therefore \lambda = \frac{1}{\bar{\nu}} = \frac{16}{1\cdot1 \times 10^7 \times 15}\, m$$

$$= 9\cdot697 \times 10^{-8}\text{ m} = \mathbf{96\cdot97\ nm}$$

Problem 19. **Calculate the wave number for the shortest wave length transition in the Balmer series of atomic hydrogen.** ***(I.I.T. 1996)***

Solution. For Balmer series, $n_1 = 2$. Hence

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

$\bar{\nu} = \frac{1}{\lambda}$. Hence λ will be shortest when $\bar{\nu}$ is largest which in turn will be largest if n_2 is highest *i.e.* $n_2 = \infty$.

Hence $\bar{\nu} = 109,677\left(\frac{1}{2^2} - \frac{1}{\infty^2}\right)$

$$= \mathbf{27419\cdot25\ cm^{-1}}$$

Problem 20. **Calculate the energy required to excite one litre of hydrogen gas at 1 atm and 298 K to the first excited state of atomic hydrogen. The energy for the dissociation of H—H bonds is 436 kJ mol^{-1}.** ***(I.I.T. 2000)***

Solution. No. of moles of H_2 gas, $n = \frac{PV}{RT}$

$$= \frac{1 \times 1}{0\cdot0821 \times 298} = 0\cdot0409$$

∴ Energy required to dissociate them into atoms

$$= 0\cdot0409 \times 436 = 17\cdot83\text{ kJ}$$

No. of moles of H atom $= 2 \times 0\cdot0409 = 0\cdot0818$

$$E_n = -\frac{1312}{n^2}\text{ kJ mol}^{-1}$$

∴ Energy required for excitation of 0·0818 moles of H-atoms from ground state to first excited state

$$= (E_2 - E_1) \times 0\cdot0818\text{ kJ}$$

$$= \left[-\frac{1312}{2^2} - \left(-\frac{1312}{1^2}\right)\right] \times 0\cdot0818\text{ kJ}$$

$$= 80\cdot49\text{ kJ}$$

∴ Total energy required $= 17\cdot83 + 80\cdot49 = \mathbf{98\cdot32\ kJ}$.

Problem 21. **Calculate the energy associated with the first orbit of He$^+$. Also calculate the radius of this orbit.**

Solution. $E_n = -\frac{21\cdot8 \times 10^{-19}\, Z^2}{n^2}$ J

$$= -\frac{21\cdot8 \times 10^{-19} \times 2^2}{1^2} = -87\cdot2 \times 10^{-19}\text{ J}$$

$$r_n = \frac{0\cdot529 \times n^2}{Z}\text{ Å}$$

$$= \frac{0\cdot529 \times 1^2}{2} = 0\cdot2645\text{ Å}.$$

Problem 22. **Wavelength of high energy transition of H-atoms is 91·2 nm. Calculate the corresponding wavelength of He$^+$ ion.** ***(I.I.T. 2003)***

Solution. For H-like particles,

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

For H atom, Z = 1

$$\therefore \quad \frac{1}{\lambda_H} = R\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \times 1^2$$

For He$^+$ ion, Z = 2. Hence for the same transition,

$$\frac{1}{\lambda_{He^+}} = R\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \times 2^2$$

$$\therefore \quad \frac{1/\lambda_H}{1/\lambda_{He^+}} = \frac{1^2}{2^2} = \frac{1}{4} \quad\text{or}\quad \frac{\lambda_{He^+}}{\lambda_H} = \frac{1}{4}$$

$$\therefore \quad \lambda_{He^+} = \frac{\lambda_H}{4} = \frac{91\cdot2}{4} = \mathbf{22\cdot8\ nm}.$$

Problem 23. **Find the wavelength of 100 g particle moving with velocity 100 ms^{-1}.** ***(I.I.T. 2004)***

Solution. $\lambda = \frac{h}{mv} = \frac{6\cdot626 \times 10^{-34}\text{ kg}\, m^2 s^{-1}}{0\cdot1\text{ kg} \times 100\text{ ms}^{-1}}$

$$= 6\cdot626 \times 10^{-35}\, m.$$

MULTIPLE CHOICE QUESTIONS

For CBSE– PMT (Preliminary), IIT Screening, AIEEE, AIIMS, AFMC, DPMT, CPMT, BHU and All Other Competitive Examinations

1. The charge on the electron was found by
   (*a*) J.J. Thomson (*b*) Millikan
   (*c*) Faraday (*d*) Goldstein.

2. The discovery of nucleus was done by
   (*a*) J.J. Thomson (*b*) Chadwick
   (*c*) Rutherford (*d*) Moseley.

3. When α-rays strike a thin foil of gold
   (*a*) Most of the α-rays are deflected back
   (*b*) All the α-rays pass through the foil
   (*c*) Most of the α-rays are deflected through small angle
   (*d*) Most of the α-rays pass through without any deflection.

4. The series of lines present in the visible region of the hydrogen spectrum is
   (*a*) Lyman (*b*) Balmer
   (*c*) Paschen (*d*) Brackett.

5. Paschen series are produced when electrons from the outer orbits jump to
   (*a*) 2nd orbit (*b*) 3rd orbit
   (*c*) 4th orbit (*d*) 5th orbit.

6. The electronic configuration of an element is $1s^2\,2s^2\,2p^3$. The number of unpaired electrons in this atom are
   (*a*) 3 (*b*) 5 (*c*) 7 (*d*) 1.

7. Which of the following is the correct electronic configuration of scandium (atomic number = 21)?
   (*a*) $1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,3d^3$
   (*b*) $1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,3d^1\,4s^2$
   (*c*) $1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,3d^2\,4s^1$
   (*d*) $1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,4s^2\,4p^1$.

8. Which of the following is the correct electronic configuration of Fe^{2+} ion (Z for Fe = 26) ?
   (*a*) $1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,3d^4\,4s^2$
   (*b*) $1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,3d^6$
   (*c*) $1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,4s^2\,4p^4$
   (*d*) $1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,3d^5\,4s^1$.

9. The ratio of energy of photon of λ = 2000 Å to that of λ = 4000 Å is
   [✓ (*a*) 2] (*b*) 1/4
   (*c*) 4 (*d*) $\frac{1}{2}$. *(I.I.T. 1980)*

10. Any *p*-orbital can accommodate upto
    (*a*) four electrons
    (*b*) two electrons with parallel spin
    [✓ (*c*) six electrons]
    [✓ (*d*) two electrons with anti-parallel spin.] *(I.I.T. 1983)*

11. Rutherford's scattering experiment is related to the size of the
    [✓ (*a*) nucleus] (*b*) atom
    (*c*) electron (*d*) neutron. *(I.I.T. 1983)*

12. When α-particles are sent through a thin metal foil, most of them go straight through the foil because (one or more)
    (*a*) α-particles are much heavier than electrons
    (*b*) α-particles are positively charged
    [✓ (*c*) Most part of atom is empty space]
    (*d*) α-particles move with high speed. *(I.I.T. 1984)*

13. ✓ The correct set of quantum numbers for the unpaired electron of Cl atom is
    (*a*) 2, 0, 0, $+\frac{1}{2}$ (*b*) 2, 1, —1, $+\frac{1}{2}$
    [✓ (*c*) 3, 1, 1, $\pm\frac{1}{2}$] (*d*) 3, 0, 0, $\pm\frac{1}{2}$. *(I.I.T. 1989)*

14. The outer shell configuration of the most electronegative element is
    (*a*) $ns^2\,np^3$ (*b*) $ns^2\,np^4$
    [✓ (*c*) $n^2\,np^5$] (*d*) $ns^2\,np^6$. *(I.I.T. 1990)*

15. A *p*-orbital can accommodate
    (*a*) 4 electrons [✓ (*b*) 6 electrons]
    (*c*) 2 electrons with parallel spins
    [✓ (*d*) 2 electrons with opposite spins.] *(M.L.N.R. Allahabad 1990)*

ANSWERS

1. *b* **2.** *c* **3.** *d* **4.** *b* **5.** *b* **6.** *a* **7.** *b* **8.** *b* **9.** *a* **10.** *d*
11. *a* **12.** *a,c* **13.** *c* **14.** *c* **15.** *d*

16. The principal quantum number of an electron represents

(*a*) size of the orbital

(*b*) spin angular momentum

(*c*) orbital angular momentum

(*d*) space orientation of the orbital.

(M.L.N.R. Allahabad 1990)

17. Electromagnetic radiation with maximum wavelength is

(*a*) Infrared (*b*) Radio waves

(*c*) X-rays (*d*) Ultraviolet

18. Which of the following represents a correct set of quantum numbers of a 4 *d* electron ?

(*a*) 4, 3, 2, + 1/2 (*b*) 4, 2, 1, 0

(*c*) 4, 3, —2, + 1/2 (*d*) 4, 2, 1, —1/2

(M.L.N.R. Allahabad 1990, B.I.T. Ranchi 1992)

19. Which of the following electronic jump in a hydrogen atom will require the largest amount of energy ?

(*a*) From $n = 1$ to $n = 2$

(*b*) From $n = 2$ to $n = 3$

(*c*) From $n = \infty$ to $n = 1$

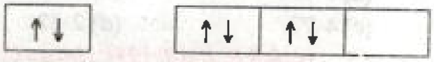
(*d*) From $n = 3$ to $n = 5$.

(M.L.N.R. Allahabad 1992)

20. The orbital diagram in which both the Pauli's exclusion principle and Hund's rule are violated is

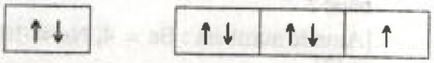
(*a*)

(*b*)



(*c*)

(*d*)



(B.I.T. Ranchi 1992)

21. Which of the following has maximum number of unpaired electrons ?

(*a*) Zn (*b*) Fe^{2+}

(*c*) Ni^{3+} (*d*) Cu^+.

(B.I.T. Ranchi 1992)

22. Which of the following does not characterise X-rays?

(*a*) The radiation can ionise the gas

(*b*) It causes ZnS to fluoresce

(*c*) It is deflected by electric and magnetic field

(*d*) They have wave length shorter than ultra violet rays.

(I.I.T. 1992)

23. The first use of quantum theory to explain the structure of atom was made by

(*a*) Heisenberg (*b*) Bohr

(*c*) Planck (*d*) Einstien. *(I.I.T. 1992)*

24. Which of the following statements is not correct for an electron that has the quantum numbers $n = 4$ and $m = 2$?

(*a*) The electron may have the quantum number $s = +\frac{1}{2}$

(*b*) The electron may have the quantum number $l = 2$

(*c*) The electron may have the quantum number $m = -2$

(*d*) The electron may have the quantum number $l = 0, 1, 2, 3$. *(M.L.N.R. Allahabad 1993)*

25. The set of quantum numbers not applicable to an electron in an atom is :

(*a*) $n = 1, l = 1, m = 1, s = +\frac{1}{2}$

(*b*) $n = 1, l = 0, 0, m = 0, s = +\frac{1}{2}$

(*c*) $n = 1, l = 0, m = 0, s = +\frac{1}{2}$

(*d*) $n = 2, l = 0, m = 0, s = +\frac{1}{2}$.

(M.L.N.R. Allahabad 1994)

26. In what ratio should $^{37}_{17}$Cl and $^{35}_{17}$Cl be present so as to obtain $^{35\cdot5}_{17}$Cl ?

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

(*c*) 1 : 3 (*d*) 3 : 1.

(Haryana C.E.E.T. 1994)

27. Bohr radius of hydrogen atom is

(*a*) $0{\cdot}529 \times 10^{-8}$ m (*b*) $0{\cdot}529 \times 10^{-10}$ m

(*c*) $5{\cdot}29 \times 10^{-8}$ m (*d*) $5{\cdot}29 \times 10^{-10}$ m

(Haryana C.E.E.T. 1994)

28. Which of the following sets of quantum number is/are not permitted ?

(*a*) $n = 3, l = 3, m = 0, s = +\frac{1}{2}$

(*b*) $n = 3, l = 2, m = +2, s = -\frac{1}{2}$

ANSWERS

16. *a* **17.** *b* **18.** *d* **19.** *a* **20.** *a* **21.** *b* **22.** *c* **23.** *b* **24.** *d* **25.** *a*
26. *c* **27.** *b*

(*c*) $n = 3, l = 1, m = -2, s = -\frac{1}{2}$

(*d*) $n = 3, l = 0, m = 0, s = +\frac{1}{2}$

(I.S.M. Dhanbad, 1994)

29. The electronic configuration of neon is

(*a*) $1s^2$ (*b*) $1s^2\,2s^2\,2p^4$

(*c*) $1s^2\,2s^2\,2p^6$ (*d*) $1s^2\,2s^2\,2p^8$

(M.L.N.R. Allahabad 1995)

30. The introduction of a neutron into the nuclear composition of an atom would lead to a change in

(*a*) The number of electrons also

(*b*) The chemical nature of the atom

(*c*) Its atomic number

(*d*) Its atomic weight *(M.L.N.R. Allahabad 1995)*

31. The wavelengths of which series lie towards the ultraviolet

(*a*) Lymann (*b*) Balmer

(*c*) Paschen (*d*) None of the above.

(U.P. C.E.E. 1996)

32. Which of the following statement does not form a part of Bohr's model of hydrogen atom ?

(*a*) Energy of the electron in the orbit is quantized

(*b*) The electron in the orbit nearst to the nucleus has the lower energy

(*c*) Angular momentum of the electron in the orbit is quantised

(*d*) The position and velocity of the electrons in the orbit cannot be determined simultaneously.

(U.P. C.E.E. 1996)

33. Which of the following statement regarding spectral series is correct ?

(*a*) The lines in the Balmer series correspond to the electronic transition from the energy level higher than $n = 1$ energy level

(*b*) Paschen series appear in the infrared region

(*c*) The lines of Lyman series appear in the visible region

(*d*) Transition from higher energy levels to 5th energy level produces Pfund series which fall in the infrared region *(U.P. C.E.E. 1996)*

34. The number of nodal planes '5*d*' orbital has is

(*a*) zero (*b*) one

(*c*) two (*d*) three.

(Haryana C.E.E.T. 1996)

35. The orbital angular momentum of an electron in 2 *s* orbital is

(*a*) $+\frac{1}{2}\frac{h}{2\pi}$ (*b*) zero

(*c*) $\frac{h}{2\pi}$ (*d*) $\sqrt{2}\,\frac{h}{2\pi}$. *(I.I.T. 1996)*

36. For a *d* electron, the orbital angular momentum is

(*a*) $\sqrt{6}\ \hbar$ (*b*) $\sqrt{2}\ \hbar$

(*c*) $\hbar$ (*d*) $2\ \hbar$. *(I.I.T. 1997)*

37. If the electron falls from $n = 3$ to $n = 2$ in the H-atom, then emitted energy is

(*a*) 10·2 eV (*b*) 12·09 eV

(*c*) 1·9 eV (*d*) 0·65 eV

(A.F.M.C. Pune 1997)

38. The total number of orbitals in a shell having principal quantum number *n* is

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

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

(A.I.I.M.S. 1997, Haryana C.E.E.T. 2000)

39. The ion that is isoelectronic with CO is

(*a*) O_2^- (*b*) N_2^+

(*c*) CN^- (*d*) O_2^+

(C.B.S.E. P.M.T. 1997)

40. The Bohr orbit radius for the H—atom ($n = 1$) is approximately 0·530 Å. The radius for the first excited state ($n = 2$) orbit is (in Å).

(*a*) 0·13 (*b*) 1·06

(*c*) 4·77 (*d*) 2·12.

(C.B.S.E. P.M.T. 1998 ; Bihar C.E.C.E. 2004)

41. Among the following which one is not paramagnetic ?

[Atomic numbers : Be = 4, Ne = 10, As = 33, Cl = 17]

(*a*) Cl^- (*b*) Be^-

(*c*) Ne^{2+} (*d*) As^+

(C.B.S.E. P.M.T. 1998)

42. The maximum number of electrons in an orbit with $l = 2, n = 3$ is

(*a*) 2 (*b*) 6

(*c*) 12 (*d*) 10 *(M.P. P.M.T. 1998)*

43. Which of the following statement(s) is (are) correct?

ANSWERS

28. *a,c* **29.** *c* **30.** *d* **31.** *a* **32.** *d* **33.** *b* **34.** *c* **35.** *b* **36.** *a* **37.** *c*

38. *b* **39.** *c* **40.** *d* **41.** *a* **42.** *d* (*a*) The electronic configuration of Cr is $[Ar]\,3d^5\,4s^1$ (At. no. of Cr = 24)

(*b*) The magnetic quantum number may have a negative value.

(*c*) In silver atom, 23 electrons have spin of one type and 24 of the opposite type (At. no. of Ag = 47)

(*d*) The oxidation state of nitrogen in NH_3 is —3.

(I.I.T. 1998)

44. The energy of an electron in the first Bohr orbit of H atom is —13·6 eV. The possible energy value (s) of the excited state(s) for electron in Bohr orbits of hydrogen is(are)

(*a*) —3·4 eV (*b*) —4·2 eV

(*c*) —6·8 eV (*d*) + 6·8 eV *(I.I.T. 1998)*

45. Who modified Bohr's theory by introducing elliptical orbits for electron path ?

(*a*) Hund (*b*) Thomson

(*c*) Rutherford (*d*) Sommerfeld.

(C.B.S.E. P.M.T. 1999)

46. Which is the correct statement about proton ?

(*a*) Proton is nucleus of deuterium

(*b*) Proton is α-particle

(*c*) Proton is ionized hydrogen molecule

(*d*) Proton is ionized hydrogen.

(M.P. C.E.E. 1999)

47. Magnetic quantum number specifies

(*a*) Size of orbitals (*b*) Shape of orbitals

(*c*) Orientation of orbitals

(*d*) Nuclear stability. *(M.P. C.E.E. 1999)*

48. The electrons, identified by quantum numbers *n* and *l* (*i*) $n = 4, l = 1$ (*ii*) $n = 4, l = 0$ (*iii*) $n = 3, l = 2$ (*iv*) $n = 3, l = 1$ can be placed in order of increasing energy, from the lowest to the highest as

(*a*) (*iv*) < (*ii*) < (*iii*) < (*i*)

(*b*) (*ii*) < (*iv*) < (*i*) < (*iii*)

(*c*) (*i*) < (*iii*) < (*ii*) < (*iv*)

(*d*) (*iii*) < (*i*) < (*iv*) < (*ii*) *(I.I.T. 1999)*

49. The number of nodal planes in a p_x orbital is

(*a*) one (*b*) two

(*c*) three (*d*) zero. *(I.I.T. 2000)*

50. The electronic configuration of an element is $1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,3d^5\,4s^1$. This represents its

(*a*) excited state (*b*) ground state

(*c*) cationic form (*d*) anionic form.

(I.I.T. 2000)

51. Among the following groupings which represents the collection of isoelectronic species ?

(*a*) $NO^+, C_2^{2-}, O_2^-, CO$

(*b*) N_2, C_2^{2-}, CO, NO

(*c*) CO, NO^+, CN^-, C_2^{2-}

(*d*) NO, CN^-, N_2, O_2^-. *(C.B.S.E. P.M.T. 2000)*

52. The energy of a photon is given as

$\Delta E/\text{atom} = 3{\cdot}03 \times 10^{-19}\ \text{J atom}^{-1}$. Then the wavelength ($\lambda$) of the photon is

(*a*) 65·6 *nm* (*b*) 656 *nm*

(*c*) 0·656 *nm* (*d*) 6·56 *nm*.

(C.B.S.E. P.M.T. 2000)

53. Principal, azimuthal and magnetic quantum numbers are respectively related to

(*a*) Size, orientation and shape

(*b*) Size, shape and orientation

(*c*) Shape, size and orientation

(*d*) None of these. *(A.I.I.M.S. 2000)*

54. For which of the following species, Bohr's theory is not applicable ?

(*a*) Be^{3+} (*b*) Li^{2+}

(*c*) He^{2+} (*d*) H. *(D.C.E.E. 2000)*

55. Which of the following is not possible ?

(*a*) $n = 3, l = 0, m = 0$ (*b*) $n = 3, l = 1, m = -1$

(*c*) $n = 2, l = 0, m = -1$ (*d*) $n = 2, l = 1, m = 0$.

(B.H.U. 2000)

56. The number of unpaired electrons in Mn^{2+} is

(*a*) 1 (*b*) 7

(*c*) 3 (*d*) 5. *(C.P.M.T. 2000)*

57. Which of the following atom has no neutron in its nucleus ?

(*a*) Helium (*b*) Lithium

(*c*) Protium (*d*) Tritium.

(C.P.M.T. 2000)

58. If the radius of first Bohr orbit be a_0, then the radius of the third orbit would be

(*a*) $3 \times a_0$ (*b*) $6 \times a_0$

(*c*) $9 \times a_0$ (*d*) $1/9 \times a_0$.

(C.P.M.T. 2000)

ANSWERS

43. *a,b,c*	**44.** *a*	**45.** *d*	**46.** *d*	**47.** *c*	**48.** *a*	**49.** *a*	**50.** *b*	**51.** *c*	**52.** *b*
53. *b*	**54.** *c*	**55.** *c*	**56.** *d*	**57.** *c*	**58.** *c*				

59. In Cu (At. No. 29)

(*a*) 13 electrons have spin in one direction and 16 electrons in other direction

(*b*) 14 electrons have spin one direction and 15 electrons in other direction

(*c*) one electron can have spin only in the clockwise direction

(*d*) none of the above is correct.

(Haryana C.E.E.T. 2000)

60. The following quantum numbers are possible for how many orbitals ? $n = 3, l = 2, m = +2$

(*a*) 1 (*b*) 2
(*c*) 3 (*d*) 4

(C.B.S.E. P.M.T. 2001)

61. In the ground state, an element has 13 electrons in its M-shell. The element is

(*a*) Manganese (*b*) Chromium
(*c*) Nickel (*d*) Iron

(E.A.M.C.E.T. 2001)

62. Which one of the following pairs of ions have the same electronic configuration ?

(*a*) Cr^{3+}, Fe^{3+} (*b*) Fe^{3+}, Mn^{2+}
(*c*) Fe^{3+}, Co^{3+} (*d*) Sc^{3+}, Cr^{3+}

(E.A.M.C.E.T. 2001)

63. As the nuclear charge increases from neon to calcium, the orbitals energies

(*a*) increase (*b*) increase very rapidly

(*c*) increase very slowly

(*d*) fall

(*e*) energy remains constant

(Kerala M.E.E. 2002)

64. Chloride ion and potassium ion are isoelectronic. Then

(*a*) their sizes are same

(*b*) chloride ion is bigger than potassium ion

(*c*) potassium ion is relatively bigger

(*d*) depends upon the other cation or anion

(K.C.E.T. 2002)

65. The spectrum of He is expected to be similar to that of

(*a*) H (*b*) Na
(*c*) He^+ (*d*) Li^+

(M.P. P.M.T. 2002)

66. Which of the following ions has the maximum magnetic moment ?

(*a*) Mn^{2+} (*b*) Fe^{2+}
(*c*) Ti^{2+} (*d*) Cr^{2+}

(A.I.E.E.E. 2002)

67. Which of the following element outermost orbit's last electron has magnetic quantum number $m = 0$?

(*a*) Na (*b*) O
(*c*) Cl (*d*) N

(Rajasthan P.M.T. 2002)

68. In hydrogen atom, energy of the first excited state is — 3·4 eV. Then find out the K.E. of the same orbit of H-atom

(*a*) + 3·4 eV (*b*) + 6·8 eV
(*c*) — 13·6 eV (*d*) + 13·6 eV

(C.B.S.E. P.M.T. 2002)

69. In the Bohr's orbit, what is the ratio of total kinetic energy and the total energy of the electron ?

(*a*) — 1 (*b*) — 2 (*c*) + 1 (*d*) + 2

(Rajasthan P.M.T. 2002)

70. Rutherford's experiment, which established the nuclear model of the atom, used a beam of

(*a*) β-particles which impinged on a metal foil and got absorbed.

(*b*) γ-rays, which impinged on a metal foil and ejected electrons

(*c*) helium atoms, which impinged on a metal foil and got scattered

(*d*) helium nuclei, which impinged on a metal foil and got scattered *(I.I.T. 2002)*

71. If the Nitrogen atom had electronic configuration $1s^7$, it would have energy lower than that of the normal ground state configuration $1s^2 2s^2 2p^3$, because the electrons would be closer to the nucleus. Yet $1s^7$ is not observed because it violates

(*a*) Heisenberg's uncertainty principle

(*b*) Hund's rule

(*c*) Pauli exclusion principle

(*d*) Bohr postulate of stationary orbits *(I.I.T. 2002)*

72. In Bohr series of lines of hydrogen spectrum, the third line from the red end corresponds to which one of the following inter-orbit jumps of the electron for Bohr orbits in an atom of hydrogen ?

(*a*) $5 \longrightarrow 2$ (*b*) $4 \longrightarrow 1$
(*c*) $2 \longrightarrow 5$ (*d*) $13 \longrightarrow 2$

(A.I.E.E.E. 2003)

73. The number of *d*-electrons retained in Fe^{2+} (At. No. of Fe = 26) ion is

(*a*) 4 (*b*) 5

ANSWERS

59. *b* **60.** *a* **61.** *b* **62.** *b* **63.** *b* **64.** *b* **65.** *d* **66.** *a* **67.** *a* **68.** *a*
69. *a* **70.** *d* **71.** *c* **72.** *a*

(c) 6 (d) 3 *(A.I.E.E.E. 2003)*

74. The value of Planck's constant is $6 \cdot 63 \times 10^{-34}$ Js. The velocity of light is $3 \cdot 0 \times 10^{8}$ ms^{-1}. Which value is closest to the wavelength in nanometers of a quantum of light with frequency of 8×10^{15} s^{-1} ?

(a) 2×10^{-25} (b) 5×10^{-18}

(c) 4×10^{1} (d) 3×10^{7}

(C.B.S.E. P.M.T. 2003)

75. A species having only one electron has ionization energy of 11810 kJ mol^{-1}. The number of protons in its nucleus will be

(a) 1 (b) 2 (c) 3 (d) 4

76. For principal quantum number $n = 4$, the total number of orbitals having $l = 3$ is

(a) 3 (b) 5

(c) 7 (d) 9 *(A.I.I.M.S. 2004)*

77. The frequency of the radiation emitted when the electron falls from $n = 4$ to $n = 1$ in a hydrogen atom will be (Given ionization energy of H

$= 2 \cdot 18 \times 10^{-18}$ J atom^{-1} and

$h = 6 \cdot 625 \times 10^{-34}$ Js)

(a) $1 \cdot 54 \times 10^{15}$ s^{-1} (b) $1 \cdot 03 \times 10^{15}$ Js^{-1}

(c) $3 \cdot 08 \times 10^{15}$ s^{-1} (d) $2 \cdot 0 \times 10^{15}$ s^{-1}

(C.B.S.E. P.M.T. 2004)

78. The radius of which of the following orbit is same as that of the first Bohr's orbit of hydrogen atom ?

(a) He^{+} ($n = 2$) (b) Li^{2+} ($n = 2$)

(c) Li^{2+} ($n = 3$) (d) Be^{3+} ($n = 2$)

(I.I.T. 2004)

79. Consider the ground state of Cr atom (Z = 24). The number of electrons with the azimuthal quantum numbers $l = 1$ and 2 are respectively

(a) 12 and 4 (b) 12 and 5

(c) 16 and 4 (d) 16 and 5

(A.I.E.E.E. 2004)

80. Proton was discovered by

(a) Chadwick (b) Thomson

(c) Goldstein (d) Bohr *(A.F.M.C. 2004)*

81. The number of 2*p* electrons having spin quantum number $s = -1/2$ are

(a) 6 (b) 0

(c) 2 (d) 3

(Karnataka C.E.T. 2004)

82. Correct energy value order is

(a) *ns np nd* $(n - 1) f$

(b) *ns np* $(n - 1) d$ $(n - 2) f$

(c) *ns np* $(n - 1) d$ $(n - 1) f$

(d) *ns* $(n - 1) d$ *np* $(n - 1) f$ *(Orissa J.E.E. 2004)*

83. Correct order of radii is

(a) N < Be < B (b) $F^{-} < O^{2-} < N^{3-}$

(c) Na < Li < K (d) $Fe^{3+} < Fe^{2+} < Fe^{4+}$

(J & K C.E.T. 2004)

84. The correct set of quantum numbers (*n*, *l* and *m* respectively) for the unpaired electron of chlorine atom is

(a) 2, 1, 0 (b) 2, 1, 1 (c) 3, 1, 1 (d) 3, 2, 1

(e) 3, 2, –1 *(Kerala C.E.E. 2004)*

85. The one electron species having ionization energy of $54 \cdot 4$ *e*V is

(a) H (b) He^{+} (c) B^{4+} (d) Li^{2+}

(e) Be^{2+} *(Kerala C.E.E. 2004)*

86. Time taken for an electron to complete one revolution in the Bohr orbit of hydrogen atom is

(a) $\frac{4\pi^2 mr^2}{nh}$ (b) $\frac{nh}{4\pi^2 mr}$ (c) $\frac{2\pi mr}{n^2 h^2}$

(d) $\frac{h}{2\pi mr}$ (e) $\frac{nh}{4\pi^2 mr^2}$ *(Kerala P.M.T. 2004)*

87. If the ionization energy of hydrogen atom is $13 \cdot 6$ *e*V, the energy required to excite it from ground state to the next higher state is nearly

(a) $3 \cdot 4$ *e*V (b) $10 \cdot 2$ *e*V

(c) $12 \cdot 1$ *e*V (d) $1 \cdot 5$ *e*V

(e) 15 *e*V *(Kerala M.E.E. 2004)*

88. If $n = 3, l = 0, m = 0$, then atomic number is

(a) 12, 13 (b) 13, 14

(c) 10, 11 (d) 11, 12

(Bihar C.E.C.E. 2004)

89. Which is the isotone of $^{76}_{32}Ge$?

(a) $^{77}_{32}Ge$ (b) $^{78}_{34}Se$ (c) $^{79}_{36}Kr$ (d) $^{78}_{32}Ge$

(Haryana P.M.T. 2004)

90. The number of *d*-electrons in Ni (at no. = 28) is equal to that of the

(a) *s* and *p* electrons in F^{-}

(b) *p* electrons in Ar (at. no. = 18)

(c) *d*-electrons in Ni^{2+}

(d) Total electrons in N (at. no. = 7)

(U.P. C.P.M.T. 2004)

ANSWERS

73. *c*	74. *c*	75. *c*	76. *c*	77. *c*	78. *d*	79. *b*	80. *c*	81. *d*	82. *d*
83. *b*	84. *c*	85. *b*	86. *a*	87. *b*	88. *d*	89. *b*	90. *c*		

HINTS/EXPLANATIONS to Multiple Choice Questions

9. $E = h\nu = h\frac{c}{\lambda}$

$$\therefore \frac{E_1}{E_2} = \frac{\lambda_2}{\lambda_1} = \frac{4000\ \text{Å}}{2000\ \text{Å}} = 2$$

12. α-particles are heavier than electrons and, therefore, cannot be stopped by electrons. Moreover most part of the atom is empty space.

13. The unpaired electron in Cl is $3p^1$ for which $n = 3$, $l = 1, m = -1$ or 0 or $+1, s = +\frac{1}{2}$ or $-\frac{1}{2}$.

Hence (*c*) is correct.

14. $ns^2\,np^5$ represents halogen which is most electronegative.

19. $E_n = -\frac{1312}{n^2}$ kJ mol^{-1}

$$E_{n_2} - E_{n_1} = -1312\left(\frac{1}{n_2^2} - \frac{1}{n_1^2}\right)$$

$$= 1312\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

$E_{n_2} - E_{n_1}$ is maximum when $\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$ is maximum.

Jump from $n = \infty$ to $n = 1$ will not require energy. Rather energy will be released.

21.

	Unpaired electrons
$_{30}Zn = 1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,3d^{10}\,4s^2$	0
$_{26}Fe^{2+} = 1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,3d^6$	4
$_{28}Ni^{3+} = 1s^2\,2s^2\,2p^6\,3s^6\,3p^6\,3d^7$	3
$_{29}Cu^{+} = 1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,3d^{10}$	0

22. X-rays are not deflected by electric and magnetic fields.

24. When $m = 2$, l cannot be 0 or 1.

25. When $n = .1$, l cannot be 1. So (*a*) is wrong.

26. Mean of 37 and 35 comes out to be 35·5 only when they are in the ratio 1 : 3.

28. When $n = 3$, l cannot be $= 3$.

So (*a*) is not permitted.

When $l = 1$, m cannot be $= -2$.

So (*c*) is not permitted

30. As protons remain the same, introduction of neutron changes only the atomic weight.

34. A *d*-orbital has two nodal planes. (Number of radial nodes in $5\,d = (n - l - 1) = (5 - 2 - 1) = 2$).

35. Orbital angular momentum $= \sqrt{l\,(l+1)}\,\frac{h}{2\pi}$.

For $2\,s$ electron, $l = 0$. Hence orbital angular momentum $= 0$.

36. For *d*-electron, $l = 2$. Orbital angular momentum $= \sqrt{l\,(l+1)}\,\hbar = \sqrt{2\,(2+1)}\,\hbar = \sqrt{6}\,\hbar$

37. $E_n = -\frac{13\cdot6}{n^2}\,eV$

$$E_3 - E_2 = 13\cdot6\left(\frac{1}{2^2} - \frac{1}{3^2}\right) eV = 13\cdot6 \times \left(\frac{1}{4} - \frac{1}{9}\right)$$

$$= 1\cdot9\,eV$$

39. Electrons in CO = 6 + 8 = 14

O_2^- has $e^- = 8 + 8 + 1 = 17$

N_2^+ has $e^- = 7 + 7 = -1 = 13$

CN^- has $e^- = 6 + 7 + 1 = 14$

O_2^+ has $e^- = 8 + 8 - 1 = 15$

40. $r_n = 0\cdot53\,n^2 = 0\cdot53 \times 2^2 = 2\cdot12$ Å

41. $_{17}Cl^- = 1s^2\,2s^2\,2p^6\,3s^2\,3p_x^2\,3p_y^2\,3p_z^2$ (No unpaired electron is present)

42. $n = 3, l = 2$ means 3*d*-subshell. Maximum number of electrons present in it = 10.

43. The oxidation state of N in NH_3 is +3.

44. $E_n = -\frac{13\cdot6}{n^2}\,eV$.

When $n = 2$,

$E_2 = -\frac{13\cdot6}{4} = -3\cdot4\,eV$

48. (*i*) $4\,p$ (*ii*) $4\,s$ (*iii*) $3\,d$ (*iv*) $3\,p$. In order of increasing energies $3\,p < 4\,s < 3\,d < 4\,p$ *i.e.* (*iv*) < (*ii*) < (*iii*) < (*i*).

50. The given E.C. is for ground state of chromium.

51. In (*c*) electrons in each species are equal.

CO = 6 + 8 = 14,

$NO^+ = 7 + 8 - 1 = 14$,

$CN^- = 6 + 7 + 1 = 14$,

$C_2^{2-} = 6 + 6 + 2 = 14$

52. $E = h\nu = h\frac{c}{\lambda}$

$$\text{or } \lambda = \frac{hc}{E} = \frac{(6\cdot63 \times 10^{-34}\ Js)\,(3 \times 10^8\ ms^{-1})}{(3\cdot03 \times 10^{-19}\ J)}$$

$$= 6\cdot56 \times 10^{-7}\ m$$

$$= 656\ nm$$

54. He^{2+} contains no electron. All others contain one electron each.

55. In (*c*), as $l = 0, m$ cannot be equal to —1.

56. $_{25}Mn^{2+} = [Ar]^{18}\,3d^5$. No. of unpaired electrons = 5.

58. $r_n = a_0 \times n^2$ *i.e.* $r_3 = a_0 \times 3^2 = 9\,a_0$

59. $_{29}Cu = [Ar]^{18}\,3d^{10}\,4s^1$

All electrons are paired except $4s^1$. Hence $14\,e^-$ have spin one direction and $15\,e^-$ in the other.

60. One set of quantum numbers is only for one orbital. In an atom, the two orbitals can have the same set of quantum numbers.

61. $13\,e^-$ in M (3rd) shell means $3s^2\,3p^6\,3d^5$. Hence complete configuration will be

$1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,4s^1\,3d^5$

i.e. total $e^- = 24$. Hence the element is chromium.

62. $_{26}Fe^{3+} = [Ar]^{18}\,3d^5$, $_{25}Mn^{2+} = [Ar]^{18}\,3d^5$.

63. Energies of the orbitals $\propto Z^2$. With increase in nuclear charge, energies of the orbitals increase very rapidly.

64. Cl^- ion has 17 protons in the nucleus while K^+ ion has 19 protons. Thus nuclear charge of K^+ is greater and hence its size is smaller.

65. He has two electrons. Li^+ also has two electrons.

66. $_{25}Mn = [Ar]^{18}\,3d^5\,4s^2 \quad \therefore \quad Mn^{2+} = [Ar]^{18}\,3d^5$

$_{26}Fe = [Ar]^{18}\,3d^6\,4s^2 \quad \therefore \quad Fe^{2+} = [Ar]^{18}\,3d^6$

$_{22}Ti = [Ar]^{18}\,3d^2\,4s^2 \quad \therefore \quad Ti^{2+} = [Ar]^{18}\,3d^2$

$_{24}Cr = [Ar]^{18}\,3d^5\,4s^1 \quad \therefore \quad Cr^{2+} = [Ar]^{18}\,3d^4$

Thus Mn^{2+} has maximum number of unpaired electrons.

67. $_{11}Na = 1s^2\,2s^2\,2p^6\,3s^1$ *i.e.* for last electron $l = 0$

$\therefore \quad m = 0.$

68. Energy in the excited state is nothing but K.E.

69. K.E. $= \frac{1}{2}mv^2$, P.E. $= -\frac{Ze^2}{r}$

But electrostatic force, $\frac{Ze^2}{r^2} = \frac{mv^2}{r}$ (centrifugal force)

$\therefore \quad$ P.E. $= -mv^2$

Total energy $= \frac{1}{2}mv^2 - mv^2 = -\frac{1}{2}mv^2$

$\therefore \quad$ K.E./Total energy = —1.

70. In Rutherford's experiment, α-rays were used which are helium nuclei.

71. According to Pauli exclusion principle, an orbital cannot have more than two electrons and these too with opposite spin.

72. The lines at the red end belong to Balmer series. These are obtained for jumps to $n = 2$ from outer orbits (1st line from $n = 3$, 2nd line from $n = 4$, 3rd line from $n = 5$).

73. E.C. of $_{26}Fe = [Ar]^{18}\,3d^6\,4s^2$

E.C. of $Fe^{2+} = [Ar]^{18}\,3d^6$

$\therefore$ *d*-electrons = 6.

74. $\lambda = \frac{c}{\nu} = \frac{3 \times 10^8\ ms^{-1}}{8 \times 10^{15}\ s^{-1}} = 0{\cdot}375 \times 10^{-7}\,m$

$= 37{\cdot}5 \times 10^{-9}\,m = 37{\cdot}5\ nm = 4{\cdot}0 \times 10\ nm.$

75. I.E. $= \frac{1312}{n^2} \times Z^2$

For one electron species in the ground state, $n = 1$

$\therefore \quad 1312 \times Z^2 = 11810$

or $Z^2 = 9$ or $Z = 3$

76. For $n = 4$, E.C. $= 1s^2\,2s^2\,2p^6\,3s^2$,

$3p^6\,3d^{10}\,4s^2\,4p^6\,4d^{10}\,4f^{14}$.

$l = 3$ means *f* subshell which has 7 orbitals.

77. I.E. $= E_\infty - E_1 = 0 - E_1$

$= 2{\cdot}18 \times 10^{-18}$ J atom^{-1}.

Thus, $E_n = -\frac{2{\cdot}18 \times 10^{-18}}{n^2}$ J atom^{-1}

$$\Delta E = E_4 - E_1 = -2{\cdot}18 \times 10^{-18}\left(\frac{1}{4^2} - \frac{1}{1^2}\right)$$

$$= 2{\cdot}044 \times 10^{-18}\ \text{J atom}^{-1}$$

$$\Delta E = h\nu \quad \text{or} \quad \nu = \frac{\Delta E}{h} = \frac{2{\cdot}044 \times 10^{-18}\ J}{6{\cdot}625 \times 10^{-34}\ Js}$$

$$= 3{\cdot}085 \times 10^{15}\ s^{-1}.$$

78. $r_n = \frac{0{\cdot}529\,n^2}{Z}$ Å

$\therefore \quad r_1\,(H) = \frac{0{\cdot}529 \times 1^2}{1} = 0{\cdot}529$ Å

$r_2\,(Be^{3+}) = \frac{0{\cdot}529 \times 2^2}{4} = 0{\cdot}529$ Å.

79. $_{24}Cr = 1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,3d^5\,4s^1$

$l = 1$ means *p*-subshell and $l = 2$ means *d*-subshell

$l = 1$ is for $2p^6$ and $3p^6$ $\therefore$ Total electrons = 12

$l = 2$ is for $3d^5$. $\therefore$ Total electrons = 5

81. There are three $2p$ orbitals containing 3 electrons with spin + 1/2 and 3 with spin − 1/2.

82. Apply $(n + l)$ rule. For $(n - 1)f$, minimum $n = 5$. For $(n - 2)f$, minimum $n = 6$. For (*d*) $n = 5$. $\therefore$ E.C. is $5s\,4d\,5p\,4f$. $(n + l)$ values are $5 + 0, 4 + 2, 5 + 1, 4 + 3$ *i.e.* 5, 6, 6, 7

83. F^-, O^{2+}, N^{3-} are isoelectronic. Greater the nuclear charge, greater is the attraction on the electrons, smaller is the size.

84. $_{17}Cl = 1s^2\, 2s^2\, 2p^6\, 3s^2\, 3p_x^2\, 3p_y^2\, 3p_z^1$. For $3p^1$ electron $n = 3, l = 1, m = -1, 0$ or $+1$.

85. $\text{I.E.} = \dfrac{13{\cdot}6\, Z^2}{n^2}\, eV = 13{\cdot}6\, Z^2$ for one-electron species.

$\therefore 13{\cdot}6\, Z^2 = 54{\cdot}4$ or $Z^2 = 4$ or $Z = 2$ *i.e.* He^+

86. By Bohr postulate, $mvr = n\dfrac{h}{2\pi}$ or $v = \dfrac{nh}{2\pi mr}$

No. of revolutions per sec

$$= \frac{\text{Velocity}}{\text{Circumference of the orbit}}$$

$$= \frac{v}{2\pi r} = \frac{nh}{2\pi mr} \times \frac{1}{2\pi r} = \frac{nh}{4\pi^2 mr^2}$$

$\therefore$ Time taken for one revolution $= \dfrac{4\pi^2 mr^2}{nh}$

87. $E_n = -\dfrac{13{\cdot}6}{n^2}\, eV,\ \Delta E = E_2 - E_1$

$$= -13{\cdot}6\left(\frac{1}{2^2} - \frac{1}{1^2}\right) = 13{\cdot}6 \times \frac{3}{4} = 10{\cdot}2\ eV$$

88. $n = 3, l = 0$ means last shell is $3s$

$\therefore$ E.C. will be $1s^2\, 2s^2\, 2p^6\, 3s^{1-2}$.

Atomic no. is 11 or 12.

89. Isotones are atoms containing the same number of neutrons (No. of n = A − Z). No. of neutrons in $^{76}_{32}Ge = 76 - 32 = 44$. $^{78}_{34}Se$ has neutrons $= 78 - 34 = 44$.

90. E.C. of $_{28}Ni = 1s^2\, 2s^2\, 2p^6\, 3s^2\, 3p^6\, 3d^8\, 4s^2$

$Ni^{2+} = 1s^2\, 2s^6\, 3s^2\, 3p^6\, 3d^8$

Thus d-electrons in Ni and Ni^{2+} are same.

ADDITIONAL QUESTIONS

For All Competitive Examinations

Assertion-Reason Type Questions

The following questions consist of two statements each printed as Assertion and Reason. While answering these questions, you are required to choose any one of the following five responses.

(*a*) If both Assertion and Reason are true and the Reason is a correct explanation of the Assertion.

(*b*) If both Assertion and Reason are true but Reason is not a correct explanation of the Assertion.

(*c*) If Assertion is true but the Reason is false. **(*d*) If the Assertion is false but the Reason is true.**

(*e*) If both Assertion and Reason are false.

	Assertion	**Reason**
1.	An orbital cannot have more than two electrons.	Two electrons in an orbital create opposite magnetic field.
2.	The configuration of Be atom cannot be $1s^2\, 3s^2$.	Hund's rule demands that the configuration should display maximum multiplicity.
3.	p-orbital is dumb-bell shaped.	Electrons present in p-orbital can have any one of the three values of magnetic quantum number *i.e.* +1, 0, —1.
4.	Wave number of a spectral line for an electronic transition is quantised.	It is proportional to the velocity of the electron undergoing the transition.
5.	A spectral line will be seen for a $2p_x - 2p_y$ transition.	Energy is released in the form of waves of light when the electron drops from $2p_x$ to $2p_y$ orbital. ***(A.I.I.M.S. 1996)***
6.	Hydrogen has one electron in its orbit but it produces several spectral lines.	There are many excited energy levels available. ***(A.I.I.M.S. 1997)***
7.	The energy of an electron is largely determined by its principal quantum number.	The principal quantum number (n) is a measure of the most probable distance of finding the electron around the nucleus. ***(A.I.I.M.S. 1998)***
8.	The 19th electron in potassium atom enters into $4s$-orbital and not the $3d$-orbital.	($n + l$) rule is followed for determining the orbital of the lowest energy state. ***(A.I.I.M.S. 1999)***
9.	The free gaseous Cr atom has six unpaired electrons.	Half-filled s orbital has greater stability. ***(A.I.I.M.S. 2004)***

True/False Statements

Which of the following statements are true ?

1. No current flows through the discharge tube when the pressure of the gas inside is one atmosphere.
2. The charge on the particles constituting the anode rays does not depend upon the nature of the gas taken.
3. Anode rays originate from the anode.
4. The magnitude of charge on an electron and a proton is the same.
5. The mass of proton is nearly same as that of hydrogen atom.
6. All electromagnetic waves travel with the velocity of light.
7. There is no difference between line spectrum and atomic spectrum.
8. Rutherford's model can explain the line spectrum of hydrogen.
9. The energy levels are called stationary states because the electrons are stationary in these levels.
10. The energies of different shells are in the order K > L > M > N......
11. Electronic energy is negative because electron has negative charge.
12. Bohr's model is not in accordance with de Broglie concept and Heisenberg's uncertainity principle.
13. The boundary of an atomic orbital cannot be defined with absolute accuracy.
14. All orbitals have directional characteristics.

Fill In The Blanks

1. Cathode rays produce.......rays when strike against the surface of a hard metal like tungsten.
2. Cathode rays produce.......on striking a ZnS screen.
3. Anode rays are deflected towards.......plate of the electric field.
4. Proton was discovered by.......... .
5. The nucleus is nearly.......in size as compared to the total size of the atom.
6. Neutron was discovered by........ .
7. The arrangement of different electromagnetic waves in order of their wavelengths is called....... .
8. The quantum of light is called....... .
9. The lowest energy state of an atom is called......and after absorbing energy it is said to be in.......... .
10. The splitting of lines in the magnetic field is called ....
11. Bohr's model of atom is based upon.........whereas wave mechanical model is based upon......... and ....
12. The numbers which give complete information about the electron are called........ .
13. The number of sub-shells in the nth main shell is.........and the number of orbitals is........ .
14. The orbitals having the same energy are called.... .
15. For $n = 3, l =$ ......, ..., ...
16. For $l = 2, m =$ ....., ..., ..., ...
17. The energy of a $4s$ orbital is......than that of $3d$ orbital.
18. s-orbitals have.......shape whereas p-orbitals have ......shape.
19. $\frac{h}{\pi}$ is the angular momentum of the electron in the ....orbit of He^+. *(Roorkee 1990)*
20. The transition of the electron in the hydrogen atom from fourth to first energy state emits a spectral line which falls in......series. *(Roorkee 1990)*
21. The light radiations with discrete quantities of energy are called....... *(I.I.T. 1993)*
22. Wave functions of electrons in atoms and molecules are called....... *(I.I.T. 1993)*
23. The $2p_x$, $2p_y$ and $2p_z$ orbitals of atoms have identical shapes but differ in their........ *(I.I.T. 1993)*
24. The outermost electronic configuration of Cr is .... *(I.I.T. 1994)*
25. The values of the quantum numbers n, l and m for the last electron of an element having the electronic configuration 2, 8, 3 are......... *(Bihar 1997)*
26. The probability of finding the electron at any point around the nucleus is found from the values of............ .

Matching Type Questions

Match the entries of column I with appropriate entries of column II.

Column I		Column II
1. Orbitals are filled in order of increasing energy	1.	Hund's rule
2. Degenerate orbitals are first singly occupied	2.	Pauli exclusion principle
3. An orbital can have maximum two electrons	3.	Aufbau principle
4. Position and momentum of a small particle cannot be measured simultaneously with absolute accuracy.	4.	Heisenberg principle.

ANSWERS

ASSERTION-REASON TYPE QUESTIONS

1. *b* **2.** *b* **3.** *b* **4.** *c* **5.** *e* **6.** *a* **7.** *a* **8.** *a* **9.** *c*

TRUE-FALSE STATEMENTS

1, 4, 5, 6, 7, 12, 13.

FILL IN THE BLANKS

1. X-rays **2.** green fluorescence **3.** negative **4.** Goldstein **5.** 1/100,000th **5.** Chadwick **7.** Electromagnetic spectrum **8.** photon **9.** ground state, excited state **10.** Zeeman effect **11.** Planck's quantum theory, de Broglie concept and Heisenberg's uncertainty principle **12.** quantum numbers **13.** n, n^2 **14.** degenerate orbitals. **15.** 0, 1, 2 **16.** —2, —1, 0, +1, +2 **17.** lower **18.** spherical, dumb-bell **19.** 2nd **20.** Lyman **21.** photons **22.** orbitals **23.** orientation **24.** $3d^5\ 4s^1$. **25.** 3, 1, —1 (or +1 or 0). **26.** ψ^2.

MATCHING TYPE QUESTIONS

1—3, 2—1, 3—2, 4—4.

HINTS/EXPLANATIONS to Assertion-Reason Type Questions

4. $\bar{\nu} = R\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$. Thus $\bar{\nu}$ depends only upon the orbits (n_1 and n_2) between which the transition takes place and not on the velocity of the electron.

5. $2p_x$ and $2p_y$ are degenerate orbitals *i.e.* have equal energies.

9. $_{24}\text{Cr} = [\text{Ar}]\, 3d^5\, 4s^1$ *i.e.* it has six unpaired electrons. Fully-filled *s*-orbital has greater stability.