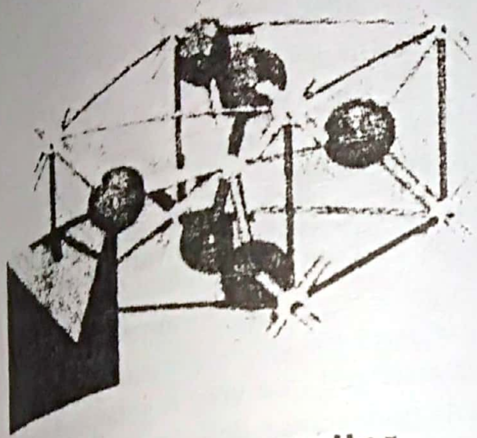
12 CHAPTER

Solid State Physics



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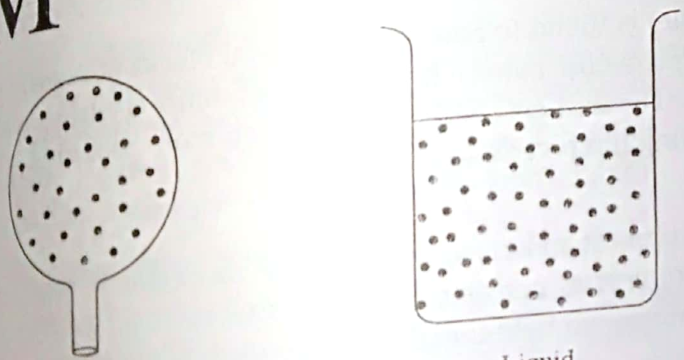
12.1. Definition of Matter

Matter is anything which has mass and occupies space. It can exist in any of the following three states :

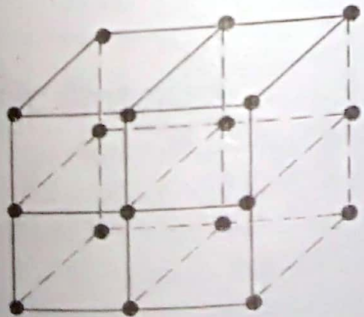


Gas

(a)

Liquid

(b)



Solid

(c)

Fig. 12.1

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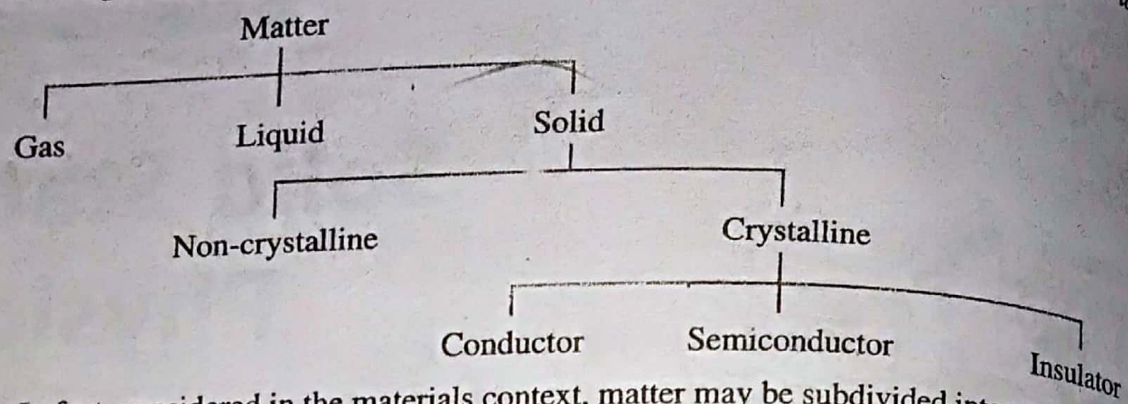
1. solid 2. liquid 3. gas

In the gaseous state, the atoms or molecules are separated from each other by comparatively *large* distances and are *haphazardly arranged* as shown in Fig.12.1 (*a*). In the liquid state, they are somewhat closer but are still arranged haphazardly as shown in Fig. 12.1 (*b*). In the solid state, atoms are the *closest* and take on an orderly three-dimensional geometric pattern called *crystal lattice* as shown in Fig. 12.1 (*c*).



In fact, considered in the materials context, matter may be subdivided into various categories, shown above.

12.2. Crystalline Solids

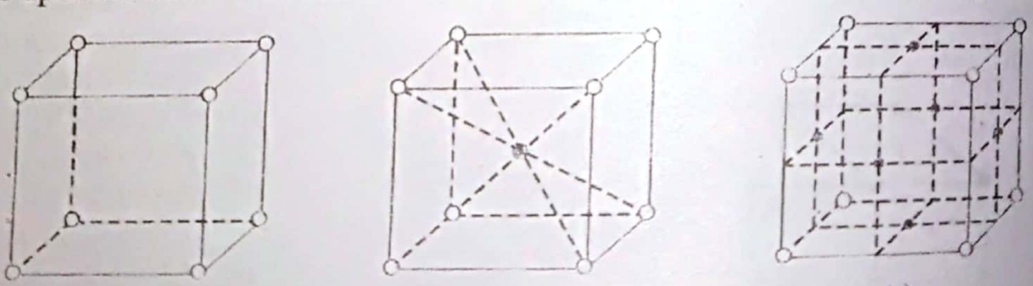
These are the solids in which atoms or molecules are arranged in a very regular and orderly fashion in a three-dimensional pattern. Each atom or molecule is fixed at a definite point in space at a definite distance and in a definite direction from all others surrounding it. In fact, there is an internal spatial symmetry of atomic orientation within a crystalline solid. This spatial pattern of atoms is called *space lattice* or *lattice array*.

12.3. Unit Cell

The entire lattice structure of a crystal is found to consist of identical blocks of atoms or unit cells. This unit cell is the smallest block or geometric pattern from which the entire crystalline solid is built up by repetition in three dimensions. The unit cell with which we are more concerned in this chapter has cubic structure with the following three variations :

(*a*) Simple Cube

This unit cell or space lattice is the simplest and consists of 8 atoms located at the corners of a cube as shown in Fig. 12.2 (*a*). The entire crystal consists of millions of such cubical unit cells stacked one upon the other. The different atoms are held together by atomic binding forces.

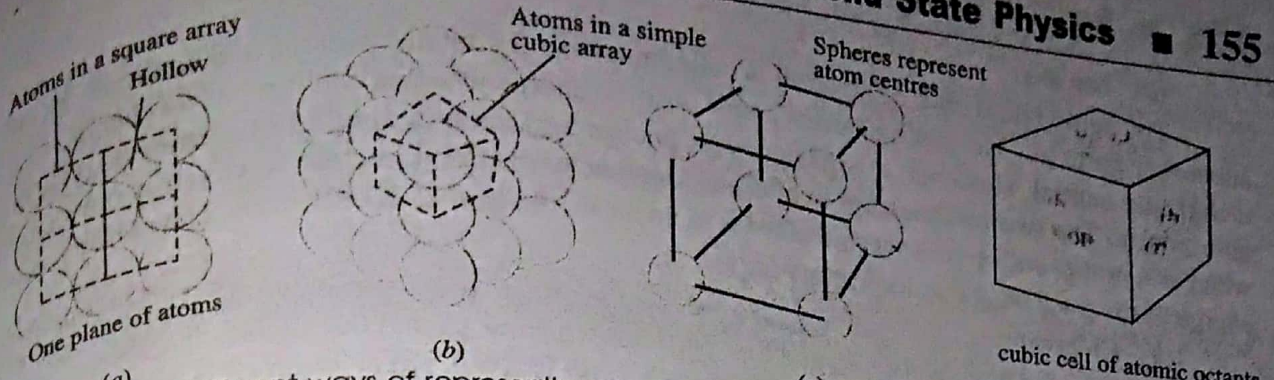


(*a*) (*b*) (*c*)

Fig. 12.2

(*b*) Body Centred Cube

In this unit cell, apart from 8 corner atoms, there is one additional atom at the centre of the cube as shown in Fig. 12.2 (*b*). Obviously, in this case, 9 atoms are involved as compared to 8 atoms in a simple cubic lattice. The two most important semiconductor materials silicon and germanium form this type of cubic crystal lattice.



(a) (b) (c) (d)

Different ways of representing a simple cubic structure.

(c) Face Centred Cube

In this arrangement, apart from the 8 corner atoms, there is one atom each at the centre of the six faces of the cube as shown in Fig. 12.2 (c). In all, there are $(8 + 6) = 14$ atoms which are bonded together by atomic forces. Copper forms this type of lattice.

12.4. Forms of Matter

In nature, matter is found in the form of either elements or compounds.

(a) Element

It is a substance which cannot be broken down any further by chemical methods into a simpler substance.

For example, copper can neither be decomposed into simpler substances nor can it be built up from any simpler substances. Elements are identified by such properties as colour, density and melting temperature etc. Common examples of elements are : oxygen, bromine, aluminium, coppe., silicon, germanium and uranium etc. They all are made up of identical atoms which themselves consist of electrons, protons and neutrons etc. Till today, 106 elements have been discovered.

(b) Compound

It is a substance which consists of more than one element in chemical combination. For example, water is formed from the chemical union of two elements *i.e.*, hydrogen and oxygen. Sodium carbonate is an example of a compound formed from the union of three elements *i.e.*, sodium, carbon and oxygen. The smallest part of a compound which retains its chemical characteristics is called a *molecule*.

12.5. Atom and Molecule

The atoms of most elements cannot exist by themselves, hence they generally combine to form molecules. A molecule is the smallest particle of a substance that retains all the characteristic properties of the original substance. Molecules are composed of one or more atoms and are called monoatomic, diatomic and triatomic molecules etc.

12.6. Atomic Structure

Our present planetary atomic model was proposed by Niels Bohr in 1913. According to this model, an atom is composed of negatively-charged electrons moving in fixed circular or elliptical orbits around a heavy positively-charged nucleus made up of protons and neutrons as shown by the three-dimensional diagram of Fig. 12.3.

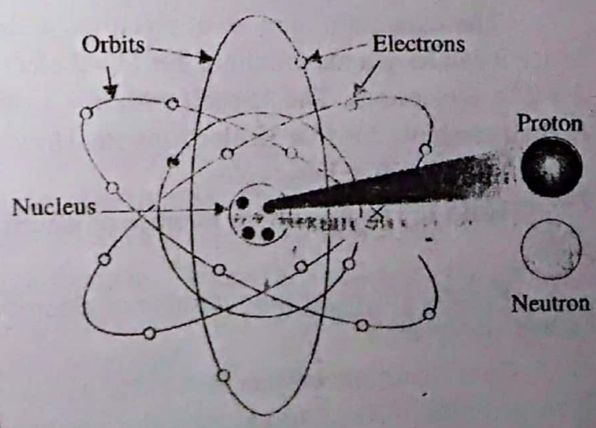


Fig. 12.3

(*a*) **Nucleus**

The central hard core of an atom is called nucleus. It contains protons and neutrons and other subatomic particles. The proton carries a unit positive charge whereas neutron has no charge *i.e.*, it is electrically neutral. However, it is as heavy as proton and each is about 1840 times heavier than an electron. The two particles are held close together with strong nuclear forces. It is obvious that whereas a proton adds both charge and mass to an atom, neutron adds only mass. Hence, the positive charge of the nucleus is due to protons only.

(*b*) **Electrons**

These are the negatively-charged tiny particles whirling around the nucleus in different elliptical orbits at fantastic speeds. Their number in each orbit is fixed. An electron carries a unit negative charge ($= -1.6 \times 10^{-19}$ C) but has negligible mass. There are as many orbital electrons as there are protons in a given atom which, therefore, makes the entire atom electrically neutral.

The centripetal force ($= mv^2/r$) necessary to keep electrons rotating round the nucleus is supplied by the force of attraction between their opposite charges as given by Coulomb's Law. It is obvious that nearer an electron is to the nucleus, greater is the force with which it is bound to it.

12.7. Atomic Number (Z)

It is equal to the number of protons (or electrons) contained in an atom.

For example, hydrogen (*H*) atom has one proton in the nucleus (and of course, one orbital electron). Hence, for hydrogen, $Z = 1$. For carbon (*C*), $Z = 6$, for copper (*Cu*), $Z = 29$, for silicon (*Si*) $Z = 14$ and for germanium (*Ge*), $Z = 32$.

12.8. Atomic Mass Number (A)

It gives the total number of protons and neutrons contained in the nucleus of an atom. For example, Si has 14 protons and 14 neutrons in its nucleus. Hence, its $A = 28$. Similarly, Ge has 32 protons and 41 neutrons thereby having $A = 73$.

The atomic weight is the *actual* weight of an atom and numerically differs slightly from the atomic mass number.

12.9. Electron Orbits or Shells

According to Planck's Quantum Theory, an electron cannot revolve round the nucleus in any arbitrary orbit but in only certain definite discrete and fixed orbits. These orbits are designated by alphabetical letters *K, L, M, N, O, P* etc., starting from the nucleus outwards. The orbit (or shell) closest to nucleus is called *K*-shell, the next farther one is called *L*-shell and so on. These shells are also known by their principal quantum number n which can have values of $n = 1$ for *K*-shell, $n = 2$ for *L*-shell and so on.

The maximum number of electrons a shell can have $= 2n^2$. For example, for *K*-shell, $n = 1$, hence it can have a maximum of $2 \times 1^2 = 2$ electrons. Similarly, *L*-shell with $n = 2$, can accommodate $2 \times 2^2 = 8$ electrons. The *M*-shell with $n = 3$ can have a maximum of $2 \times 3^2 = 18$ electrons whereas *N*-shell can have $2 \times 4^2 = 32$ electrons etc. However, this electronic distribution in all atoms is subject to the following two basic rules :

Rule 1. The maximum number of electrons in the outermost shell of an atom cannot exceed eight.

Rule 2. The maximum number of electrons in the shell just prior to the outermost shell cannot exceed eighteen.

Each electronic orbit is associated with a certain definite amount of energy. While revolving in these permitted orbits, an electron does not radiate out any energy. But it does radiate out some definite energy when *jumping from one orbit to another*. If E_2 and E_1 are the energies corresponding to the two orbits before and after the jump, the frequency of the emitted radiation is given by the relation

$$E_2 - E_1 = hf \quad \text{or} \quad \Delta E = hf$$

where h = Planck's constant
$= 6.625 \times 10^{-34}$ J-s.

12.10. Electron Distribution of Different Atoms

In Fig. 12.4 is shown the two-dimensional schematic distribution of electrons in different orbits for hydrogen, boron, silicon and germanium atoms. Following facts are clear from the diagram.

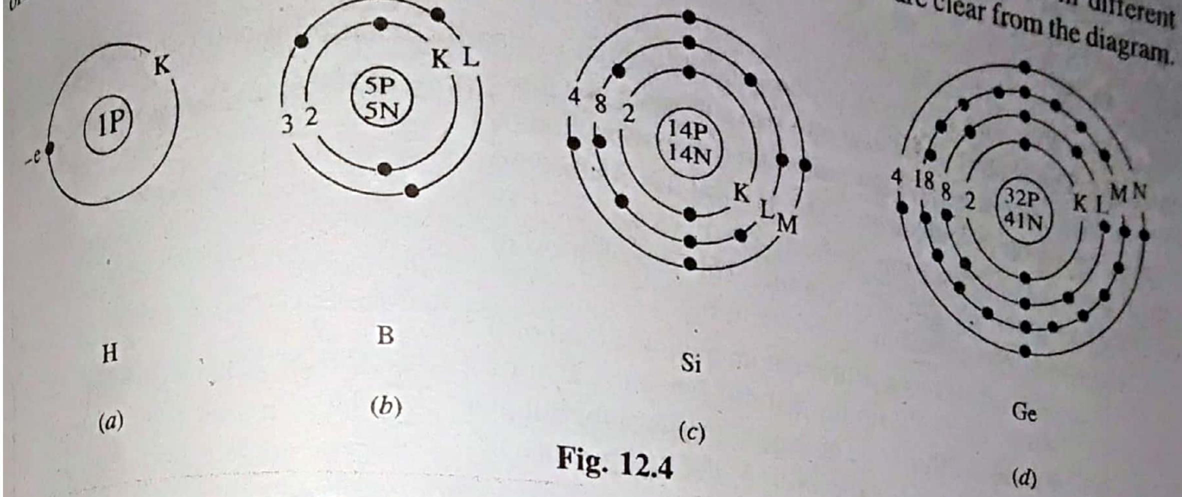


Fig. 12.4

The hydrogen atom [Fig. 12.4 (*a*)] has one positive proton in its nucleus symbolised as "IP". To balance this charge, it has one electron revolving in the extra-nuclear *K*-shell.

As shown in Fig. 12.4 (*b*), a boron atom has 5 protons and 5 neutrons inside its nucleus and 5 electrons outside it. Two electrons occupy *K*-shell which is then said to be completely- or fully-occupied because it cannot hold more electrons as per the $2n^2$ formula. The other three electrons occupy the next *L*-shell which, obviously, is not full or completely-occupied because it can hold a total of 8 electrons.

The Si atom of 12.4 (*c*) has *K*- and *L*-shells completely filled whereas *M*-shell is partially-occupied because it has only four electrons*.

Similarly, Ge atom of Fig. 12.4 (*d*) has first three orbits fully occupied whereas the fourth (and the outermost) orbit is partially filled. It could also have at least four additional electrons (Rule 1 of Art. 12.9).

12.11. Electrons Suborbits or Subshells

It has been found that each electron orbit actually contains a number of *suborbits* with the exception of the $n = 1$ or *K*-orbit which is its own suborbit. The number of suborbits in an orbit equals its principal quantum number, *n*. For example, *K*-orbit (n = 1) has one suborbit, *L*-orbit (n = 2) has two suborbits and *M*-orbit (n = 3) consists of three suborbits etc. These orbits and suborbits are also respectively known as shells and subshell. The total number of electrons (which equals $2n^2$) gets distributed amongst these subshells as shown on next page in Table 12.1.

* Being the outermost orbit, it could have at least 4 more electrons (Art. 12.9).

Table 12.1

Orbit	Total No. of electrons	No. of suborbits	Electron distribution in suborbits
K ($n = 1$)	2	1	2
L ($n = 2$)	8	2	2,6
M ($n = 3$)	18	3	2, 6, 10
N ($n = 4$)	32	4	2, 6, 10, 14

It is seen that *K*-orbit has one suborbit which is also the main orbit and contains only two electrons. The *L*-orbit is divided into two suborbits, the inner one having 2 electrons and the outer one 6 electrons thereby making up a total of 8 electrons. The *M*-orbit has 3 suborbits which have 2, 6, 10 electrons respectively, the total being 18 electrons as given by the $2n^2$ formula. This distribution of electrons in various suborbits is shown in Fig. 12.5.

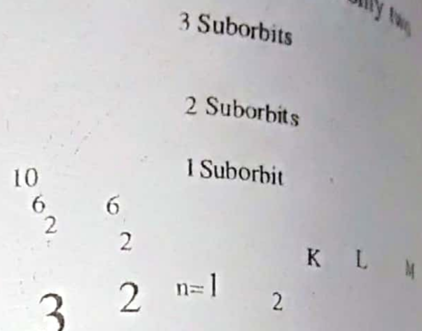
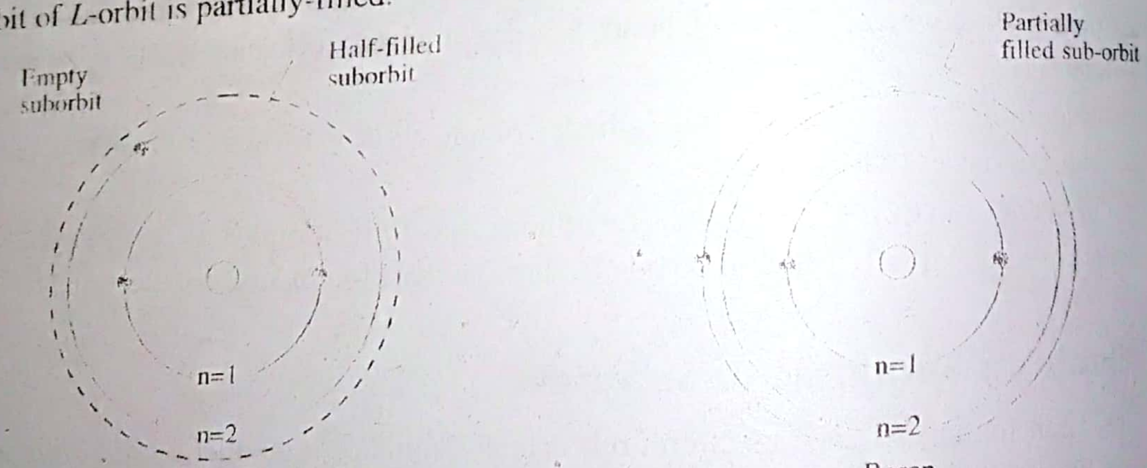


Fig. 12.5

Fig. 12.6 (*a*) shows a lithium atom having a total of 3 electrons. Two of these fill up the *K*-orbit (which is also its own suborbit) and the third one occupies the first suborbit of the *L*-orbit. Obviously, this suborbit is half-filled because it needs one more electron to fill it completely.

Fig. 12.6 (*b*) shows electron distribution in a boron atom. As seen, this atom has a total of 5 electrons. As usual, *K*-orbit has 2 electrons. The first suborbit of *L*-orbit has 2 electrons and the next suborbit has just one electron (though it could have five more). Hence, second suborbit of *L*-orbit is partially-filled.



Lithium (*a*)

Boron (*b*)

Fig. 12.6

Example 12.1. *The atomic number of copper is 29. Give its electronic distribution.*

Solution. Since atomic number represents protons, it means that the number of protons in the nucleus of Cu is 29. This is also the number of orbiting electrons which are distributed orbitwise as under :

K-orbit =	2 electrons	— full
L-orbit =	8 electrons	— full
M-orbit =	18 electrons	— full
N-orbit =	1 electron	— incomplete
Total =	29 electrons	

Example 12.2. *Silicon atom has Z = 14. Give its electronic distribution indicating which orbits are full and which are not.*

Solution. There are 14 electrons per atom. They are distributed as under :

K-orbit =	2 electrons	— full
L-orbit =	8 electrons	— full
M-orbit =	4 electrons	– incomplete

Example 12.3. *Xenon atom has Z = 54. Determine its electronic distribution. Also find out if it is chemically stable. What is the number of its valence electron?*

Solution. The 54 electrons are distributed as under :

Shell	:	K	L	M	N	O
No. of electrons	:	2	8	18	18	8

It is seen that it has 8 valence electrons. Hence, its valence or outermost orbit has maximum possible number of electrons as permitted by Rule 1 of Art. 12.9. Consequently, Xenon atom is chemically highly stable and is also an insulator.

12.12. Valence Electrons

Most of the atoms of different elements do not have their outermost shells completely-filled *i.e.*, they do not have eight electrons in their outermost orbit as permitted by Rule 1 of Art. 12.9. The electrons occupying the outermost orbit or shell of an atom are called *valence* electrons. They determine the chemical and electrical properties of the element. Elements deficient in valence electrons are highly active in the sense that they are always ready to chemically combine with other elements. Those elements which have one or two valence electrons are good conductors of electricity. These valence electrons are responsible for forming atomic bonds (Art. 12.18). The number of valence electrons in an atom also determines the valency of the element whose atom it is. For example, boron is trivalent whereas both Si and Ge are tetravalent *i.e.*, they have four valence electrons each.

12.13. Orbital Energy

The total energy (both kinetic and potential) possessed by an electron when it revolves in the nth orbit of an atom with atomic number Z is given by

$$E_n = -21.76 \times 10^{-19} \frac{Z}{n^2} \text{ joule}$$

Now, 1 electron-volt (eV) = 1.6×10^{-19} J

$$\therefore \quad E_n = -\left(\frac{21.76 \times 10^{-19}}{1.6 \times 10^{-19}}\right)\frac{Z^2}{n^2} \text{ eV} = -13.6 \frac{Z^2}{n^2} \text{ eV}$$

From the above equation, it is seen that

1. Total energy of the electron is *negative i.e.*, it is a *binding* energy.
2. Total energy is inversely proportional to the square of the principal quantum number. It means that the *binding* energy of electrons is less when they revolve in higher orbits. Consequently, it is easier to remove electrons from M-shell than from L-shell and also from N-shell than from the M-shell and so on.
3. Total energy of the electron varies as Z^2. It means that electrons in the atoms of heavier elements have much greater binding energy than those in the lighter elements when revolving in the same orbit.

12.14. Normal, Excited and Ionised Atom

Consider the case of the simplest atom *i.e.*, hydrogen atom which has only one orbital electron. When this electron occupies the innermost orbit *i.e.*, *K*-orbit ($n = 1$), the atom is said to be in its *normal* or *ground* or *unexcited* state as shown in Fig. 12.7 (a). Generally, it is this condition in which most of the free hydrogen atoms in a gas are found to exist at normal temperature and pressure. However, if a spark is passed through hydrogen gas contained in a vessel, the high-speed electrons produced by this spark collide with the hydrogen electron and may either raise it from its normal $n = 1$ orbit to higher permitted orbits with $n = 2, 3, 4$ etc. [Fig. 12.7 (b)] or may altogether remove it from the atom itself and make it a free electron which is no longer bond to the atom as shown in Fig. 12.7 (c).

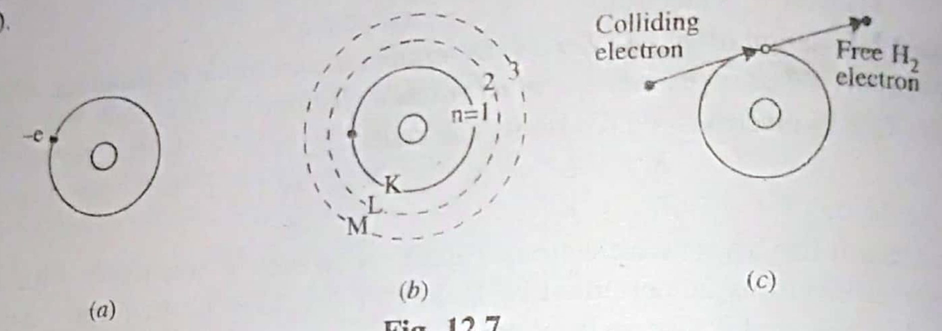


Fig. 12.7

As shown in Fig. 12.8, the hydrogen electron can be raised to higher permitted orbits provided it is given the right amount of energy. In that case, the hydrogen atom is said to be *excited* or be in an *excited* state. However, the atom does not remain in the excited state longer than 10^{-8} second because the raised electron tends to come back to its normal or ground state. In so doing, it gives out the energy (it had gained earlier during collision) in the form of radiations which may or may not be visible. The raised electron may return by several jumps instead of one thereby emitting many radiations of different frequencies (and, hence wavelengths).

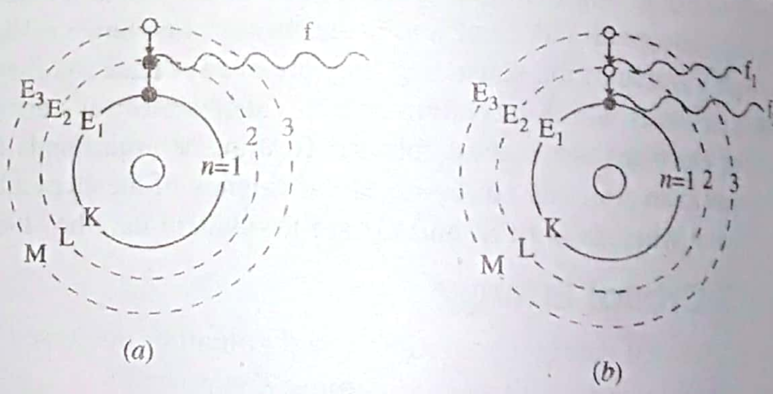


Fig. 12.8

As shown in Fig. 12.8, suppose that the electron had been raised to $n = 3$ orbit where its energy is E_3. It can, now, come back to its normal $n = 1$ orbit either directly by one jump [Fig. 12.8 (a) thereby giving out radiations of single frequency or by two jumps [Fig. 12.8 (b)] thereby giving out two radiations of different frequencies.

In Fig. 12.8 (a), $\quad E_3 - E_1 = hf$

In Fig. 12.8 (b), $\quad E_3 - E_2 = hf_1$

$$E_2 - E_1 = hf_2$$

If, as shown in Fig. 12.7 (c), the electron is completely removed from the atom, the atom is said to be *ionised i.e.*, it becomes a positively-charged ion. The energy required to remove the electron away from its parent atom is called *ionisation energy*.

12.15. Orbital Energies in Hydrogen Atom

The general expression for total energy of an electron in an atom is

$$E_n = -13.6 \frac{Z^2}{n^2} \text{ eV}$$

For hydrogen $Z = 1$

$$E_n = -\frac{13.6}{n^2} \text{ eV}$$

∴ (i) For K-shell, $n = 1$

$$E_1 = -\frac{13.6}{1^2} = -13.6 \text{ eV}$$

∴ (ii) For L-shell, $n = 2$

$$E_2 = -\frac{13.6}{2^2} = -3.4 \text{ eV}$$

∴ (iii) For M-shell, $n = 3$

$$E_3 = -\frac{13.6}{3^2} = -1.51 \text{ eV etc.}$$

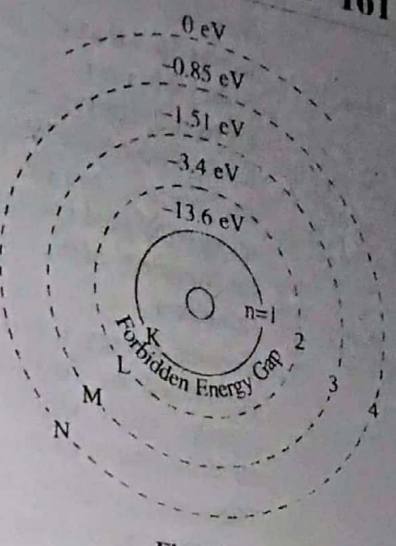


Fig. 12.9

The different permitted orbits with their associated electronic energies are shown in Fig. 12.9. It is seen that the electrons can have certain specific amounts of energy only. In the $n = 1$ orbit, it can have an energy of -13.6 eV and in the $n = 2$ orbit, it can have -3.4 eV. It cannot have any energy *lying in between these two values*. For example, we will have to give it an extra amount of energy = (13.6) – (3.4) = 10.2 eV to raise it from the lower $n = 1$ orbit to the higher $n = 2$ orbit. If we try to give it, say, 8 eV, it will simply not accept it because it is forbidden (by Quantum Theory) to lie anywhere in between the permitted orbits.

Example 12.4. *Determine the frequency of radiation emitted by an electron in an excited hydrogen atom when it jumps from $n = 3$ orbit to $n = 2$ orbit. Take $h = 6.625 \times 10^{-34}$ J-s.*

Solution. As seen from Art. 12.5, $E_3 = -1.51$ eV and $E_2 = -3.4$ eV

$$\therefore \quad E_3 - E_2 = -1.51 - (-3.4) = 1.89 \text{ eV}$$

$$= 1.89 \times 1.6 \times 10^{-19} \text{ J}$$

Now, $\quad E_3 - E_2 = hf$

or $\quad 1.89 \times 1.6 \times 10^{-19} = 6.625 \times 10^{-34} \times f$

$$\therefore \quad f = \mathbf{4.57 \times 10^{14}\ Hz}$$

If required, wavelength of the radiations emitted can also be found.

Now, $\quad c = f\lambda$

where c is the velocity of light in vacuum.

$$\therefore \quad 3 \times 10^8 = 4.57 \times 10^{14} \times \lambda$$

$$\therefore \quad \lambda = \mathbf{6563 \times 10^{-10}\ m}$$

12.16. Energy Levels in an Isolated Atom

We will consider a *single isolated* atom of hydrogen *i.e.*, an atom which is so far removed from other atoms as not to be affected at all by their electric fields. In that case, energies possessed by various electrons in different orbits would remain totally unaffected by any external influence. The orbital energies have already been given in Art. 13.15 above. However, instead of drawing various orbits to the scale of their radii as in Fig. 12.9, it is customary (and also more convenient) to draw horizontal lines to an energy scale as shown in Fig. 12.10. Such a diagram is called an *energy-level diagram* (ELD) of the atom.

Each energy level is represented by a horizontal line of the same length although the length and thickness of the lines have no significance. It is seen that in this diagram

1. less negative energies are at the *top* whereas more negative ones are at the *bottom*. It means that it is easier to remove electrons from higher orbits than from lower ones.