

The other commonly used quantity specially in spectroscopy, is the **wavenumber** ($\bar{\nu}$). It is defined as the number of wavelengths per unit length. Its units are reciprocal of wavelength unit, i.e., m^{-1} . However commonly used unit is cm^{-1} (not SI unit).

Problem 2.3

The Vividh Bharati station of All India Radio, Delhi, broadcasts on a frequency of 1,368 kHz (kilo hertz). Calculate the wavelength of the electromagnetic radiation emitted by transmitter. Which part of the electromagnetic spectrum does it belong to?

Solution

The wavelength, λ , is equal to c/ν , where c is the speed of electromagnetic radiation in vacuum and ν is the frequency. Substituting the given values, we have

$$\begin{aligned}\lambda &= \frac{c}{\nu} \\ &= \frac{3.00 \times 10^8 \text{ m s}^{-1}}{1368 \text{ kHz}} \\ &= \frac{3.00 \times 10^8 \text{ m s}^{-1}}{1368 \times 10^3 \text{ s}^{-1}} \\ &= 219.3 \text{ m}\end{aligned}$$

This is a characteristic radiowave wavelength.

Problem 2.4

The wavelength range of the visible spectrum extends from violet (400 nm) to red (750 nm). Express these wavelengths in frequencies (Hz). ($1 \text{ nm} = 10^{-9} \text{ m}$)

Solution

Using equation 2.5, frequency of violet light

$$\begin{aligned}\nu &= \frac{c}{\lambda} = \frac{3.00 \times 10^8 \text{ m s}^{-1}}{400 \times 10^{-9} \text{ m}} \\ &= 7.50 \times 10^{14} \text{ Hz}\end{aligned}$$

Frequency of red light

$$\nu = \frac{c}{\lambda} = \frac{3.00 \times 10^8 \text{ m s}^{-1}}{750 \times 10^{-9} \text{ m}} = 4.00 \times 10^{14} \text{ Hz}$$

The range of visible spectrum is from 4.0×10^{14} to 7.5×10^{14} Hz in terms of frequency units.

Problem 2.5

Calculate (a) wavenumber and (b) frequency of yellow radiation having wavelength 5800 Å.

Solution

(a) Calculation of wavenumber ($\bar{\nu}$)
 $\lambda = 5800 \text{ Å} = 5800 \times 10^{-8} \text{ cm}$
 $= 5800 \times 10^{-10} \text{ m}$

$$\begin{aligned}\bar{\nu} &= \frac{1}{\lambda} = \frac{1}{5800 \times 10^{-10} \text{ m}} \\ &= 1.724 \times 10^6 \text{ m}^{-1} \\ &= 1.724 \times 10^4 \text{ cm}^{-1}\end{aligned}$$

(b) Calculation of the frequency (ν)

$$\bar{\nu} = \frac{c}{\lambda} = \frac{3 \times 10^8 \text{ m s}^{-1}}{5800 \times 10^{-10} \text{ m}} = 5.172 \times 10^{14} \text{ s}^{-1}$$

2.3.2 Particle Nature of Electromagnetic Radiation: Planck's Quantum Theory

Some of the experimental phenomenon such as diffraction* and interference** can be explained by the wave nature of the electromagnetic radiation. However, following are some of the observations which could not be explained with the help of even the electromagnetic theory of 19th century physics (known as classical physics):

- the nature of emission of radiation from hot bodies (black-body radiation)
- ejection of electrons from metal surface when radiation strikes it (photoelectric effect)
- variation of heat capacity of solids as a function of temperature

* Diffraction is the bending of wave around an obstacle.

** Interference is the combination of two waves of the same or different frequencies to give a wave whose distribution at each point in space is the algebraic or vector sum of disturbances at that point resulting from each interfering wave.

- (iv) Line spectra of atoms with special reference to hydrogen.

These phenomena indicate that the system can take energy only in discrete amounts. All possible energies cannot be taken up or radiated.

It is noteworthy that the first concrete explanation for the phenomenon of the black body radiation mentioned above was given by Max Planck in 1900. Let us first try to understand this phenomenon, which is given below:

Hot objects emit electromagnetic radiations over a wide range of wavelengths. At high temperatures, an appreciable proportion of radiation is in the visible region of the spectrum. As the temperature is raised, a higher proportion of short wavelength (blue light) is generated. For example, when an iron rod is heated in a furnace, it first turns to dull red and then progressively becomes more and more red as the temperature increases. As this is heated further, the radiation emitted becomes white and then becomes blue as the temperature becomes very high. This means that red radiation is most intense at a particular temperature and the blue radiation is more intense at another temperature. This means intensities of radiations of different wavelengths emitted by hot body depend upon its temperature. By late 1850's it was known that objects made of different material and kept at different temperatures emit different amount of radiation. Also, when the surface of an object is irradiated with light (electromagnetic radiation), a part of radiant energy is generally reflected as such, a part is absorbed and a part of it is transmitted. The reason for incomplete absorption is that ordinary objects are as a rule imperfect absorbers of radiation. *An ideal body, which emits and absorbs radiations of all frequencies uniformly, is called a black body and the radiation emitted by such a body is called black body radiation.* In practice, no such body exists. Carbon black approximates fairly closely to black body. A good physical approximation to a black body is a cavity with a tiny hole, which has no other opening. Any ray

entering the hole will be reflected by the cavity walls and will be eventually absorbed by the walls. A black body is also a perfect radiator of radiant energy. Furthermore, a black body is in thermal equilibrium with its surroundings. It radiates same amount of energy per unit area as it absorbs from its surrounding in any given time. The amount of light emitted (intensity of radiation) from a black body and its spectral distribution depends only on its temperature. At a given temperature, intensity of radiation emitted increases with the increase of wavelength, reaches a maximum value at a given wavelength and then starts decreasing with further increase of wavelength, as shown in Fig. 2.8. Also, as the temperature increases, maxima of the curve shifts to short wavelength. Several attempts were made to predict the intensity of radiation as a function of wavelength.

But the results of the above experiment could not be explained satisfactorily on the basis of the wave theory of light. Max Planck arrived at a satisfactory relationship

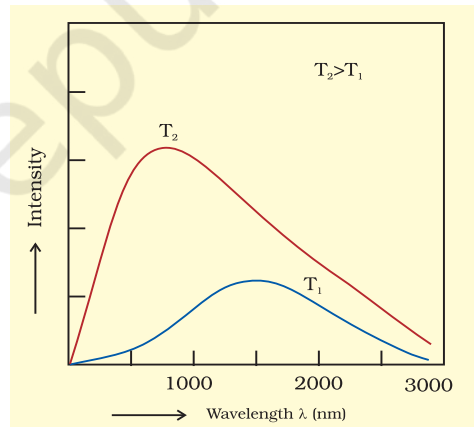


Fig. 2.8 Wavelength-intensity relationship

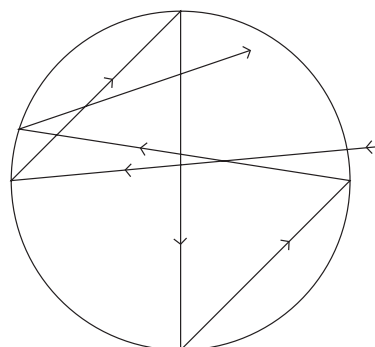


Fig. 2.8(a) Black body

by making an assumption that absorption and emission of radiation arises from oscillator i.e., atoms in the wall of black body. Their frequency of oscillation is changed by interaction with oscillators of electromagnetic radiation. Planck assumed that radiation could be sub-divided into discrete chunks of energy. He suggested that atoms and molecules could emit or absorb energy only in discrete quantities and not in a continuous manner. He gave the name **quantum** to the smallest quantity of energy that can be emitted or absorbed in the form of electromagnetic radiation. The energy (E) of a quantum of radiation is proportional to its frequency (ν) and is expressed by equation (2.6).

$$E = h\nu \quad (2.6)$$

The proportionality constant, ' h ' is known as Planck's constant and has the value $6.626 \times 10^{-34} \text{ J s}$.

With this theory, Planck was able to explain the distribution of intensity in the radiation from black body as a function of frequency or wavelength at different temperatures.

Quantisation has been compared to standing on a staircase. A person can stand on any step of a staircase, but it is not possible for him/her to stand in between the two steps. The energy can take any one of the values from the following set, but cannot take on any values between them.

$$E = 0, h\nu, 2h\nu, 3h\nu, \dots, nh\nu, \dots$$

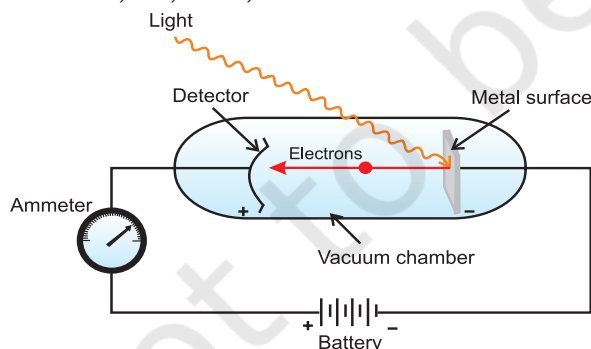


Fig. 2.9 Equipment for studying the photoelectric effect. Light of a particular frequency strikes a clean metal surface inside a vacuum chamber. Electrons are ejected from the metal and are counted by a detector that measures their kinetic energy.



Max Planck (1858–1947)

Max Planck, a German physicist, received his Ph.D in theoretical physics from the University of Munich in 1879. In 1888, he was appointed Director of the Institute of Theoretical Physics at the University of Berlin.

Planck was awarded the Nobel Prize in Physics in 1918 for his quantum theory. Planck also made significant contributions in thermodynamics and other areas of physics.

Photoelectric Effect

In 1887, H. Hertz performed a very interesting experiment in which electrons (or electric current) were ejected when certain metals (for example potassium, rubidium, caesium etc.) were exposed to a beam of light as shown in Fig. 2.9. The phenomenon is called **Photoelectric effect**. The results observed in this experiment were:

- (i) The electrons are ejected from the metal surface as soon as the beam of light strikes the surface, i.e., there is no time lag between the striking of light beam and the ejection of electrons from the metal surface.
- (ii) The number of electrons ejected is proportional to the intensity or brightness of light.
- (iii) For each metal, there is a characteristic minimum frequency, ν_0 (also known as **threshold frequency**) below which photoelectric effect is not observed. At a frequency $\nu > \nu_0$, the ejected electrons come out with certain kinetic energy. The kinetic energies of these electrons increase with the increase of frequency of the light used.

All the above results could not be explained on the basis of laws of classical physics. According to latter, the energy content of the beam of light depends upon the brightness of the light. In other words, number of electrons ejected and kinetic energy associated with them should depend on the brightness of light. It has been observed that though the number

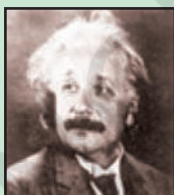
Table 2.2 Values of Work Function (W_0) for a Few Metals

Metal	Li	Na	K	Mg	Cu	Ag
W_0 /eV	2.42	2.3	2.25	3.7	4.8	4.3

of electrons ejected does depend upon the brightness of light, the kinetic energy of the ejected electrons does not. For example, red light [$\nu = (4.3 \text{ to } 4.6) \times 10^{14} \text{ Hz}$] of any brightness (intensity) may shine on a piece of potassium metal for hours but no photoelectrons are ejected. But, as soon as even a very weak yellow light ($\nu = 5.1\text{--}5.2 \times 10^{14} \text{ Hz}$) shines on the potassium metal, the photoelectric effect is observed. The threshold frequency (ν_0) for potassium metal is $5.0 \times 10^{14} \text{ Hz}$.

Einstein (1905) was able to explain the photoelectric effect using Planck's quantum theory of electromagnetic radiation as a starting point.

Albert Einstein, a German born American physicist, is regarded by many as one of the two great physicists the world has known (the other is Isaac Newton). His three research papers (on special relativity, Brownian motion and the photoelectric effect) which he published in 1905, while he was employed as a technical assistant in a Swiss patent office in Berne have profoundly influenced the development of physics. He received the Nobel Prize in Physics in 1921 for his explanation of the photoelectric effect.



Albert Einstein
(1879–1955)

Shining a beam of light on to a metal surface can, therefore, be viewed as shooting a beam of particles, the photons. When a photon of sufficient energy strikes an electron in the atom of the metal, it transfers its energy instantaneously to the electron during the collision and the electron is ejected without any time lag or delay. Greater the energy possessed by the photon, greater will be transfer of energy to the electron and greater the kinetic energy of the ejected electron. In other words, kinetic energy of the ejected electron is proportional to the frequency of the electromagnetic radiation. Since the striking photon has energy equal to $h\nu$ and

the minimum energy required to eject the electron is $h\nu_0$ (also called work function, W_0 ; Table 2.2), then the difference in energy ($h\nu - h\nu_0$) is transferred as the kinetic energy of the photoelectron. Following the conservation of energy principle, the kinetic energy of the ejected electron is given by the equation 2.7.

$$h\nu = h\nu_0 + \frac{1}{2} m_e v^2 \quad (2.7)$$

where m_e is the mass of the electron and v is the velocity associated with the ejected electron. Lastly, a more intense beam of light consists of larger number of photons, consequently the number of electrons ejected is also larger as compared to that in an experiment in which a beam of weaker intensity of light is employed.

Dual Behaviour of Electromagnetic Radiation

The particle nature of light posed a dilemma for scientists. On the one hand, it could explain the black body radiation and photoelectric effect satisfactorily but on the other hand, it was not consistent with the known wave behaviour of light which could account for the phenomena of interference and diffraction. The only way to resolve the dilemma was to accept the idea that light possesses both particle and wave-like properties, i.e., light has dual behaviour. Depending on the experiment, we find that light behaves either as a wave or as a stream of particles. Whenever radiation interacts with matter, it displays particle like properties in contrast to the wavelike properties (interference and diffraction), which it exhibits when it propagates. This concept was totally alien to the way the scientists thought about matter and radiation and it took them a long time to become convinced of its validity. It turns out, as you shall see later, that some microscopic particles like electrons also exhibit this wave-particle duality.

Problem 2.6

Calculate energy of one mole of photons of radiation whose frequency is 5×10^{14} Hz.

Solution

Energy (E) of one photon is given by the expression

$$E = h\nu$$

$$h = 6.626 \times 10^{-34} \text{ J s}$$

$$\nu = 5 \times 10^{14} \text{ s}^{-1} \text{ (given)}$$

$$E = (6.626 \times 10^{-34} \text{ J s}) \times (5 \times 10^{14} \text{ s}^{-1})$$

$$= 3.313 \times 10^{-19} \text{ J}$$

Energy of one mole of photons

$$= (3.313 \times 10^{-19} \text{ J}) \times (6.022 \times 10^{23} \text{ mol}^{-1})$$

$$= 199.51 \text{ kJ mol}^{-1}$$

Problem 2.7

A 100 watt bulb emits monochromatic light of wavelength 400 nm. Calculate the number of photons emitted per second by the bulb.

Solution

$$\text{Power of the bulb} = 100 \text{ watt}$$

$$= 100 \text{ J s}^{-1}$$

$$\text{Energy of one photon } E = h\nu = hc/\lambda$$

$$= \frac{6.626 \times 10^{-34} \text{ J s} \times 3 \times 10^8 \text{ m s}^{-1}}{400 \times 10^{-9} \text{ m}}$$

$$= 4.969 \times 10^{-19} \text{ J}$$

Number of photons emitted

$$\frac{100 \text{ J s}^{-1}}{4.969 \times 10^{-19} \text{ J}} = 2.012 \times 10^{20} \text{ s}^{-1}$$

Problem 2.8

When electromagnetic radiation of wavelength 300 nm falls on the surface of sodium, electrons are emitted with a kinetic energy of $1.68 \times 10^5 \text{ J mol}^{-1}$. 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?

Solution

The energy (E) of a 300 nm photon is given by

$$h\nu = hc/\lambda$$

$$= \frac{6.626 \times 10^{-34} \text{ J s} \times 3.0 \times 10^8 \text{ m s}^{-1}}{300 \times 10^{-9} \text{ m}}$$

$$= 6.626 \times 10^{-19} \text{ J}$$

The energy of one mole of photons

$$= 6.626 \times 10^{-19} \text{ J} \times 6.022 \times 10^{23} \text{ mol}^{-1}$$

$$= 3.99 \times 10^5 \text{ J mol}^{-1}$$

The minimum energy needed to remove one mole of electrons from sodium

$$= (3.99 - 1.68) \times 10^5 \text{ J mol}^{-1}$$

$$= 2.31 \times 10^5 \text{ J mol}^{-1}$$

The minimum energy for one electron

$$= \frac{2.31 \times 10^5 \text{ J mol}^{-1}}{6.022 \times 10^{23} \text{ electrons mol}^{-1}}$$

$$= 3.84 \times 10^{-19} \text{ J}$$

This corresponds to the wavelength

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

$$= \frac{6.626 \times 10^{-34} \text{ J s} \times 3.0 \times 10^8 \text{ m s}^{-1}}{3.84 \times 10^{-19} \text{ J}}$$

$$= 517 \text{ nm}$$

(This corresponds to green light)

Problem 2.9

The threshold frequency ν_0 for a metal is $7.0 \times 10^{14} \text{ s}^{-1}$. Calculate the kinetic energy of an electron emitted when radiation of frequency $\nu = 1.0 \times 10^{15} \text{ s}^{-1}$ hits the metal.

Solution

According to Einstein's equation

$$\text{Kinetic energy} = \frac{1}{2} m_e v^2 = h(\nu - \nu_0)$$

$$= (6.626 \times 10^{-34} \text{ J s}) (1.0 \times 10^{15} \text{ s}^{-1} - 7.0 \times 10^{14} \text{ s}^{-1})$$

$$= (6.626 \times 10^{-34} \text{ J s}) (10.0 \times 10^{14} \text{ s}^{-1} - 7.0 \times 10^{14} \text{ s}^{-1})$$

$$= (6.626 \times 10^{-34} \text{ J s}) \times (3.0 \times 10^{14} \text{ s}^{-1})$$

$$= 1.988 \times 10^{-19} \text{ J}$$

2.3.3 Evidence for the quantized* Electronic Energy Levels: Atomic spectra

The speed of light depends upon the nature of the medium through which it passes. As a result, the beam of light is deviated or refracted from its original path as it passes from one medium to another. It is observed that when a ray of white light is passed through a prism, the wave with shorter wavelength bends more than the one with a longer wavelength. Since ordinary white light consists of waves with all the wavelengths in the visible range, a ray of white light is spread out into a series of coloured bands called **spectrum**. The light of red colour which has longest wavelength is deviated the least while the violet light, which has shortest wavelength is deviated the most. The spectrum of white light, that we can see, ranges from violet at 7.50×10^{14} Hz to red at 4×10^{14} Hz. Such a spectrum is called **continuous spectrum**. Continuous because violet merges into blue, blue into green and so on. A similar spectrum is produced when a rainbow forms in the sky. Remember that visible light is just a small portion of the electromagnetic radiation (Fig.2.7). When electromagnetic radiation interacts with matter, atoms and molecules may absorb energy and reach to a higher energy state. With higher energy, these are in an unstable state. For returning to their normal (more stable, lower energy states) energy state, the atoms and molecules emit radiations in various regions of the electromagnetic spectrum.

Emission and Absorption Spectra

The spectrum of radiation emitted by a substance that has absorbed energy is called an **emission spectrum**. Atoms, molecules or ions that have absorbed radiation are said to be **“excited”**. To produce an emission spectrum, energy is supplied to a sample by heating it or irradiating it and the wavelength (or frequency) of the radiation emitted, as the sample gives up the absorbed energy, is recorded.

An absorption spectrum is like the photographic negative of an emission

spectrum. A continuum of radiation is passed through a sample which absorbs radiation of certain wavelengths. The missing wavelength which corresponds to the radiation absorbed by the matter, leave dark spaces in the bright continuous spectrum.

The study of emission or absorption spectra is referred to as **spectroscopy**. The spectrum of the visible light, as discussed above, was continuous as all wavelengths (red to violet) of the visible light are represented in the spectra. The emission spectra of atoms in the gas phase, on the other hand, do not show a continuous spread of wavelength from red to violet, rather they emit light only at specific wavelengths with dark spaces between them. Such spectra are called **line spectra** or **atomic spectra** because the emitted radiation is identified by the appearance of bright lines in the spectra (Fig. 2.10 page 45).

Line emission spectra are of great interest in the study of electronic structure. Each element has a unique line emission spectrum. The characteristic lines in atomic spectra can be used in chemical analysis to identify unknown atoms in the same way as fingerprints are used to identify people. The exact matching of lines of the emission spectrum of the atoms of a known element with the lines from an unknown sample quickly establishes the identity of the latter, German chemist, Robert Bunsen (1811-1899) was one of the first investigators to use line spectra to identify elements.

Elements like rubidium (Rb), caesium (Cs) thallium (Tl), indium (In), gallium (Ga) and scandium (Sc) were discovered when their minerals were analysed by spectroscopic methods. The element helium (He) was discovered in the sun by spectroscopic method.

Line Spectrum of Hydrogen

When an electric discharge is passed through gaseous hydrogen, the H_2 molecules dissociate and the energetically excited hydrogen atoms produced emit electromagnetic radiation of *discrete frequencies*. The hydrogen spectrum consists of several series of *lines* named after their discoverers. Balmer showed in 1885 on the basis of experimental observations

* The restriction of any property to discrete values is called quantization.

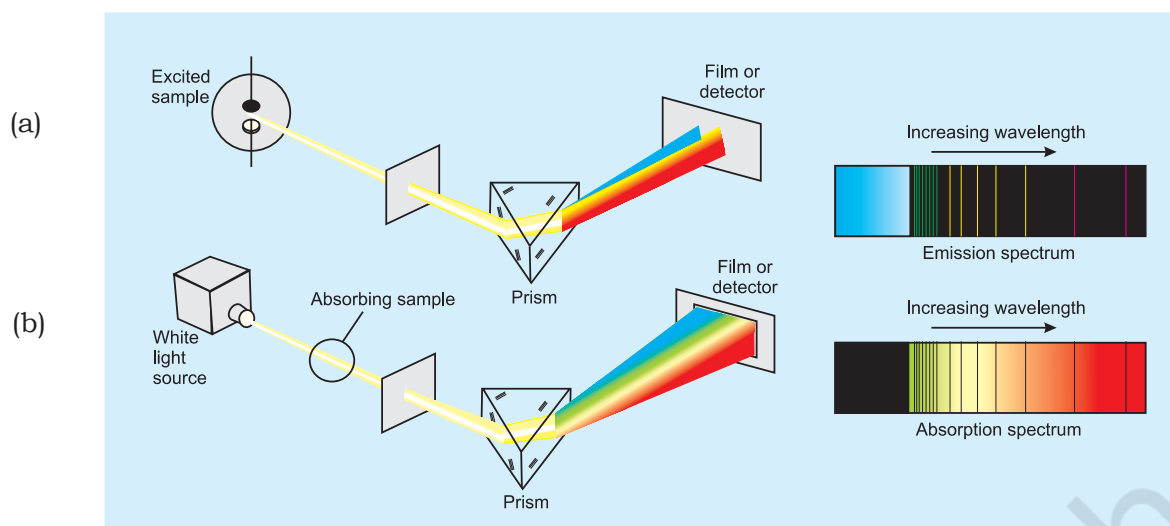


Fig. 2.10 (a) Atomic emission. The light emitted by a sample of excited hydrogen atoms (or any other element) can be passed through a prism and separated into certain discrete wavelengths. Thus an emission spectrum, which is a photographic recording of the separated wavelengths is called as line spectrum. Any sample of reasonable size contains an enormous number of atoms. Although a single atom can be in only one excited state at a time, the collection of atoms contains all possible excited states. The light emitted as these atoms fall to lower energy states is responsible for the spectrum. **(b) Atomic absorption.** When white light is passed through unexcited atomic hydrogen and then through a slit and prism, the transmitted light is lacking in intensity at the same wavelengths as are emitted in (a). The recorded absorption spectrum is also a line spectrum and the photographic negative of the emission spectrum.

that if spectral lines are expressed in terms of wavenumber ($\bar{\nu}$), then the visible lines of the hydrogen spectrum obey the following formula:

$$\bar{\nu} = 109,677 \left(\frac{1}{2^2} - \frac{1}{n^2} \right) \text{ cm}^{-1} \quad (2.8)$$

where n is an integer equal to or greater than 3 (i.e., $n = 3, 4, 5, \dots$)

The series of lines described by this formula are called the **Balmer series**. The Balmer series of lines are the only lines in the hydrogen spectrum which appear in the visible region of the electromagnetic spectrum. The Swedish spectroscopist, Johannes Rydberg, noted that all series of lines in the hydrogen spectrum could be described by the following expression :

$$\bar{\nu} = 109,677 \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \text{ cm}^{-1} \quad (2.9)$$

where $n_1 = 1, 2, \dots$

$n_2 = n_1 + 1, n_1 + 2, \dots$

The value $109,677 \text{ cm}^{-1}$ is called the **Rydberg constant** for hydrogen. The first five series of lines that correspond to $n_1 = 1, 2, 3, 4, 5$ are known as Lyman, Balmer, Paschen, Brackett and Pfund series, respectively. Table 2.3 shows these series of transitions in the hydrogen spectrum. Fig. 2.11 (page, 46) shows the Lyman, Balmer and Paschen series of transitions for hydrogen atom.

Of all the elements, hydrogen atom has the simplest line spectrum. Line spectrum

Table 2.3 The Spectral Lines for Atomic Hydrogen

Series	n_1	n_2	Spectral Region
Lyman	1	2, 3, ...	Ultraviolet
Balmer	2	3, 4, ...	Visible
Paschen	3	4, 5, ...	Infrared
Brackett	4	5, 6, ...	Infrared
Pfund	5	6, 7, ...	Infrared

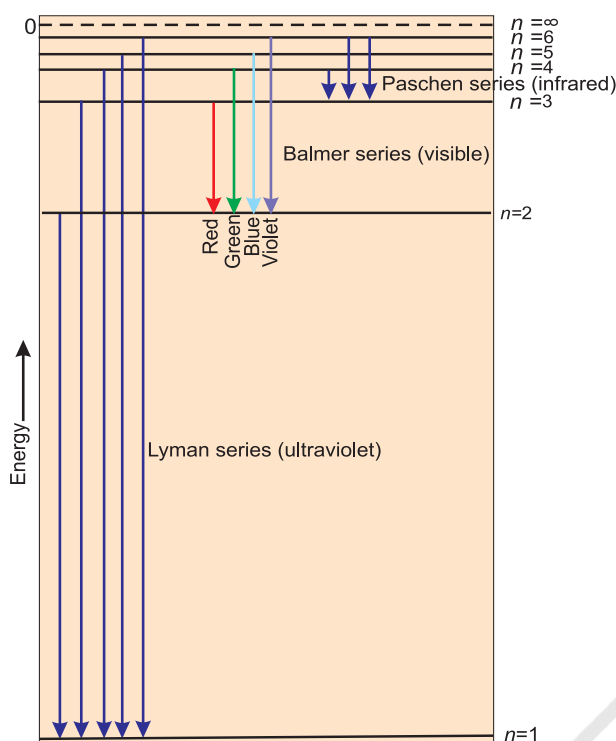


Fig. 2.11 Transitions of the electron in the hydrogen atom (The diagram shows the Lyman, Balmer and Paschen series of transitions)

becomes more and more complex for heavier atom. There are, however, certain features which are common to all line spectra, i.e., (i) line spectrum of element is unique and (ii) there is regularity in the line spectrum of each element. The questions which arise are: What are the reasons for these similarities? Is it something to do with the electronic structure of atoms? These are the questions need to be answered. We shall find later that the answers to these questions provide the key in understanding electronic structure of these elements.

2.4 BOHR'S MODEL FOR HYDROGEN ATOM

Neils Bohr (1913) was the first to explain quantitatively the general features of the structure of hydrogen atom and its spectrum. He used Planck's concept of quantisation of energy. Though the theory is not the modern quantum mechanics, it can still be used to rationalize many points in the

atomic structure and spectra. Bohr's model for hydrogen atom is based on the following postulates:

- The electron in the hydrogen atom can move around the nucleus in a circular path of fixed radius and energy. These paths are called **orbits**, stationary states or allowed energy states. These orbits are arranged concentrically around the nucleus.
- The energy of an electron in the orbit does not change with time. However, the electron will move from a lower stationary state to a higher stationary state when required amount of energy is absorbed by the electron or energy is emitted when electron moves from higher stationary state to lower stationary state (equation 2.16). The energy change does not take place in a continuous manner.

Angular Momentum

Just as linear momentum is the product of mass (m) and linear velocity (v), angular momentum is the product of moment of inertia (I) and angular velocity (ω). For an electron of mass m_e , moving in a circular path of radius r around the nucleus,

$$\text{angular momentum} = I \times \omega$$

Since $I = m_e r^2$, and $\omega = v/r$ where v is the linear velocity,

$$\therefore \text{angular momentum} = m_e r^2 \times v/r = m_e v r$$

- The frequency of radiation absorbed or emitted when transition occurs between two stationary states that differ in energy by ΔE , is given by:

$$n = \frac{\Delta E}{h} = \frac{E_2 - E_1}{h} \quad (2.10)$$

Where E_1 and E_2 are the energies of the lower and higher allowed energy states respectively. This expression is commonly known as Bohr's frequency rule.

- The angular momentum of an electron is quantised. In a given stationary state it can be expressed as in equation (2.11)

$$m_e v r = n \cdot \frac{h}{2\pi} \quad n = 1, 2, 3, \dots \quad (2.11)$$

Where m_e is the mass of electron, v is the velocity and r is the radius of the orbit in which electron is moving.

Thus an electron can move only in those orbits for which its angular momentum is integral multiple of $h/2\pi$. That means angular momentum is quantised. Radiation is emitted or absorbed only when transition of electron takes place from one quantised value of angular momentum to another. Therefore, Maxwell's electromagnetic theory does not apply here that is why only certain fixed orbits are allowed.

The details regarding the derivation of energies of the stationary states used by Bohr, are quite complicated and will be discussed in higher classes. However, according to Bohr's theory for hydrogen atom:

a) The stationary states for electron are numbered $n = 1, 2, 3, \dots$. These integral numbers (Section 2.6.2) are known as **Principal quantum numbers**.

b) The radii of the stationary states are expressed as:

$$r_n = n^2 a_0 \quad (2.12)$$

where $a_0 = 52.9$ pm. Thus the radius of the first stationary state, called the **Bohr orbit**, is 52.9 pm. Normally the electron in the hydrogen atom is found in this orbit (that is $n=1$). As n increases the value of r will increase. In other words the electron will be present away from the nucleus.

c) The most important property associated with the electron, is the energy of its stationary state. It is given by the expression.

$$E_n = -R_H \left(\frac{1}{n^2} \right) \quad n = 1, 2, 3, \dots \quad (2.13)$$

where R_H is called **Rydberg constant** and its value is 2.18×10^{-18} J. The energy of the lowest state, also called as the ground state, is

$$E_1 = -2.18 \times 10^{-18} \left(\frac{1}{1^2} \right) = -2.18 \times 10^{-18} \text{ J.}$$

The energy of the stationary state for $n = 2$, will

$$\text{be : } E_2 = -2.18 \times 10^{-18} \text{ J} \left(\frac{1}{2^2} \right) = -0.545 \times 10^{-18} \text{ J.}$$



Niels Bohr
(1885–1962)

Niels Bohr, a Danish physicist received his Ph.D. from the University of Copenhagen in 1911. He then spent a year with J.J. Thomson and Ernest Rutherford in England. In 1913, he returned to Copenhagen where he remained for the rest of his life. In 1920 he was named Director of the Institute of theoretical Physics. After first World War, Bohr worked energetically for peaceful uses of atomic energy. He received the first Atoms for Peace award in 1957. Bohr was awarded the Nobel Prize in Physics in 1922.

Fig. 2.11 depicts the energies of different stationary states or energy levels of hydrogen atom. This representation is called an energy level diagram.

When the electron is free from the influence of nucleus, the energy is taken as zero. The electron in this situation is associated with the stationary state of Principal Quantum number $= n = \infty$ and is called as ionized hydrogen atom. When the electron is attracted by the nucleus and is present in orbit n , the energy is emitted and its energy is lowered. That is the reason

What does the negative electronic energy (E_n) for hydrogen atom mean?

The energy of the electron in a hydrogen atom has a negative sign for all possible orbits (eq. 2.13). What does this negative sign convey? This negative sign means that the energy of the electron in the atom is lower than the energy of a free electron at rest. A free electron at rest is an electron that is infinitely far away from the nucleus and is assigned the energy value of zero. Mathematically, this corresponds to setting n equal to infinity in the equation (2.13) so that $E_\infty = 0$. As the electron gets closer to the nucleus (as n decreases), E_n becomes larger in absolute value and more and more negative. The most negative energy value is given by $n=1$ which corresponds to the most stable orbit. We call this the ground state.

for the presence of negative sign in equation (2.13) and depicts its stability relative to the reference state of zero energy and $n = \infty$.

- d) Bohr's theory can also be applied to the ions containing only one electron, similar to that present in hydrogen atom. For example, He^+ , Li^{2+} , Be^{3+} and so on. The energies of the stationary states associated with these kinds of ions (also known as hydrogen like species) are given by the expression.

$$E_n = -2.18 \times 10^{-18} \left(\frac{Z^2}{n^2} \right) \text{J} \quad (2.14)$$

and radii by the expression

$$r_n = \frac{52.9(n^2)}{Z} \text{pm} \quad (2.15)$$

where Z is the atomic number and has values 2,3 for the helium and lithium atoms respectively. From the above equations, it is evident that the value of energy becomes more negative and that of radius becomes smaller with increase of Z . This means that electron will be tightly bound to the nucleus.

- e) It is also possible to calculate the velocities of electrons moving in these orbits. Although the precise equation is not given here, qualitatively the magnitude of velocity of electron increases with increase of positive charge on the nucleus and decreases with increase of principal quantum number.

2.4.1 Explanation of Line Spectrum of Hydrogen

Line spectrum observed in case of hydrogen atom, as mentioned in section 2.3.3, can be explained quantitatively using Bohr's model. According to assumption 2, radiation (energy) is absorbed if the electron moves from the orbit of smaller Principal quantum number to the orbit of higher Principal quantum number, whereas the radiation (energy) is emitted if the electron moves from higher orbit to lower orbit. The energy gap between the two orbits is given by equation (2.16)

$$\Delta E = E_f - E_i \quad (2.16)$$

Combining equations (2.13) and (2.16)

$$\Delta E = \left(-\frac{R_H}{n_f^2} \right) - \left(-\frac{R_H}{n_i^2} \right) \quad (\text{where } n_i \text{ and } n_f$$

stand for initial orbit and final orbits)

$$\Delta E = R_H \left(\frac{1}{n_i^2} - \frac{1}{n_f^2} \right) = 2.18 \times 10^{-18} \text{J} \left(\frac{1}{n_i^2} - \frac{1}{n_f^2} \right) \quad (2.17)$$

The frequency (ν) associated with the absorption and emission of the photon can be evaluated by using equation (2.18)

$$\begin{aligned} \nu &= \frac{\Delta E}{h} = \frac{R_H}{h} \left(\frac{1}{n_i^2} - \frac{1}{n_f^2} \right) \\ &= \frac{2.18 \times 10^{-18} \text{J}}{6.626 \times 10^{-34} \text{Js}} \left(\frac{1}{n_i^2} - \frac{1}{n_f^2} \right) \end{aligned} \quad (2.18)$$

$$= 3.29 \times 10^{15} \left(\frac{1}{n_i^2} - \frac{1}{n_f^2} \right) \text{Hz} \quad (2.19)$$

and in terms of wavenumbers ($\bar{\nu}$)

$$\begin{aligned} \bar{\nu} &= \frac{\nu}{c} = \frac{R_H}{hc} \left(\frac{1}{n_i^2} - \frac{1}{n_f^2} \right) \\ &= \frac{3.29 \times 10^{15} \text{s}^{-1}}{3 \times 10^8 \text{ms}^{-1}} \left(\frac{1}{n_i^2} - \frac{1}{n_f^2} \right) \\ &= 1.09677 \times 10^7 \left(\frac{1}{n_i^2} - \frac{1}{n_f^2} \right) \text{m}^{-1} \end{aligned} \quad (2.20)$$

In case of absorption spectrum, $n_f > n_i$ and the term in the parenthesis is positive and energy is absorbed. On the other hand in case of emission spectrum $n_i > n_f$, ΔE is negative and energy is released.

The expression (2.17) is similar to that used by Rydberg (2.9) derived empirically using the experimental data available at that time. Further, each spectral line, whether in absorption or emission spectrum, can be associated to the particular transition in hydrogen atom. In case of large number of hydrogen atoms, different possible transitions can be observed and thus leading to large number of spectral lines. The brightness or intensity of spectral lines depends upon the number of photons of same wavelength or frequency absorbed or emitted.

Problem 2.10

What are the frequency and wavelength of a photon emitted during a transition from $n = 5$ state to the $n = 2$ state in the hydrogen atom?

Solution

Since $n_i = 5$ and $n_f = 2$, this transition gives rise to a spectral line in the visible region of the Balmer series. From equation (2.17)

$$\Delta E = 2.18 \times 10^{-18} \text{ J} \left[\frac{1}{5^2} - \frac{1}{2^2} \right]$$

$$= -4.58 \times 10^{-19} \text{ J}$$

It is an emission energy

The frequency of the photon (taking energy in terms of magnitude) is given by

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

$$= \frac{4.58 \times 10^{-19} \text{ J}}{6.626 \times 10^{-34} \text{ J s}}$$

$$= 6.91 \times 10^{14} \text{ Hz}$$

$$\lambda = \frac{c}{\nu} = \frac{3.0 \times 10^8 \text{ m s}^{-1}}{6.91 \times 10^{14} \text{ Hz}} = 434 \text{ nm}$$

Problem 2.11

Calculate the energy associated with the first orbit of He^+ . What is the radius of this orbit?

Solution

$$E_n = -\frac{(2.18 \times 10^{-18} \text{ J})Z^2}{n^2} \text{ atom}^{-1}$$

For He^+ , $n = 1$, $Z = 2$

$$E_1 = -\frac{(2.18 \times 10^{-18} \text{ J})(2^2)}{1^2} = -8.72 \times 10^{-18} \text{ J}$$

The radius of the orbit is given by equation (2.15)

$$r_n = \frac{(0.0529 \text{ nm})n^2}{Z}$$

Since $n = 1$, and $Z = 2$

$$r_n = \frac{(0.0529 \text{ nm})1^2}{2} = 0.02645 \text{ nm}$$

2.4.2 Limitations of Bohr's Model

Bohr's model of the hydrogen atom was no doubt an improvement over Rutherford's nuclear model, as it could account for the stability and line spectra of hydrogen atom and hydrogen like ions (for example, He^+ , Li^{2+} , Be^{3+} , and so on). However, Bohr's model was too simple to account for the following points.

- It fails to account for the finer details (doublet, that is two closely spaced lines) of the hydrogen atom spectrum observed by using sophisticated spectroscopic techniques. This model is also unable to explain the spectrum of atoms other than hydrogen, for example, helium atom which possesses only two electrons. Further, Bohr's theory was also unable to explain the splitting of spectral lines in the presence of magnetic field (Zeeman effect) or an electric field (Stark effect).
- It could not explain the ability of atoms to form molecules by chemical bonds.

In other words, taking into account the points mentioned above, one needs a better theory which can explain the salient features of the structure of complex atoms.

2.5 TOWARDS QUANTUM MECHANICAL MODEL OF THE ATOM

In view of the shortcoming of the Bohr's model, attempts were made to develop a more suitable and general model for atoms. Two important developments which contributed significantly in the formulation of such a model were:

- Dual behaviour of matter,
- Heisenberg uncertainty principle.

2.5.1 Dual Behaviour of Matter

The French physicist, de Broglie, in 1924 proposed that matter, like radiation, should also exhibit dual behaviour i.e., both particle and wavelike properties. This means that just as the photon has momentum as well as wavelength, electrons should also have momentum as well as wavelength, de Broglie, from this analogy, gave the following relation between wavelength (λ) and momentum (p) of a material particle.

**Louis de Broglie
(1892–1987)**

Louis de Broglie, a French physicist, studied history as an undergraduate in the early 1910's. His interest turned to science as a result of his assignment to radio communications in World War I. He received his Dr. Sc. from the University of Paris in 1924. He was professor of theoretical physics at the University of Paris from 1932 until his retirement in 1962. He was awarded the Nobel Prize in Physics in 1929.



$$\lambda = \frac{h}{mv} = \frac{h}{p} \quad (2.22)$$

where m is the mass of the particle, v its velocity and p its momentum. de Broglie's prediction was confirmed experimentally when it was found that an electron beam undergoes diffraction, a phenomenon characteristic of waves. This fact has been put to use in making an electron microscope, which is based on the wavelike behaviour of electrons just as an ordinary microscope utilises the wave nature of light. An electron microscope is a powerful tool in modern scientific research because it achieves a magnification of about 15 million times.

It needs to be noted that according to de Broglie, every object in motion has a wave character. The wavelengths associated with ordinary objects are so short (because of their large masses) that their wave properties cannot be detected. The wavelengths associated with electrons and other subatomic particles (with very small mass) can however be detected experimentally. Results obtained from the following problems prove these points qualitatively.

Problem 2.12

What will be the wavelength of a ball of mass 0.1 kg moving with a velocity of 10 m s⁻¹?

Solution

According to de Broglie equation (2.22)

$$\lambda = \frac{h}{mv} = \frac{(6.626 \times 10^{-34} \text{ Js})}{(0.1 \text{ kg})(10 \text{ m s}^{-1})}$$

$$= 6.626 \times 10^{-34} \text{ m (J = kg m}^2 \text{ s}^{-2})$$

Problem 2.13

The mass of an electron is 9.1×10^{-31} kg. If its K.E. is 3.0×10^{-25} J, calculate its wavelength.

Solution

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

$$v = \left(\frac{2 \text{K.E.}}{m} \right)^{1/2} = \left(\frac{2 \times 3.0 \times 10^{-25} \text{ kg m}^2 \text{ s}^{-2}}{9.1 \times 10^{-31} \text{ kg}} \right)^{1/2}$$

$$= 812 \text{ m s}^{-1}$$

$$\lambda = \frac{h}{mv} = \frac{6.626 \times 10^{-34} \text{ Js}}{(9.1 \times 10^{-31} \text{ kg})(812 \text{ m s}^{-1})}$$

$$= 8967 \times 10^{-10} \text{ m} = 896.7 \text{ nm}$$

Problem 2.14

Calculate the mass of a photon with wavelength 3.6 Å.

Solution

$$\lambda = 3.6 \text{ Å} = 3.6 \times 10^{-10} \text{ m}$$

Velocity of photon = velocity of light

$$m = \frac{h}{\lambda v} = \frac{6.626 \times 10^{-34} \text{ Js}}{(3.6 \times 10^{-10} \text{ m})(3 \times 10^8 \text{ m s}^{-1})}$$

$$= 6.135 \times 10^{-29} \text{ kg}$$

2.5.2 Heisenberg's Uncertainty Principle

Werner Heisenberg a German physicist in 1927, stated uncertainty principle which is the consequence of dual behaviour of matter and radiation. **It states that it is impossible to determine simultaneously, the exact position and exact momentum (or velocity) of an electron.**

Mathematically, it can be given as in equation (2.23).

$$\Delta x \times \Delta p_x \geq \frac{h}{4\pi} \quad (2.23)$$

$$\text{or } \Delta x \times \Delta(mv_x) \geq \frac{h}{4\pi}$$

$$\text{or } \Delta x \times \Delta v_x \geq \frac{h}{4\pi m}$$

where Δx is the uncertainty in position and Δp_x (or Δv_x) is the uncertainty in momentum (or velocity) of the particle. If the position of the electron is known with high degree of accuracy (Δx is small), then the velocity of the electron will be uncertain [$\Delta(v_x)$ is large]. On the other hand, if the velocity of the electron is known precisely ($\Delta(v_x)$ is small), then the position of the electron will be uncertain (Δx will be large). Thus, if we carry out some physical measurements on the electron's position or velocity, the outcome will always depict a fuzzy or blur picture.

The uncertainty principle can be best understood with the help of an example. Suppose you are asked to measure the thickness of a sheet of paper with an unmarked metrestick. Obviously, the results obtained would be extremely inaccurate and meaningless. In order to obtain any accuracy, you should use an instrument graduated in units smaller than the thickness of a sheet of the paper. Analogously, in order to determine the position of an electron, we must use a meterstick calibrated in units of smaller than the dimensions of electron (keep in mind that an electron is considered as a point charge and is therefore, dimensionless). To observe an electron, we can illuminate it with "light" or electromagnetic radiation. The "light" used must have a wavelength smaller than the dimensions of an electron. The high

momentum photons of such light $\left(p = \frac{h}{\lambda}\right)$

would change the energy of electrons by collisions. In this process we, no doubt, would be able to calculate the position of the electron, but we would know very little about the velocity of the electron after the collision.

Significance of Uncertainty Principle

One of the important implications of the Heisenberg Uncertainty Principle is that **it rules out existence of definite paths or trajectories of electrons and other similar particles.** The trajectory of an object is determined by its location and velocity at various moments. If we know where a body is at a particular instant and if we also know its velocity and the forces acting on it at that instant, we can tell where the body would be sometime later. We, therefore, conclude that the position of an object and its velocity fix its trajectory. Since for a sub-atomic object such as an electron, it is not possible simultaneously to determine the position and velocity at any given instant to an arbitrary degree of precision, it is not possible to talk of the trajectory of an electron.

The effect of Heisenberg Uncertainty Principle is significant only for motion of microscopic objects and is negligible for that of macroscopic objects. This can be seen from the following examples.

If uncertainty principle is applied to an object of mass, say about a milligram (10^{-6} kg), then

$$\begin{aligned} \Delta v \cdot \Delta x &= \frac{h}{4\pi m} \\ &= \frac{6.626 \times 10^{-34} \text{ Js}}{4 \times 3.1416 \times 10^{-6} \text{ kg}} \approx 10^{-28} \text{ m}^2 \text{ s}^{-1} \end{aligned}$$

Werner Heisenberg (1901–1976) Werner Heisenberg (1901–1976) received his Ph.D. in physics from the University of Munich in 1923. He then spent a year working with Max Born at Gottingen and three years with Niels Bohr in Copenhagen. He was professor of physics at the University of Leipzig from 1927 to 1941. During World War II, Heisenberg was in charge of German research on the atomic bomb. After the war he was named director of Max Planck Institute for physics in Gottingen. He was also accomplished mountain climber. Heisenberg was awarded the Nobel Prize in Physics in 1932.



The value of $\Delta v \Delta x$ obtained is extremely small and is insignificant. Therefore, one may say that **in dealing with milligram-sized or heavier objects, the associated uncertainties are hardly of any real consequence.**

In the case of a microscopic object like an electron on the other hand, $\Delta v \Delta x$ obtained is much larger and such uncertainties are of real consequence. For example, for an electron whose mass is 9.11×10^{-31} kg., according to Heisenberg uncertainty principle

$$\begin{aligned}\Delta v \Delta x &= \frac{h}{4\pi m} \\ &= \frac{6.626 \times 10^{-34} \text{ Js}}{4 \times 3.1416 \times 9.11 \times 10^{-31} \text{ kg}} \\ &= 10^{-4} \text{ m}^2 \text{ s}^{-1}\end{aligned}$$

It, therefore, means that if one tries to find the exact location of the electron, say to an uncertainty of only 10^{-8} m, then the uncertainty Δv in velocity would be

$$\frac{10^{-4} \text{ m}^2 \text{ s}^{-1}}{10^{-8} \text{ m}} \approx 10^4 \text{ m s}^{-1}$$

which is so large that the classical picture of electrons moving in Bohr's orbits (fixed) cannot hold good. **It, therefore, means that the precise statements of the position and momentum of electrons have to be replaced by the statements of probability, that the electron has at a given position and momentum. This is what happens in the quantum mechanical model of atom.**

Problem 2.15

A microscope using suitable photons is employed to locate an electron in an atom within a distance of 0.1 \AA . What is the uncertainty involved in the measurement of its velocity?

Solution

$$\Delta x \Delta p = \frac{h}{4\pi} \text{ or } \Delta x \times m \Delta v = \frac{h}{4\pi}$$

$$\Delta v = \frac{h}{4\pi \Delta x m}$$

$$\begin{aligned}\Delta v &= \frac{6.626 \times 10^{-34} \text{ Js}}{4 \times 3.14 \times 0.1 \times 10^{-10} \text{ m} \times 9.11 \times 10^{-31} \text{ kg}} \\ &= 0.579 \times 10^7 \text{ m s}^{-1} \quad (1 \text{ J} = 1 \text{ kg m}^2 \text{ s}^{-2}) \\ &= 5.79 \times 10^6 \text{ m s}^{-1}\end{aligned}$$

Problem 2.16

A golf ball has a mass of 40g, and a speed of 45 m/s. If the speed can be measured within accuracy of 2%, calculate the uncertainty in the position.

Solution

The uncertainty in the speed is 2%, i.e.,

$$45 \times \frac{2}{100} = 0.9 \text{ m s}^{-1}$$

Using the equation (2.22)

$$\begin{aligned}\Delta x &= \frac{h}{4\pi m \Delta v} \\ &= \frac{6.626 \times 10^{-34} \text{ Js}}{4 \times 3.14 \times 40 \text{ g} \times 10^{-3} \text{ kg g}^{-1} (0.9 \text{ m s}^{-1})} \\ &= 1.46 \times 10^{-33} \text{ m}\end{aligned}$$

This is nearly $\sim 10^{18}$ times smaller than the diameter of a typical atomic nucleus. As mentioned earlier for large particles, the uncertainty principle sets no meaningful limit to the precision of measurements.

Reasons for the Failure of the Bohr Model

One can now understand the reasons for the failure of the Bohr model. In Bohr model, an electron is regarded as a charged particle moving in well defined circular orbits about the nucleus. The wave character of the electron is not considered in Bohr model. Further, an orbit is a clearly defined path and this path can completely be defined only if both the position and the velocity of the electron are known exactly at the same time. This is not possible according to the Heisenberg uncertainty principle. *Bohr model of the hydrogen atom, therefore, not only ignores dual behaviour of matter but also contradicts Heisenberg uncertainty principle.*

Erwin Schrödinger, an Austrian physicist received his Ph.D. in theoretical physics from the University of Vienna in 1910. In 1927 Schrödinger succeeded Max Planck at the University of Berlin at Planck's request. In 1933, Schrödinger left Berlin because of his opposition to Hitler and Nazi policies and returned to Austria in 1936. After the invasion of Austria by Germany, Schrödinger was forcibly removed from his professorship. He then moved to Dublin, Ireland where he remained for seventeen years. Schrödinger shared the Nobel Prize for Physics with P.A.M. Dirac in 1933.



Erwin Schrödinger
(1887–1961)

In view of these inherent weaknesses in the Bohr model, there was no point in extending Bohr model to other atoms. In fact an insight into the structure of the atom was needed which could account for wave-particle duality of matter and be consistent with Heisenberg uncertainty principle. This came with the advent of quantum mechanics.

2.6 QUANTUM MECHANICAL MODEL OF ATOM

Classical mechanics, based on Newton's laws of motion, successfully describes the motion of all macroscopic objects such as a falling stone, orbiting planets etc., which have essentially a particle-like behaviour as shown in the previous section. However it fails when applied to microscopic objects like electrons, atoms, molecules etc. This is mainly because of the fact that classical mechanics ignores the concept of dual behaviour of matter especially for sub-atomic particles and the uncertainty principle. The branch of science that takes into account this dual behaviour of matter is called **quantum mechanics**.

Quantum mechanics is a theoretical science that deals with the study of the motions of the microscopic objects that have both observable wave like and particle like properties. It specifies the laws of motion that

these objects obey. When quantum mechanics is applied to macroscopic objects (for which wave like properties are insignificant) the results are the same as those from the classical mechanics.

Quantum mechanics was developed independently in 1926 by Werner Heisenberg and Erwin Schrödinger. Here, however, we shall be discussing the quantum mechanics which is based on the ideas of wave motion. The fundamental equation of quantum mechanics was developed by Schrödinger and it won him the Nobel Prize in Physics in 1933. This equation which incorporates wave-particle duality of matter as proposed by de Broglie is quite complex and knowledge of higher mathematics is needed to solve it. You will learn its solutions for different systems in higher classes.

For a system (such as an atom or a molecule whose energy does not change with time) the **Schrödinger equation** is written as $\hat{H}\Psi = E\Psi$ where \hat{H} is a mathematical operator called Hamiltonian. Schrödinger gave a recipe of constructing this operator from the expression for the total energy of the system. The total energy of the system takes into account the kinetic energies of all the sub-atomic particles (electrons, nuclei), attractive potential between the electrons and nuclei and repulsive potential among the electrons and nuclei individually. Solution of this equation gives E and ψ .

Hydrogen Atom and the Schrödinger Equation

When Schrödinger equation is solved for hydrogen atom, the solution gives the possible energy levels the electron can occupy and the corresponding wave function(s) (ψ) of the electron associated with each energy level. These quantized energy states and corresponding wave functions which are characterized by a set of three quantum numbers (**principal quantum number n , azimuthal quantum number l and magnetic quantum number m_l**) arise as a natural consequence in the solution of the Schrödinger equation. When an electron is in any energy state, the wave function

corresponding to that energy state contains all information about the electron. The wave function is a mathematical function whose value depends upon the coordinates of the electron in the atom and does not carry any physical meaning. Such wave functions of hydrogen or hydrogen like species with one electron are called **atomic orbitals**. Such wave functions pertaining to one-electron species are called one-electron systems. The probability of finding an electron at a point within an atom is proportional to the $|\psi|^2$ at that point. The quantum mechanical results of the hydrogen atom successfully predict all aspects of the hydrogen atom spectrum including some phenomena that could not be explained by the Bohr model.

Application of Schrödinger equation to multi-electron atoms presents a difficulty: the Schrödinger equation cannot be solved exactly for a multi-electron atom. This difficulty can be overcome by using approximate methods. Such calculations with the aid of modern computers show that orbitals in atoms other than hydrogen do not differ in any radical way from the hydrogen orbitals discussed above. The principal difference lies in the consequence of increased nuclear charge. Because of this all the orbitals are somewhat contracted. Further, as you shall see later (in subsections 2.6.3 and 2.6.4), unlike orbitals of hydrogen or hydrogen like species, whose energies depend only on the quantum number n , the energies of the orbitals in multi-electron atoms depend on quantum numbers n and l .

Important Features of the Quantum Mechanical Model of Atom

Quantum mechanical model of atom is the picture of the structure of the atom, which emerges from the application of the Schrödinger equation to atoms. The following are the important features of the quantum-mechanical model of atom:

1. The energy of electrons in atoms is quantized (i.e., can only have certain specific values), for example when electrons are bound to the nucleus in atoms.

2. The existence of quantised electronic energy levels is a direct result of the wave like properties of electrons and are allowed solutions of Schrödinger wave equation.
3. Both the exact position and exact velocity of an electron in an atom cannot be determined simultaneously (Heisenberg uncertainty principle). The path of an electron in an atom therefore, can never be determined or known accurately. That is why, as you shall see later on, one talks of only probability of finding the electron at different points in an atom.
4. **An atomic orbital is the wave function ψ for an electron in an atom.** Whenever an electron is described by a wave function, we say that the electron occupies that orbital. Since many such wave functions are possible for an electron, there are many atomic orbitals in an atom. These “one electron orbital wave functions” or orbitals form the basis of the electronic structure of atoms. In each orbital, the electron has a definite energy. An orbital cannot contain more than two electrons. In a multi-electron atom, the electrons are filled in various orbitals in the order of increasing energy. For each electron of a multi-electron atom, there shall, therefore, be an orbital wave function characteristic of the orbital it occupies. All the information about the electron in an atom is stored in its orbital wave function ψ and quantum mechanics makes it possible to extract this information out of ψ .
5. The probability of finding an electron at a point within an atom is proportional to the square of the orbital wave function i.e., $|\psi|^2$ at that point. $|\psi|^2$ is known as **probability density** and is always positive. **From the value of $|\psi|^2$ at different points within an atom, it is possible to predict the region around the nucleus where electron will most probably be found.**

2.6.1 Orbitals and Quantum Numbers

A large number of orbitals are possible in an atom. Qualitatively these orbitals can

be distinguished by their size, shape and orientation. An orbital of smaller size means there is more chance of finding the electron near the nucleus. Similarly shape and orientation mean that there is more probability of finding the electron along certain directions than along others. Atomic orbitals are precisely distinguished by what are known as quantum numbers. Each orbital is designated by three quantum numbers labelled as n , l and m_l .

The principal quantum number ‘ n ’ is a positive integer with value of $n = 1, 2, 3, \dots$. The principal quantum number determines the *size and to large extent the energy of the orbital*. For hydrogen atom and hydrogen like species (He^+ , Li^{2+} , etc.) energy and size of the orbital depends only on ‘ n ’.

The principal quantum number also identifies the **shell**. With the increase in the value of ‘ n ’, the number of allowed orbital increases and **are given by ‘ n^2 ’**. **All the orbitals of a given value of ‘ n ’ constitute a single shell of atom** and are represented by the following letters

$n = 1 \quad 2 \quad 3 \quad 4 \quad \dots$

Shell = K L M N \dots

Size of an orbital increases with increase of principal quantum number ‘ n ’. In other words the electron will be located away from the nucleus. Since energy is required in shifting away the negatively charged electron from the positively charged nucleus, the energy of the orbital will increase with increase of n .

Azimuthal quantum number. ‘ l ’ is also known as **orbital angular momentum or subsidiary quantum number**. It defines the three-dimensional shape of the orbital. For a given value of n , l can have n values ranging from 0 to $n - 1$, that is, for a given value of n , the possible value of l are : $l = 0, 1, 2, \dots, (n-1)$

For example, when $n = 1$, value of l is only 0. For $n = 2$, the possible value of l can be 0 and 1. For $n = 3$, the possible l values are 0, 1 and 2.

Each shell consists of one or more **sub-shells** or **sub-levels**. The number of

sub-shells in a principal shell is equal to the value of n . For example in the first shell ($n = 1$), there is only one sub-shell which corresponds to $l = 0$. There are two sub-shells ($l = 0, 1$) in the second shell ($n = 2$), three ($l = 0, 1, 2$) in third shell ($n = 3$) and so on. Each sub-shell is assigned an azimuthal quantum number (l). Sub-shells corresponding to different values of l are represented by the following symbols. Value for l : 0 1 2 3 4 5 \dots
notation for s p d f g h \dots
sub-shell

Table 2.4 shows the permissible values of ‘ l ’ for a given principal quantum number and the corresponding sub-shell notation.

Table 2.4 Subshell Notations

n	l	Subshell notation
1	0	1s
2	0	2s
2	1	2p
3	0	3s
3	1	3p
3	2	3d
4	0	4s
4	1	4p
4	2	4d
4	3	4f

Magnetic orbital quantum number. ‘ m_l ’ gives information about the **spatial orientation of the orbital with respect to standard set of co-ordinate axis**. For any **sub-shell (defined by ‘ l ’ value)** $2l+1$ values of m_l are possible and these values are given by : $m_l = -l, -(l-1), -(l-2) \dots 0, 1 \dots (l-2), (l-1), l$

Thus for $l = 0$, the only permitted value of $m_l = 0$, [$2(0)+1 = 1$, one s orbital]. For $l = 1$, m_l can be $-1, 0$ and $+1$ [$2(1)+1 = 3$, three p orbitals]. For $l = 2$, $m_l = -2, -1, 0, +1$ and $+2$, [$2(2)+1 = 5$, five d orbitals]. It should be noted that the values of m_l are derived from l and that the value of l are derived from n .

Each orbital in an atom, therefore, is defined by a set of values for n , l and m_l . An orbital described by the quantum numbers $n = 2$, $l = 1$, $m_l = 0$ is an orbital in the p subshell of the second shell. The following chart gives the relation between the subshell and the number of orbitals associated with it.

Value of l	0	1	2	3	4	5
Subshell notation	s	p	d	f	g	h
number of orbitals	1	3	5	7	9	11

Electron spin ‘s’ : The three quantum numbers labelling an atomic orbital can be used equally well to define its energy, shape and orientation. But all these quantum numbers are not enough to explain the line spectra observed in the case of multi-electron atoms, that is, some of the lines actually occur in doublets (two lines closely spaced), triplets (three lines, closely spaced) etc. This suggests the presence of a few more energy levels than predicted by the three quantum numbers.

In 1925, George Uhlenbeck and Samuel Goudsmit proposed the presence of the fourth quantum number known as the **electron spin quantum number (m_s)**. An electron spins around its own axis, much in a similar way as earth spins around its own axis while revolving around the sun. In other words, an electron has, besides charge and mass, intrinsic spin angular quantum number. Spin

angular momentum of the electron — a vector quantity, can have two orientations relative to the chosen axis. These two orientations are distinguished by the spin quantum numbers m_s which can take the values of $+\frac{1}{2}$ or $-\frac{1}{2}$. These are called the **two spin states of the electron** and are normally represented by two arrows, \uparrow (spin up) and \downarrow (spin down). Two electrons that have different m_s values (one $+\frac{1}{2}$ and the other $-\frac{1}{2}$) are said to have opposite spins. An orbital cannot hold more than two electrons and these two electrons should have opposite spins.

To sum up, the four quantum numbers provide the following information :

- n defines the shell, determines the size of the orbital and also to a large extent the energy of the orbital.
- There are n subshells in the n^{th} shell. l identifies the subshell and determines the shape of the orbital (see section 2.6.2). There are $(2l+1)$ orbitals of each type in a subshell, that is, one s orbital ($l = 0$), three p orbitals ($l = 1$) and five d orbitals ($l = 2$) per subshell. To some extent l also determines the energy of the orbital in a multi-electron atom.
- m_l designates the orientation of the orbital. For a given value of l , m_l has $(2l+1)$ values, the same as the number of orbitals per subshell. It means that

Orbit, orbital and its importance

Orbit and orbital are not synonymous. An orbit, as proposed by Bohr, is a circular path around the nucleus in which an electron moves. A precise description of this path of the electron is impossible according to Heisenberg uncertainty principle. Bohr orbits, therefore, have no real meaning and their existence can never be demonstrated experimentally. An atomic orbital, on the other hand, is a quantum mechanical concept and refers to the one electron wave function ψ in an atom. It is characterized by three quantum numbers (n , l and m_l) and its value depends upon the coordinates of the electron. ψ has, by itself, no physical meaning. It is the square of the wave function i.e., $|\psi|^2$ which has a physical meaning. $|\psi|^2$ at any point in an atom gives the value of probability density at that point. Probability density ($|\psi|^2$) is the probability per unit volume and the product of $|\psi|^2$ and a small volume (called a volume element) yields the probability of finding the electron in that volume (the reason for specifying a small volume element is that $|\psi|^2$ varies from one region to another in space but its value can be assumed to be constant within a small volume element). The total probability of finding the electron in a given volume can then be calculated by the sum of all the products of $|\psi|^2$ and the corresponding volume elements. It is thus possible to get the probable distribution of an electron in an orbital.

the number of orbitals is equal to the number of ways in which they are oriented.

- iv) m_s refers to orientation of the spin of the electron.

Problem 2.17

What is the total number of orbitals associated with the principal quantum number $n = 3$?

Solution

For $n = 3$, the possible values of l are 0, 1 and 2. Thus there is one 3s orbital ($n = 3, l = 0$ and $m_l = 0$); there are three 3p orbitals ($n = 3, l = 1$ and $m_l = -1, 0, +1$); there are five 3d orbitals ($n = 3, l = 2$ and $m_l = -2, -1, 0, +1, +2$).

Therefore, the total number of orbitals is $1+3+5 = 9$

The same value can also be obtained by using the relation; number of orbitals = n^2 , i.e. $3^2 = 9$.

Problem 2.18

Using s, p, d, f notations, describe the orbital with the following quantum numbers

- (a) $n = 2, l = 1$, (b) $n = 4, l = 0$, (c) $n = 5, l = 3$, (d) $n = 3, l = 2$

Solution

	n	l	orbital
a)	2	1	2p
b)	4	0	4s
c)	5	3	5f
d)	3	2	3d

2.6.2 Shapes of Atomic Orbitals

The orbital wave function or ψ for an electron in an atom has no physical meaning. It is simply a mathematical function of the coordinates of the electron. However, for different orbitals the plots of corresponding wave functions as a function of r (the distance from the nucleus) are different. Fig. 2.12(a), gives such plots for 1s ($n = 1, l = 0$) and 2s ($n = 2, l = 0$) orbitals.

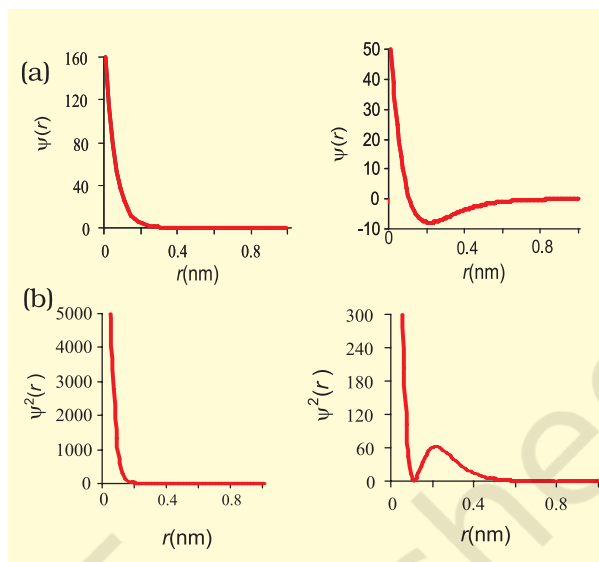


Fig. 2.12 The plots of (a) the orbital wave function $\psi(r)$; (b) the variation of probability density $\psi^2(r)$ as a function of distance r of the electron from the nucleus for 1s and 2s orbitals.

According to the German physicist, Max Born, the square of the wave function (i.e., ψ^2) at a point gives the probability density of the electron at that point. The variation of ψ^2 as a function of r for 1s and 2s orbitals is given in Fig. 2.12(b). Here again, you may note that the curves for 1s and 2s orbitals are different.

It may be noted that for 1s orbital the probability density is maximum at the nucleus and it decreases sharply as we move away from it. On the other hand, for 2s orbital the probability density first decreases sharply to zero and again starts increasing. After reaching a small maxima it decreases again and approaches zero as the value of r increases further. The region where this probability density function reduces to zero is called **nodal surfaces** or simply **nodes**. In general, it has been found that ns -orbital has $(n - 1)$ nodes, that is, number of nodes increases with increase of principal quantum number n . In other words, number of nodes for 2s orbital is one, two for 3s and so on.

These probability density variation can be visualised in terms of charge cloud diagrams [Fig. 2.13(a)]. In these diagrams, the density

of the dots in a region represents electron probability density in that region.

Boundary surface diagrams of constant probability density for different orbitals give a fairly good representation of the shapes of the orbitals. In this representation, a boundary surface or contour surface is drawn in space for an orbital on which the value of probability density $|\psi|^2$ is constant. In principle many such boundary surfaces may be possible. However, for a given orbital, only that boundary surface diagram of constant probability density* is taken to be good representation of the shape of the orbital which encloses a region or volume in which the probability of finding the electron is very high, say, 90%. The boundary surface diagram for 1s and 2s orbitals are given in Fig. 2.13(b). One may ask a question : Why do we not draw a boundary surface diagram, which bounds a region in which the probability of finding the electron is, 100 %? The answer to this question is that the probability density $|\psi|^2$ has always some value, however small it may be, at any finite distance from the nucleus. It is therefore, not possible to draw a boundary surface diagram of a rigid size in which the probability of finding the electron is 100%. Boundary surface diagram for a s orbital is actually a sphere centred on the nucleus. In two dimensions, this sphere looks like a circle. It encloses a region in which probability of finding the electron is about 90%.

Thus, we see that 1s and 2s orbitals are spherical in shape. In reality all the s-orbitals are spherically symmetric, that is, the probability of finding the electron at a given distance is equal in all the directions. It is also observed that the size of the s orbital increases with increase in n , that is, $4s > 3s > 2s > 1s$ and the electron is located further away from the nucleus as the principal quantum number increases.

Boundary surface diagrams for three $2p$ orbitals ($l = 1$) are shown in Fig. 2.14. In

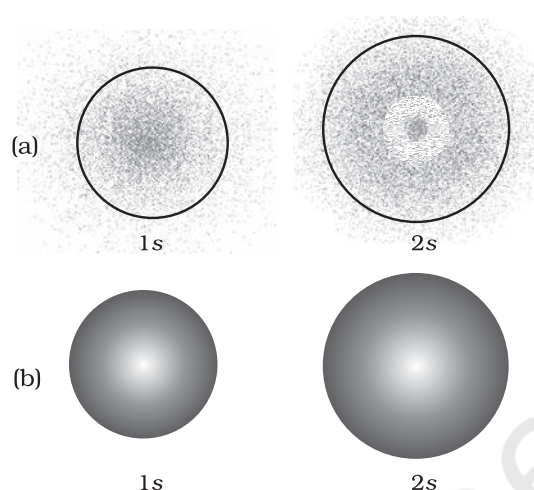


Fig. 2.13 (a) Probability density plots of 1s and 2s atomic orbitals. The density of the dots represents the probability density of finding the electron in that region. (b) Boundary surface diagram for 1s and 2s orbitals.

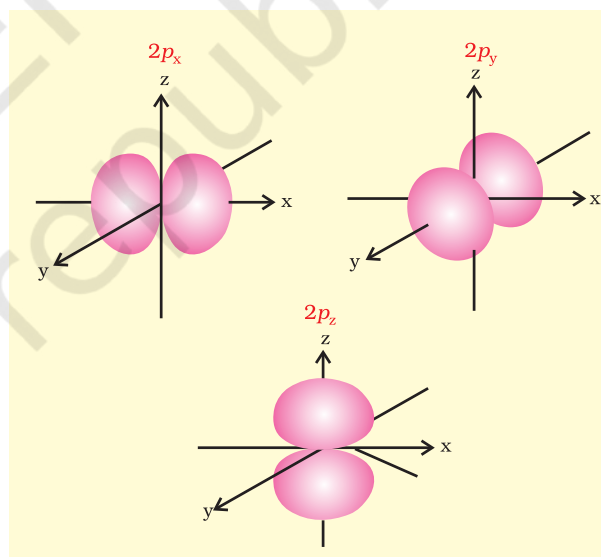


Fig. 2.14 Boundary surface diagrams of the three $2p$ orbitals.

these diagrams, the nucleus is at the origin. Here, unlike s-orbitals, the boundary surface diagrams are not spherical. Instead each p orbital consists of two sections called lobes that are on either side of the plane that passes through the nucleus. The probability density

* If probability density $|\psi|^2$ is constant on a given surface, $|\psi|$ is also constant over the surface. The boundary surface for $|\psi|^2$ and $|\psi|$ are identical.

function is zero on the plane where the two lobes touch each other. The size, shape and energy of the three orbitals are identical. They differ however, in the way the lobes are oriented. Since the lobes may be considered to lie along the x , y or z axis, they are given the designations $2p_x$, $2p_y$, and $2p_z$. It should be understood, however, that *there is no simple relation between the values of m_l (-1 , 0 and $+1$) and the x , y and z directions.* For our purpose,

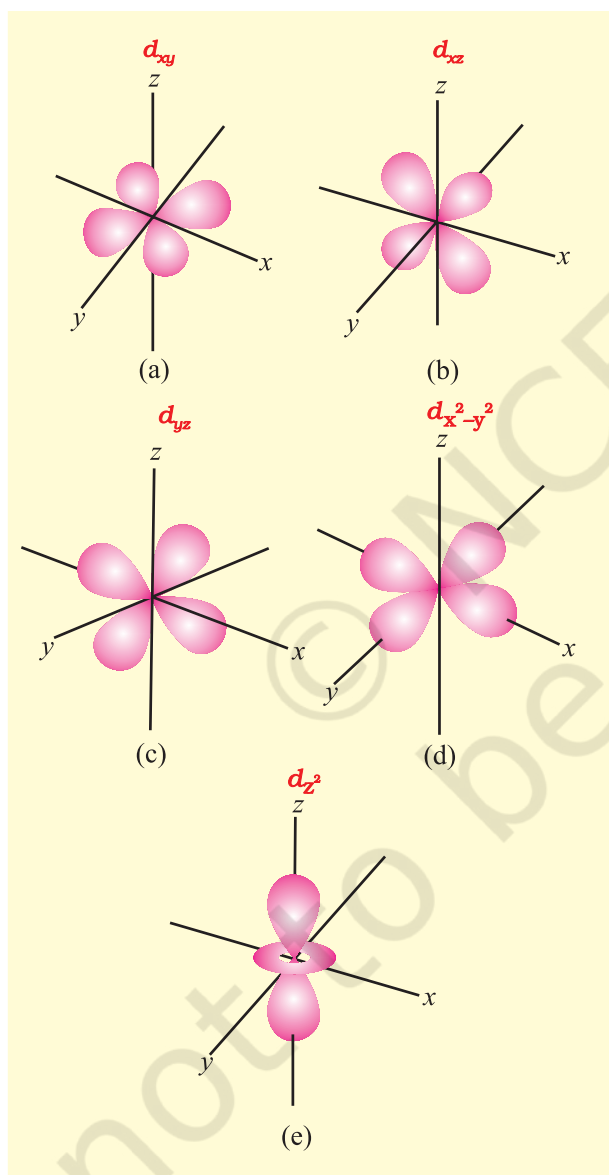


Fig. 2.15 Boundary surface diagrams of the five $3d$ orbitals.

it is sufficient to remember that, because there are three possible values of m_l , there are, therefore, three p orbitals whose axes are mutually perpendicular. Like s orbitals, p orbitals increase in size and energy with increase in the principal quantum number and hence the order of the energy and size of various p orbitals is $4p > 3p > 2p$. Further, like s orbitals, the probability density functions for p -orbital also pass through value zero, besides at zero and infinite distance, as the distance from the nucleus increases. The number of nodes are given by the $n - 2$, that is number of radial node is 1 for $3p$ orbital, two for $4p$ orbital and so on.

For $l = 2$, the orbital is known as d -orbital and the minimum value of principal quantum number (n) has to be 3. as the value of l cannot be greater than $n - 1$. There are five m_l values (-2 , -1 , 0 , $+1$ and $+2$) for $l = 2$ and thus there are five d orbitals. The boundary surface diagram of d orbitals are shown in Fig. 2.15.

The five d -orbitals are designated as d_{xy} , d_{yz} , d_{xz} , $d_{x^2-y^2}$ and d_{z^2} . The shapes of the first four d -orbitals are similar to each other, where as that of the fifth one, d_{z^2} , is different from others, but all five $3d$ orbitals are equivalent in energy. The d orbitals for which n is greater than 3 ($4d$, $5d$...) also have shapes similar to $3d$ orbital, but differ in energy and size.

Besides the radial nodes (i.e., probability density function is zero), the probability density functions for the np and nd orbitals are zero at the plane (s), passing through the nucleus (origin). For example, in case of p_z orbital, xy -plane is a nodal plane, in case of d_{xy} orbital, there are two nodal planes passing through the origin and bisecting the xy plane containing z -axis. These are called angular nodes and number of angular nodes are given by ' l ', i.e., one angular node for p orbitals, two angular nodes for ' d ' orbitals and so on. **The total number of nodes are given by $(n-1)$, i.e., sum of l angular nodes and $(n - l - 1)$ radial nodes.**

2.6.3 Energies of Orbitals

The energy of an electron in a hydrogen atom is determined solely by the principal quantum

number. Thus the energy of the orbitals in hydrogen atom increases as follows :

$$1s < 2s = 2p < 3s = 3p = 3d < 4s = 4p = 4d = 4f < \dots \quad (2.23)$$

and is depicted in Fig. 2.16. Although the shapes of 2s and 2p orbitals are different, an electron has the same energy when it is in the 2s orbital as when it is present in 2p orbital. The orbitals having the same energy are called **degenerate**. The 1s orbital in a hydrogen atom, as said earlier, corresponds to the most stable condition and is called the **ground state** and an electron residing in this orbital is most strongly held by the nucleus. An electron in the 2s, 2p or higher orbitals in a hydrogen atom is in **excited state**.

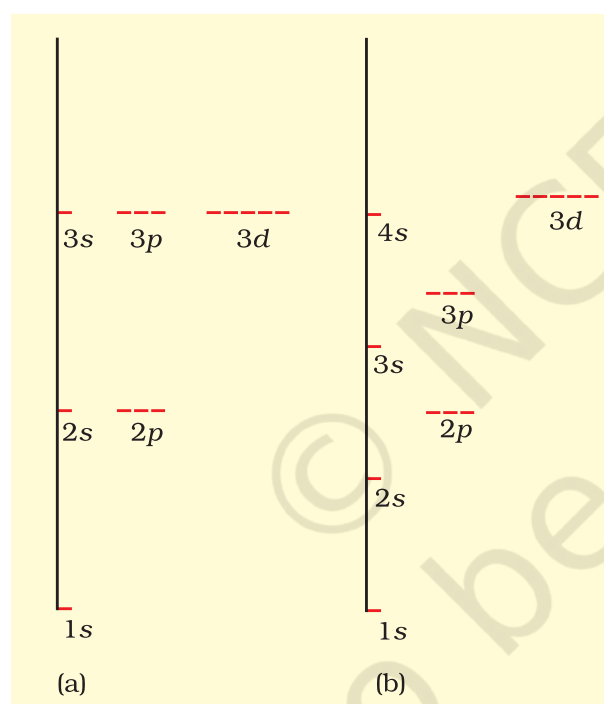


Fig. 2.16 Energy level diagrams for the few electronic shells of (a) hydrogen atom and (b) multi-electronic atoms. Note that orbitals for the same value of principal quantum number, have the same energies even for different azimuthal quantum number for hydrogen atom. In case of multi-electronic atoms, orbitals with same principal quantum number possess different energies for different azimuthal quantum numbers.

The energy of an electron in a multi-electron atom, unlike that of the hydrogen atom, depends not only on its principal quantum number (shell), but also on its azimuthal quantum number (subshell). That is, for a given principal quantum number, $s, p, d, f \dots$ all have different energies. Within a given principal quantum number, the energy of orbitals increases in the order $s < p < d < f$. For higher energy levels, these differences are sufficiently pronounced and straggling of orbital energy may result, e.g., $4s < 3d$ and $6s < 5d$; $4f < 6p$. The main reason for having different energies of the subshells is the mutual repulsion among the electrons in multi-electron atoms. The only electrical interaction present in hydrogen atom is the attraction between the negatively charged electron and the positively charged nucleus. In multi-electron atoms, besides the presence of attraction between the electron and nucleus, there are repulsion terms between every electron and other electrons present in the atom. Thus the stability of an electron in a multi-electron atom is because total attractive interactions are more than the repulsive interactions. In general, the repulsive interaction of the electrons in the outer shell with the electrons in the inner shell are more important. On the other hand, the attractive interactions of an electron increases with increase of positive charge (Ze) on the nucleus. Due to the presence of electrons in the inner shells, the electron in the outer shell will not experience the full positive charge of the nucleus (Ze). The effect will be lowered due to the partial screening of positive charge on the nucleus by the inner shell electrons. This is known as the **shielding of the outer shell electrons from the nucleus by the inner shell electrons**, and the net positive charge experienced by the outer electrons is known as **effective nuclear charge** (Z_{eff}). Despite the shielding of the outer electrons from the nucleus by the inner shell electrons, the attractive force experienced by the outer shell electrons increases with increase of nuclear charge. In other words, the energy of interaction between, the nucleus and electron

(that is orbital energy) decreases (that is more negative) with the increase of atomic number (Z).

Both the attractive and repulsive interactions depend upon the shell and shape of the orbital in which the electron is present. For example electrons present in spherical shaped, s orbital shields the outer electrons from the nucleus more effectively as compared to electrons present in p orbital. Similarly electrons present in p orbitals shield the outer electrons from the nucleus more than the electrons present in d orbitals, even though all these orbitals are present in the same shell. Further within a shell, due to spherical shape of s orbital, the s orbital electron spends more time close to the nucleus in comparison to p orbital electron which spends more time in the vicinity of nucleus in comparison to d orbital electron. In other words, for a given shell (principal quantum number), the Z_{eff} experienced by the electron decreases with increase of azimuthal quantum number (l), that is, the s orbital electron will be more tightly bound to the nucleus than p orbital electron which in turn will be better tightly bound than the d orbital electron. The energy of electrons in s orbital will be lower (more negative) than that of p orbital electron which will have less energy than that of d orbital electron and so on. Since the extent of shielding from the nucleus is different for electrons in different orbitals, it leads to the splitting of energy levels within the same shell (or same principal quantum number), that is, energy of electron in an orbital, as mentioned earlier, depends upon the values of n and l . Mathematically, the dependence of energies of the orbitals on n and l are quite complicated but one simple rule is that, **the lower the value of $(n + l)$ for an orbital, the lower is its energy. If two orbitals have the same value of $(n + l)$, the orbital with lower value of n will have the lower energy.** The Table 2.5 illustrates the $(n + l)$ rule and Fig. 2.16 depicts the energy levels of multi-electrons atoms. It may be noted that different subshells of a particular shell have different energies in case of multi-electrons atoms. However, in hydrogen atom, these have the

Table 2.5 Arrangement of Orbitals with Increasing Energy on the Basis of $(n + l)$ Rule

Orbital	Value of n	Value of l	Value of $(n + l)$	
1s	1	0	$1 + 0 = 1$	
2s	2	0	$2 + 0 = 2$	
2p	2	1	$2 + 1 = 3$	$2p$ ($n=2$) has lower energy than
3s	3	0	$3 + 0 = 3$	$3s$ ($n=3$)
3p	3	1	$3 + 1 = 4$	$3p$ ($n=3$) has lower energy than
4s	4	0	$4 + 0 = 4$	$4s$ ($n=4$)
3d	3	2	$3 + 2 = 5$	$3d$ ($n=3$) has lower energy than
4p	4	1	$4 + 1 = 5$	$4p$ ($n=4$)

same energy. Lastly it may be mentioned here that **energies of the orbitals in the same subshell decrease with increase in the atomic number (Z_{eff})**. For example, energy of $2s$ orbital of hydrogen atom is greater than that of $2s$ orbital of lithium and that of lithium is greater than that of sodium and so on, that is, $E_{2s}(\text{H}) > E_{2s}(\text{Li}) > E_{2s}(\text{Na}) > E_{2s}(\text{K})$.

2.6.4 Filling of Orbitals in Atom

The filling of electrons into the orbitals of different atoms takes place according to the *aufbau* principle which is based on the Pauli's exclusion principle, the Hund's rule of maximum multiplicity and the relative energies of the orbitals.

Aufbau Principle

The word '*aufbau*' in German means 'building up'. The building up of orbitals means the

filling up of orbitals with electrons. The principle states : **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 after the lower energy orbitals are filled. As you have learnt above, energy of a given orbital depends upon effective nuclear charge and different type of orbitals are affected to different extent. Thus, there is no single ordering of energies of orbitals which will be universally correct for all atoms.

However, following order of energies of the orbitals is extremely useful:

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

The order may be remembered by using the method given in Fig. 2.17. Starting from

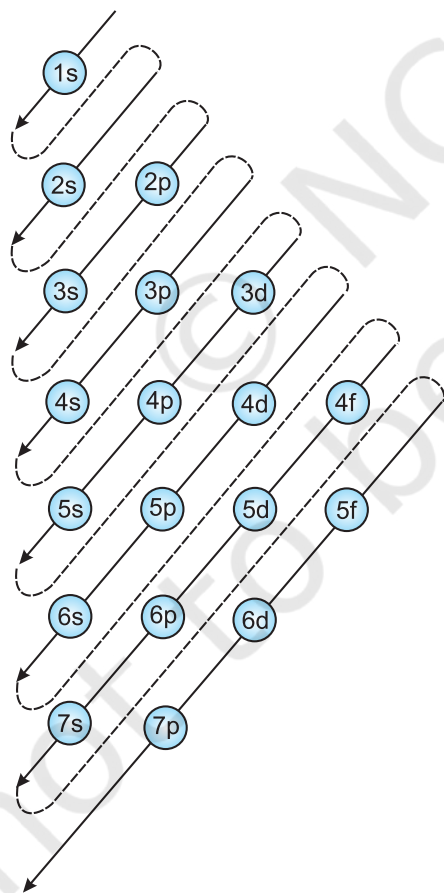


Fig.2.17 Order of filling of orbitals

the top, the direction of the arrows gives the order of filling of orbitals, that is starting from right top to bottom left. With respect to placement of outermost valence electrons, it is remarkably accurate for all atoms. For example, valence electron in potassium must choose between 3d and 4s orbitals and as predicted by this sequence, it is found in 4s orbital. The above order should be assumed to be a rough guide to the filling of energy levels. In many cases, the orbitals are similar in energy and small changes in atomic structure may bring about a change in the order of filling. Even then, the above series is a useful guide to the building of the electronic structure of an atom provided that it is remembered that exceptions may occur.

Pauli Exclusion Principle

The number of electrons to be filled in various orbitals is restricted by the exclusion principle, given by the Austrian scientist Wolfgang Pauli (1926). According to this principle : **No two electrons in an atom can have the same set of four quantum numbers.** Pauli exclusion principle can also be stated as : **“Only two electrons may exist in the same orbital and these electrons must have opposite spin.”**

This means that the two electrons can have the same value of three quantum numbers n , l and m_l , but must have the opposite spin quantum number. The restriction imposed by Pauli’s exclusion principle on the number of electrons in an orbital helps in calculating the capacity of electrons to be present in any subshell. For example, subshell 1s comprises one orbital and thus the maximum number of electrons present in 1s subshell can be two, in p and d subshells, the maximum number of electrons can be 6 and 10 and so on. This can be summed up as : **the maximum number of electrons in the shell with principal quantum number n is equal to $2n^2$.**

Hund’s Rule of Maximum Multiplicity

This rule deals with the filling of electrons into the orbitals belonging to the same subshell (that is, orbitals of equal energy, called **degenerate orbitals**). It states : **pairing of**

electrons in the orbitals belonging to the same subshell (p , d or f) does not take place until each orbital belonging to that subshell has got one electron each i.e., it 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. It has been observed that half filled and fully filled degenerate set of orbitals acquire extra stability due to their symmetry (see Section, 2.6.7).

2.6.5 Electronic Configuration of Atoms

The distribution of electrons into orbitals of an atom is called its **electronic configuration**. If one keeps in mind the basic rules which govern the filling of different atomic orbitals, the electronic configurations of different atoms can be written very easily.

The electronic configuration of different atoms can be represented in two ways. For example :

- (i) $s^a p^b d^c \dots$ notation
- (ii) Orbital diagram



In the first notation, the subshell is represented by the respective letter symbol and the number of electrons present in the subshell is depicted, as the super script, like a^2 , b^2 , c^2 , ... etc. The similar subshell represented for different shells is differentiated by writing the principal quantum number before the respective subshell. In the second notation each orbital of the subshell is represented by a box and the electron is represented by an arrow (\uparrow) a positive spin or an arrow (\downarrow) a negative spin. The advantage of second notation over the first is that it represents all the four quantum numbers.

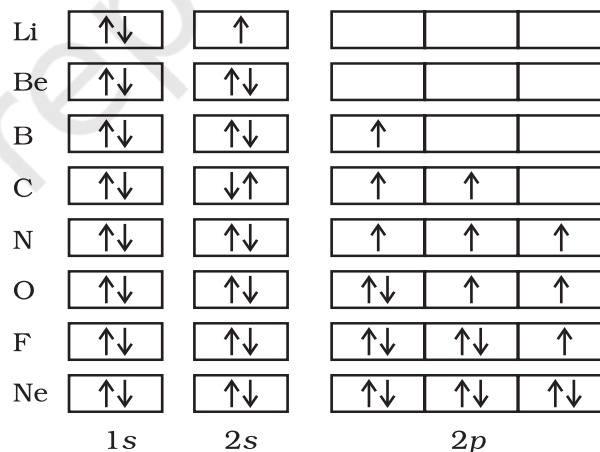
The hydrogen atom has only one electron which goes in the orbital with the lowest energy, namely 1s. The electronic configuration of the hydrogen atom is $1s^1$ meaning that it has one electron in the 1s orbital. The second electron in helium (He) can also occupy the

1s orbital. Its configuration is, therefore, $1s^2$. As mentioned above, the two electrons differ from each other with opposite spin, as can be seen from the orbital diagram.



The third electron of lithium (Li) is not allowed in the 1s orbital because of Pauli exclusion principle. It, therefore, takes the next available choice, namely the 2s orbital. The electronic configuration of Li is $1s^2 2s^1$. The 2s orbital can accommodate one more electron. The configuration of beryllium (Be) atom is, therefore, $1s^2 2s^2$ (see Table 2.6, page 66 for the electronic configurations of elements).

In the next six elements—boron (B, $1s^2 2s^2 2p^1$), carbon (C, $1s^2 2s^2 2p^2$), nitrogen (N, $1s^2 2s^2 2p^3$), oxygen (O, $1s^2 2s^2 2p^4$), fluorine (F, $1s^2 2s^2 2p^5$) and neon (Ne, $1s^2 2s^2 2p^6$), the $2p$ orbitals get progressively filled. This process is completed with the neon atom. The orbital picture of these elements can be represented as follows :



The electronic configuration of the elements sodium ($\text{Na}, 1s^2 2s^2 2p^6 3s^1$) to argon ($\text{Ar}, 1s^2 2s^2 2p^6 3s^2 3p^6$), follow exactly the same pattern as the elements from lithium to neon with the difference that the $3s$ and $3p$ orbitals are getting filled now. This process can be simplified if we represent the total number of electrons in the first two shells by the name of element neon (Ne). The electronic configuration of the elements from sodium to