



3

ATOMIC STRUCTURE

Chemistry has been defined as the study of matter in terms of its structure, composition and the properties. As you are aware, matter is made up of atoms, and therefore an understanding of the structure of atom is very important. You have studied in your earlier classes that the earliest concept of atom (smallest indivisible part of matter) was given by ancient (600-400 BC) Indian and Greek philosophers. At that time there were no experimental evidence. The origin of the concept of atom was based on their thoughts on ‘What would happen if we continuously keep dividing matter’. John Dalton revived the concept of atom in the beginning of nineteenth century in terms of his **atomic theory** which successfully explained the laws of chemical combination. Later experiments showed that the atom is not indivisible but has an internal structure.

In this lesson you will learn about the internal structure of an atom which will help you to understand the correlations between its structure and properties. You would learn about these in the later lessons.



Objectives

After reading this lesson you will be able to :

- recognize the fundamental particles of atom;
- describe Rutherford’s experiment and explain its results;
- define electromagnetic radiation;
- list and define the characteristic parameters of electromagnetic radiation;
- discuss line spectrum of hydrogen;
- explain Bohr’s postulates and discuss his model;
- draw energy level diagram of hydrogen atom showing different series of lines in its spectrum;
- explain wave particle duality of matter and radiation;
- formulate Heisenberg’s uncertainty principle;

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- explain the need for quantum mechanical model;
- draw probability pictures of an electron in an atom;
- list quantum numbers and discuss their significance;
- draw the shapes of s, p and d orbitals;
- recognize nodal plane;
- explain Pauli's exclusion principle;
- define Aufbau principle and
- explain Hund's rule of maximum multiplicity.

3.1 Fundamental Particles of Atom

In 1897 J.J. Thomson discovered **electron** as a constituent of atom. He determined that an electron had a negative charge and had very little mass as compared to that of the atom. Since an atom was found to be electrically neutral it was inferred that some source of positive charge must be present in the atom. This soon led to the experimental discovery of the proton, which is a positively charged subatomic particle. Proton was found approximately 1840 times heavier than an electron. Further experiments revealed that the atomic masses were more than that expected from the presence of just protons and electrons in the atom. For example, the mass of helium atom was expected to be double that of hydrogen atom but was actually found to be almost four times the mass of hydrogen atom. This suggested the presence of neutral particles with mass comparable to that of protons in the atom. Sir James Chadwick discovered this neutral particle and called it **neutron** subsequently in 1932. Thus we may conclude that atoms are not indivisible but are made up of three fundamental particles whose characteristics are given in Table 3.1.

Table 3.1 Fundamental particles of atom and their characteristics

Particle	Symbol	Mass/ kg	Actual Charge / C	Relative charge
Electron	<i>e</i>	$9.109\ 389 \times 10^{-31}$	$-1.602\ 177 \times 10^{-19}$	-1
Proton	<i>p</i>	$1.672\ 623 \times 10^{-27}$	$1.602\ 177 \times 10^{-19}$	+1
Neutron	<i>n</i>	$1.674\ 928 \times 10^{-27}$	0	0

Since atoms are made up of still smaller particles, they must have an internal structure. In the next section we shall take up some of the earlier ideas about the internal structure of atom.



Intext Question 3.1

1. Compare the mass of an electron with that of the proton.

.....

2. What is a fundamental particle?

.....



3. What is the name given to neutral particles in the atom?

.....

3.2 Earlier Models

Once it was established that the atom is not indivisible, the scientists made attempts to understand the structure of the atom. A number of models have been proposed for the internal structure of the atom. The first attempt to describe the structure of atom in terms of a model was made by J.J Thomson.

3.2.1 Thomson's Model

On the basis of his experiments on discharge tubes, Thomson proposed that atoms can be considered as a large positively charged body with a number of small negatively charged electrons scattered throughout it. This model (Fig.3.1) was called as plum pudding model of the atom.

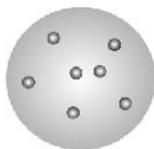


Fig. 3.1 : A pictorial representation of Thomson's plum-pudding model

The electrons represent the plums in the pudding made of positive charge. It is sometimes also called as **watermelon model**. In this, the juicy pulp of the watermelon represents the positive charge and the seeds represent the electrons.



J.J. Thomson
(1856-1940)

Won Nobel prize in Physics in 1906



Ernest Rutherford
(1871-1937)

Won Nobel prize in Chemistry in 1908

3.2.2 Rutherford's Experiment

Ernest Rutherford performed an experiment called 'Gold Foil Experiment' or 'α-ray scattering experiment' to test the structure of an atom as proposed by Thomson. In this experiment a beam of fast moving alpha particles (positively charged helium ions) was passed through a very thin foil of gold. He expected that the alpha particles would just pass straight through the gold foil and could be detected by a photographic plate. But, the actual results of the experiment (Fig. 3.2) were quite surprising. It was observed that most of the α-particles did pass straight through the foil but a number of particles were deflected from their path. Some of these deflected slightly while a few deflected through large angles and about 1 in 10,000 α-particles suffered a rebound

Atomic Structure and Chemical Bonding



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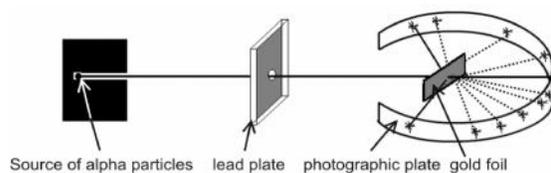


Fig 3.2: Schematic representation of Rutherford's α -ray scattering experiment.

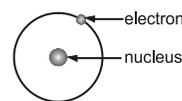


Fig 3.3 : Schematic representation of Rutherford's model

These results led Rutherford to conclude that :

- the atom contained some dense and positively charged region located at the center of the atom that he called as **nucleus**.
- all the positive charge of the atom and most of its mass was contained in the nucleus.
- the rest of the atom must be empty space which contains the much smaller and negatively charged electrons (Fig. 3.3).

The model proposed by Rutherford explained the observation in the α -ray scattering experiments as shown below in Fig 3.4.

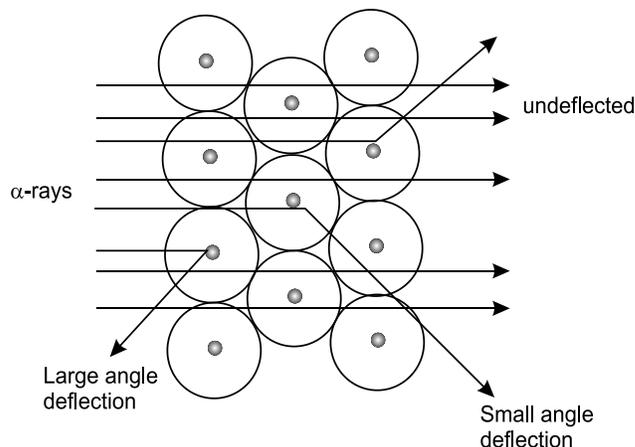


Fig 3.4 : Explanation of the results of α -ray scattering experiment.

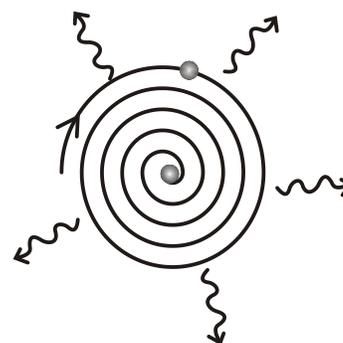


Fig 3.5 : Failure of Rutherford's model

However, there was a problem with the Rutherford's model. According to the Maxwell's theory of electromagnetic radiation, a charged particle undergoing acceleration would continuously emit radiation and lose energy. Since the electron in the atom is also a charged particle and is under acceleration, it is expected to continuously lose energy. As a consequence, the electron moving around the nucleus would approach the nucleus by a spiral path (Fig. 3.5) and the atom would collapse. However, since it does not happen we can say that the Rutherford's model failed to explain the stability of the atom.

The next attempt to suggest a model for atom was made by Neils Bohr- a student of Rutherford. This model used the concept of quantisation of energy of electrons in the atom. Since this fact was suggested by line spectrum of hydrogen atom it is worthwhile to understand the meaning of a spectrum. For this we begin with the understanding of the nature of an electromagnetic radiation.



Notes

**Intext Question 3.2**

1. List the three constituent particles of an atom.

.....

2. What was the aim of Rutherford's α -rays scattering experiment?

.....

3. Briefly describe Rutherford's model of an atom.

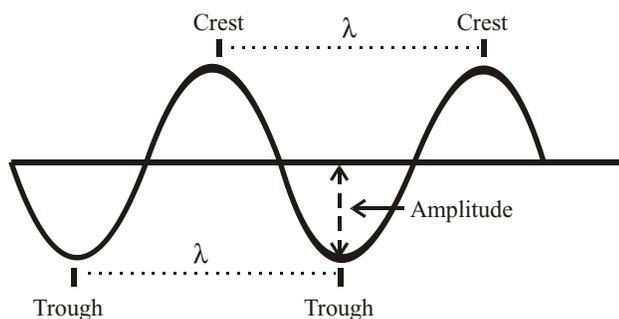
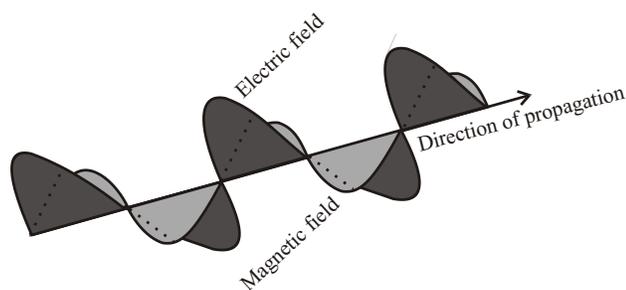
.....

4. On what basis was the Rutherford's model rejected?

.....

3.3 Electromagnetic Radiations

Electromagnetic radiation is a kind of energy, which is transmitted through space in the form of electric and magnetic fields. These do not require any medium to propagate. Visible light, radiant heat, radio waves, X-rays and gamma radiation are some of the examples of electromagnetic radiations. According to the Maxwell's theory, an electromagnetic radiation can be visualised as oscillating electric and magnetic fields. These travel as waves in the planes perpendicular to each other and also to the direction of propagation. (Fig. 3.6 (a)). These radiations travel with the velocity of light ($3.0 \times 10^8 \text{ m s}^{-1}$).



(a)

Atomic Structure and Chemical Bonding



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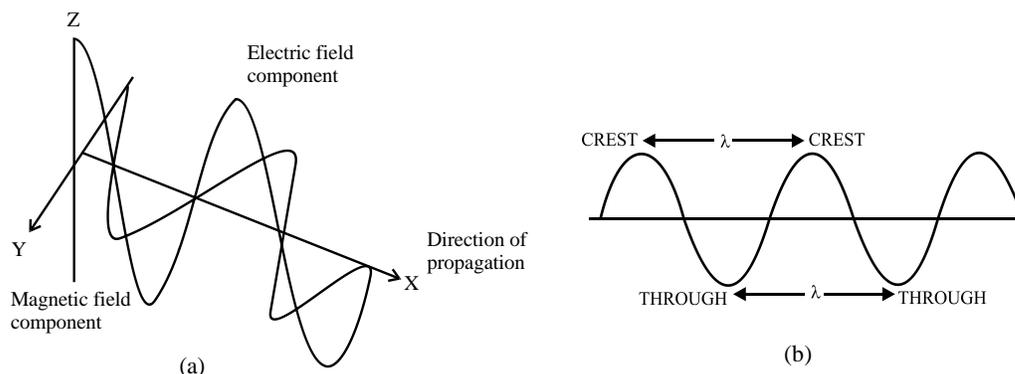


Fig. 3.6 : (a) An electromagnetic wave showing electric and magnetic fields travelling in planes perpendicular to each other and also to the direction of propagation (b) Characteristics of electromagnetic wave

3.3.1 Characteristic Parameters of Electromagnetic Radiations

The electromagnetic radiations are characterized by a number of parameters. These are

Amplitude: This refers to the **maximum height to which the wave oscillates**. It equals the height of the crests or depth of the troughs.

Wavelength : It is the linear **distance between two consecutive wave-crests or wave- troughs** as shown in Fig. 3.6(b). It is represented by a Greek letter lambda (λ) and is expressed in terms of m, cm, nm or Angstrom ($1\text{\AA} = 10^{-10}\text{ m}$).

Frequency: It is defined as the **number of wave crests or wave troughs that pass through a given point per second**. It is represented by a Greek letter nu (ν) and is expressed in terms of s^{-1} (second inverse or per second). It is also called as Hz (Hertz).

Wave number: It equals **the number of waves per unit length**. It is denoted as $\bar{\nu}$ (nu bar) and is equal to the reciprocal of the wavelength. The SI unit of $\bar{\nu}$ is m^{-1} (meter inverse). However, sometimes it is also expressed as cm^{-1} (centimeter inverse).

$$\bar{\nu} = \frac{1}{\lambda} \quad \dots (3.1)$$

Velocity: it is defined as the linear **distance travelled by the wave in one second**. The velocity in meters per second can be obtained by multiplying frequency in Hertz (s^{-1}) with wavelength in meters.

$$c = \nu \lambda \quad \text{or} \quad \nu = \frac{c}{\lambda} \quad \dots (3.2)$$

The velocity of a radiation depends on the medium. In vacuum the velocity is equal to $3.00 \times 10^8 \text{ m s}^{-1}$.

The electromagnetic radiations also show the characteristics of particles. These are called as *quanta*. These quanta are actually bundles of energy. A quantum of visible light is



called a *photon*. The energy of the quantum (or photon) is proportional to the frequency of the radiation. The two are related as

$$E = h\nu \quad \dots (3.3)$$

The energy of the quantum can also be related to the wavelength or wave number as

$$E = h\frac{c}{\lambda} \text{ or } E = hc\bar{\nu} \quad \dots (3.4)$$

the energy of photon can be readily calculated from these equations if we know the frequency, wavelength or wave number.

Example 3.1 : A microwave radiation has a frequency of 12 gigahertz. Calculate the energy of the photon corresponding to this radiation. ($h = 6.626 \times 10^{-34} \text{ J s}$ and 1 gigahertz = 10^9 Hz).

Solution: The energy is given by the expression, $E = h\nu$
Substituting the values we get,

$$E = 6.626 \times 10^{-34} \text{ Js} \times 1.2 \times 10^{10} \text{ s}^{-1} = 7.95 \times 10^{-24} \text{ J}$$

Example 3.2 : The green light has a wavelength of 535 nm. Calculate the energy of a photon of green light.

Solution: We know that

$$E = h\nu = \frac{hc}{\lambda} = \frac{(6.626 \times 10^{-34} \text{ Js}) \times (3.0 \times 10^8 \text{ ms}^{-1})}{535 \times 10^{-9} \text{ m}} = 3.71 \times 10^{-19} \text{ J}$$

3.3.2 Electromagnetic Spectrum

Depending on their characteristics (wavelength , frequency and wave number) electromagnetic radiations are of many types and constitute what is called as an electromagnetic spectrum. (Fig. 3.7) The part of the spectrum that we can see is called visible spectrum and is a very small part of the overall spectrum.

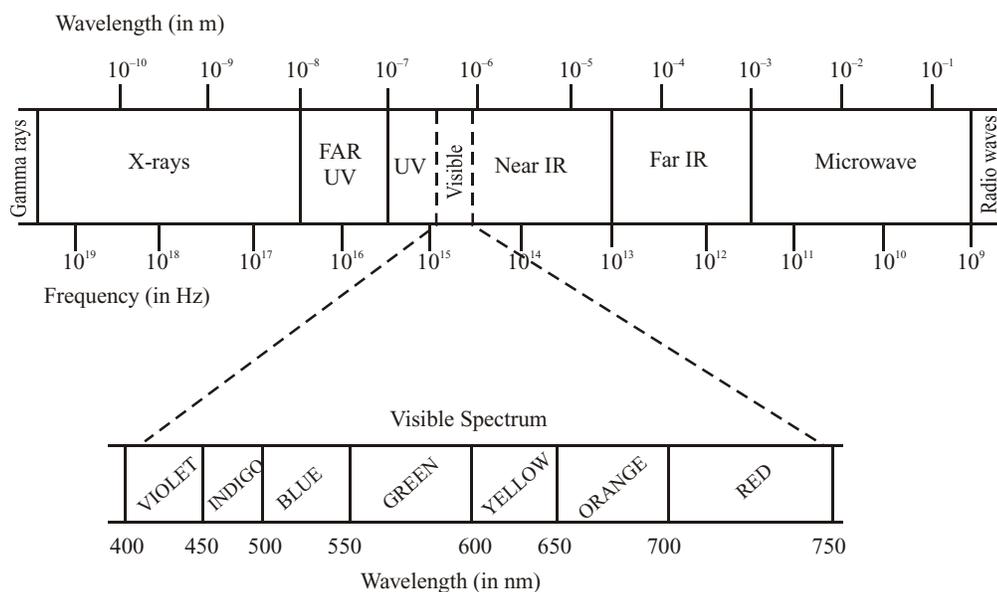


Fig. 3.7: The electromagnetic spectrum



Intext Question 3.3



Notes

1. What is an electromagnetic radiation?
.....
2. List any three characteristics of electromagnetic radiation.
.....
3. What is wave number? How is it related to wave length?
.....
4. What is the difference between a 'quantum' and a 'photon'?
.....

3.4 Line Spectrum

You know that when we pass a beam of sunlight through a prism we get a range of colours from violet to red (VIBGYOR) in the form of a spectrum (like rainbow). This is called a *continuous spectrum* because the wavelengths of the light varies continuously that is without any break. Let us take another example. You are aware of the flame tests for identifying cations in the qualitative analysis. Compounds of sodium impart a bright yellow colour to the flame, copper gives a green flame while strontium gives a crimson red coloured flame. If we pass such a light through a prism it gets separated into a set of lines. This is called as a *line spectrum*. Fig. 3.8 differentiates between a continuous and a line spectrum.

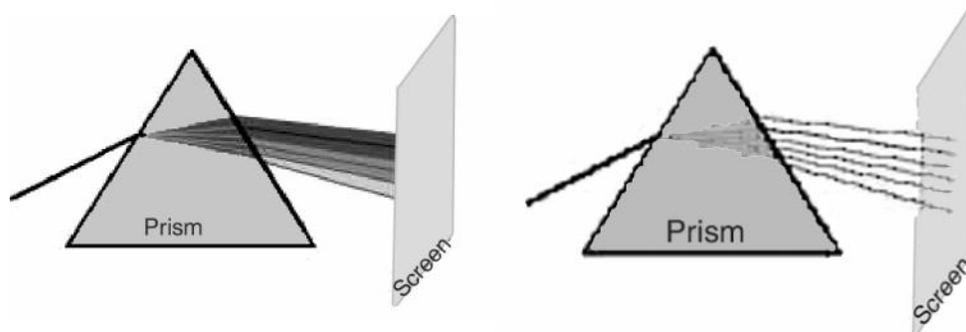


Fig. 3.8: a) a Continuous spectrum b) a Line spectrum

3.4.1 Line Spectrum of Hydrogen Atom

When an electric discharge is passed through a discharge tube containing hydrogen gas at low pressure, it emits some light. When this light is passed through a prism it splits up into a set of five lines. This spectrum is called the *line spectrum of hydrogen* (Fig. 3.9).

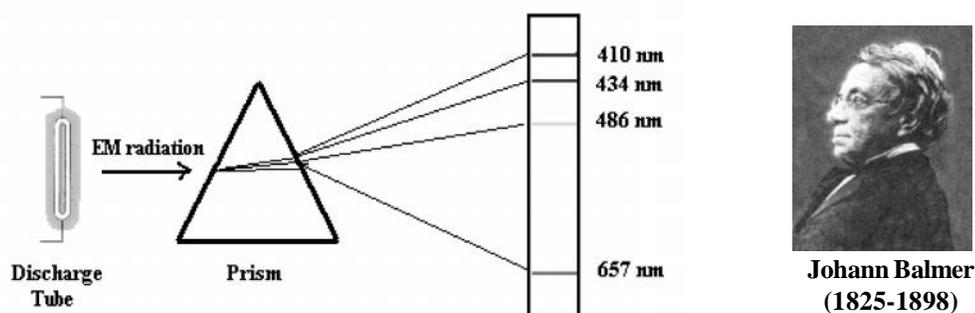


Fig. 3.9: A schematic diagram showing line spectrum of hydrogen in the visible range

On careful analysis of the hydrogen spectrum it was found to consist of a few sets of lines in the ultraviolet, visible and infrared regions. These sets of lines were observed by different scientists. These spectral emission lines could be expressed in the form of a general formula as:

$$\bar{\nu} = \frac{1}{\lambda} = R_H \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \text{ cm}^{-1}; R_H = 109677 \text{ cm}^{-1} \quad \dots(3.5)$$

Where n_1 and n_2 are positive integers ($n_1 < n_2$) and R_H is called Rydberg's constant. The different sets of lines observed in the hydrogen atom spectrum, their discoverers and the values of n_1 and n_2 are given in the Table 3.2.

Table 3.2 : Summary of the emission lines observed in hydrogen spectrum

Series	n_1	n_2	Region of spectrum
Lyman	1	2,3,4.....	Ultraviolet
Balmer	2	3,4,5.....	Visible
Paschen	3	4,5,6.....	Infrared
Bracket	4	5,6,7.....	Infrared
Pfund	5	6,7,8.....	Infrared

The line spectrum of hydrogen atom was explained by Bohr's model, which is discussed in section 3.5.

Example 3.3 : Calculate the wavelength of the Balmer line corresponding to $n_2 = 3$.

Solution: According to Balmer series $\bar{\nu} = R_H \left(\frac{1}{2^2} - \frac{1}{n_2^2} \right)$

where $R_H = 109,677 \text{ cm}^{-1}$

$$\text{For } n_2 = 3; \bar{\nu} = 109,677 \left(\frac{1}{2^2} - \frac{1}{3^2} \right) = 109,677 \left(\frac{5}{36} \right)$$

Notes





$$\begin{aligned} \text{Since, } \lambda &= \frac{1}{\nu}; \lambda = \frac{36}{109,677 \times 5} \\ &= 6.56 \times 10^{-5} \text{ cm} \\ &= 656 \text{ nm} \end{aligned}$$

3.5 Bohr's Model

In 1913, Niels Bohr (1885-1962) proposed another model of the atom where electrons move around the nucleus in circular paths. Bohr's atomic model is built upon a set of postulates, which are as follows :

- The electrons move in a definite circular paths around the nucleus (Fig 3.10). He called these circular paths as **orbits** and postulated that **as long as the electron is in a given orbit its energy does not change** (or energy remains fixed). These orbits were therefore referred to as **stationary orbits** or **stationary states** or **non radiating orbits**.



Fig. 3.10: Bohr's model



Bohr won the Nobel Prize in Physics in 1922 for his work.

- The **electron can change its orbit by absorbing or releasing energy**. An electron at a lower (initial) state of energy, E_i can go to a (final) higher state of energy, E_f by absorbing (Fig 3.11) a single photon of energy given by

$$E = h\nu = E_f - E_i \quad \dots(3.6)$$

Similarly, when electron changes its orbit from a higher initial state of energy E_i to a lower final state of energy E_f , a single photon of energy $h\nu$ is released.

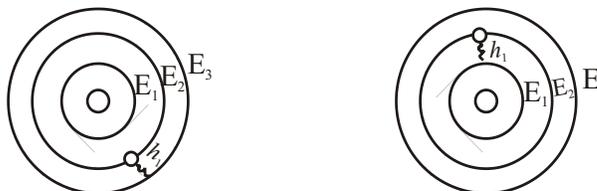


Fig. 3.11 : Absorption and emission of photon causes the electron to change its energy level.

- The **angular momentum of an electron** of mass m_e moving in a circular orbit of radius r and velocity v is an integral multiple of $h/2\pi$.

$$m_e v r = \frac{nh}{2\pi} \quad \dots (3.7)$$

where n is a positive integer, known as the **principal quantum number**.

Bohr obtained the following expressions for the energy of an electron in stationary states of hydrogen atom by using his postulates :



$$\text{Energy of the orbit, } E_n = -R_H \left(\frac{1}{n^2} \right) \quad \dots(3.8)$$

$$\text{Bohr could correlate } R_H \text{ to other properties as } R_H = \frac{mz^2e^4}{8h^2\epsilon_0^2}; \quad \dots(3.9)$$

where,

m = mass of the electron

h = Planck's constant

z = nuclear charge

ϵ_0 = permittivity of the medium

e = electronic charge

The negative sign in the energy expression means that there is an attractive interaction between the nucleus and the electron. This means that certain amount of energy (called ionisation energy) would be required to remove the electron from the influence of the nucleus in the atom. You may note here that the energies of the Bohr orbits are inversely proportional to the square of the **quantum number** n . As n increases the value of the energy increases (becomes lesser negative or more positive). It means that as we go farther from the nucleus the energy of the orbit goes on increasing.

3.5.1 Explanation of Line Spectrum of Hydrogen Atom

As per the second postulate mentioned above, the energy emitted in the transition of a single electron from an initial stationary state of energy E_i to a final stationary state of energy E_f is given as $h\nu = E_i - E_f$. Substituting the expressions for energy from Eq.1.8 we can get the formula given in eq.3.5. Thus Bohr's model provides an explanation for the observed line spectrum of hydrogen as summarized in Table 3.2. Fig. 3.12 shows the energy level diagram for hydrogen atom and the transitions responsible for the observed line spectrum.

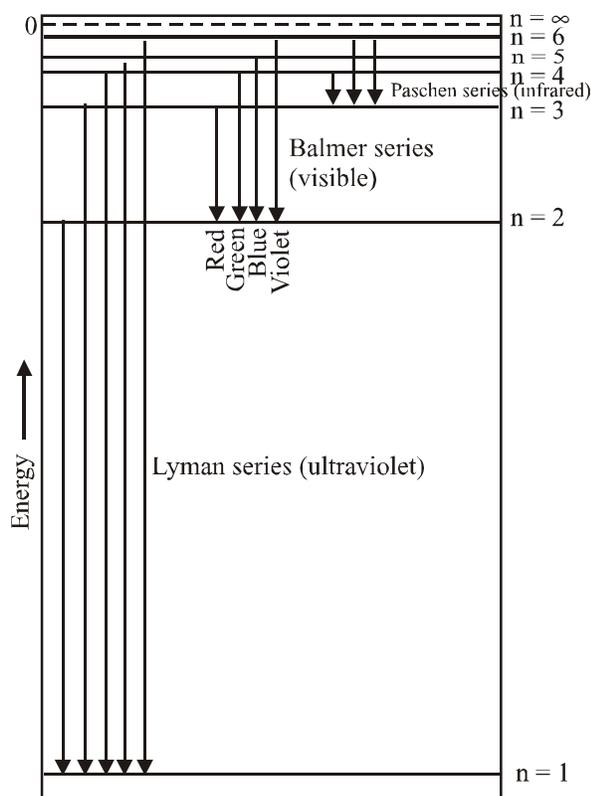


Fig. 3.12: Energy level diagram for H-atom, showing various transitions responsible for the observed line spectrum



Intext Question 3.4

1. What is the difference between a line spectrum and a continuous spectrum?
.....
2. What are the main postulates of Bohr's model?
.....
3. How does the energy of a Bohr orbit vary with the principle quantum number 'n'.
.....

3.6 Wave – Particle Duality

In section 3.3 you have learnt about the wave nature of light. As you are aware that some of the properties of light e.g., diffraction and interference can be explained on the basis of its wave nature. On the other hand some other properties like photoelectric effect and scattering of light can be explained only on the basis of particle nature of light. Thus light has a dual nature possessing the properties of both a wave and a particle, i.e., light could under some conditions behave like a particle and other conditions behave as a wave.

In 1923 a young French physicist, Louis de Broglie, argued that if light can show wave as well as particle nature, why should particles of matter (e.g., electron) not possess wave like characteristics? He proposed that matter particles should indeed have a wave nature and said that a particle of mass m moving with a velocity v has an associated wavelength, (some times called *de Broglie wavelength*) given by the formula;

$$\lambda = \frac{h}{mv} \quad \text{or} \quad \lambda = \frac{h}{p} \quad \dots(3.10)$$

Where $p (= mv)$ is the momentum of the particle. The de Broglie wavelength of a body is inversely proportional to its momentum. Since the magnitude of h is very small, the wavelength of the objects of our everyday world would be too small to be observed. Let us make a calculation to see this.

Example 3.4 : Calculate the de Broglie wavelength associated with a cricket ball weighing 380 g thrown at a speed of 140 km per hour.

Solution: Mass of the cricket ball = 380 g = 380×10^{-3} kg = 0.38 kg

$$\begin{aligned} \text{Speed or Velocity} &= 140 \text{ km/hr} = (140 \times 1000)/3600 \\ &= 38.89 \text{ m s}^{-1} \end{aligned}$$

The wavelength associated with the cricket ball will be

$$\begin{aligned} \lambda &= \frac{h}{mv} = \frac{6.626 \times 10^{-34} \text{ JS}}{(0.380 \text{ kg})(38.89 \text{ m s}^{-1})} \\ &= 4.48 \times 10^{-35} \text{ m} \quad (\text{J} = \text{kg m}^2 \text{ s}^{-2}) \end{aligned}$$



de-Broglie
(1892-1987)

de-Broglie proposed the theory of wave-particle dualism as a part of his PhD thesis in 1924. He got the physics Nobel prize in 1929



If the electrons show wave nature then a beam of these electrons is expected to show diffraction which is a property of waves. In 1927 G.P. Thomson and C.J. Davisson demonstrated the diffraction of electron waves by the crystal lattice of nickel (Fig. 3.13). Thus electrons also show a dual nature. That is, sometimes these show particle nature while at some other times they show wave nature.

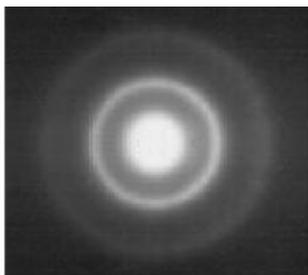


Fig. 3.13: *Electron diffraction pattern from nickel crystal*



Werner Heisenberg
(1901-1976)

Heisenberg got the phys. is Nobel prize in 1932

3.7 Heisenberg's Uncertainty Principle

An important consequence of the wave-particle duality of matter and radiation was discovered by Werner Heisenberg in 1927 and is called the **uncertainty principle**. According to this principle it is not possible to simultaneously measure both the **position** and **momentum (or velocity)** of an electron accurately. In simple words we may state that more accurately you measure a particle's position, the less accurately you're able to measure its momentum, and vice versa. Mathematically, the Heisenberg principle can be expressed in terms of an inequality

$$\Delta x \Delta p \geq \frac{h}{4\pi} \quad \dots(3.11)$$

Where Δx and Δp are the uncertainties in the measurements of position and momentum respectively. If the position of an object is known exactly (i.e., $\Delta x = 0$), then the uncertainty in the momentum must be infinite, meaning that we cannot say anything about the velocity. Similarly, if the velocity is known exactly, then the position would be entirely uncertain and the particle could be anywhere. It means that we cannot say anything about the position of the particle. In actual practice none of the two properties can be measured with certainty. Due to the small value of the Planck's constant, h (6.626×10^{-34} J s) this principle is not relevant while making measurements of large objects like car, bus or aeroplane etc.. It is relevant, only when you are making measurements on very small objects such as electrons.

Heisenberg's principle questioned the validity of Bohr's model. It is so because according to Bohr's model we can precisely calculate the radius of the orbit (i.e., the position of the electron) and the velocity of electron in it. But it is not possible according to Heisenberg's principle. It motivated many scientists to develop newer models of the atom using the dual nature of the electron. This resulted into the development of a Quantum mechanical or *Wave Mechanical Model* of the atom discussed in the next section.

**Intext Question 3.5**

1. What do you understand by wave-particle duality?
.....
2. Name the experiment that established the wave nature of electron.
.....
3. Compute the de-Broglie wavelength associated with an electron moving with a velocity of 100 km /second? ($m_e = 9.1 \times 10^{-31} \text{kg}$)
.....
4. State Heisenberg's Uncertainty Principle?
.....

3.8 Wave Mechanical Model of Atom

Wave Mechanical Model of atom was proposed by Erwin Schrödinger- an Austrian physicist in 1926. This model is basically a formalism or a mathematical recipe, which is based on some postulates that have no foundation in classical physics. The correctness of these postulates can be justified in terms of the correctness of the results predicted by them. According to this Model, the motion of electron inside the atom could be described in terms of a mathematical function called, **wave function**, (ψ) (Greek letter, psi). The wave functions are assumed to contain all the information about the electron and are obtained by solving a differential equation called Schrödinger wave equation (SWE). The square of the wave function ψ^2 is a measure of the probability of finding an electron in a three dimensional space around the nucleus.

On solving the SWE for hydrogen atom we get a number of wave functions, which are characterized by three quantum numbers viz.,

- Principal quantum number, n
- Azimuthal quantum number, l
- Magnetic quantum number, m_l

These quantum numbers arise in the process of logically solving the wave equation. Every electron in an atom has a unique (different) set of quantum numbers which help to describe the three dimensional region where there is maximum probability of finding the electron. This region is called as *atomic orbital* or simply *orbital*.

3.8.1 Significance of Quantum Numbers

The three quantum numbers describe the size, shape, and orientation of the atomic orbitals in space. There is an additional quantum number which does not follow from the Schrödinger wave equation but is introduced to account for electron spin. The fourth quantum number thus help in designating the electrons present in the atom. Let us understand the significance of each of these quantum numbers.

**Principal quantum number, n**

The principal quantum number, n describes the energy level (or principal shell) of the electron within the atom. n can have only positive non zero integral values (i.e., $n = 1, 2, 3, 4, \dots$). This means that in an atom, the electron can have only certain energies. Thus we may say that n quantizes energy of the electron. The principal quantum number also determines the mean distance of the electron from the nucleus, i.e., its size. Greater the value of n farther is the electron from the nucleus.

Each principal shell can accommodate a maximum of $2n^2$ electrons, i.e.,

$n = 1$	number of electrons : 2
$n = 2$	number of electrons : 8
$n = 3$	number of electrons : 18 and so on...

Azimuthal quantum number, l

The azimuthal quantum number, l is related to the geometrical shape of the orbital. The value of l may be zero or a positive integer less than or equal to $n-1$ (n is the principal quantum number), i.e., $l = 0, 1, 2, 3, \dots, (n-1)$. Different values of l correspond to different types of **subshells** and each subshell contains orbitals of a given shape.

$l = 0$, corresponds to **s**-subshell and contains the orbital with **spherical shape** called as **s orbital**.

$l = 1$, corresponds to **p**-subshell and contains the orbitals with a **dumb-bell shape** called as **p-orbitals**. There are three p-orbitals in each p-subshell

$l = 2$, corresponds to **d**-subshell and contains the orbitals with a **cloverleaf shape** called as **d-orbitals**.

$l = 3$, corresponds to **f**-subshell and contain **f orbitals**. There are seven f-orbitals in each f-subshell.

The shapes of s, p and d orbitals will be discussed in the next subsection.

Magnetic quantum number, m_l

The quantum number, m_l , describes the direction or orientation of the orbital in space. The quantum number m_l may have any integral value from $-l$ to $+l$. For example, for $l = 1$; m_l can have the values as $-1, 0$ and 1 .

Magnetic spin quantum number, m_s

The quantum number, m_s , describes the spin of the electron i.e., whether it is clockwise or anticlockwise. The quantum number, m_s does not arise while solving SWE. The clockwise and anticlockwise direction of electron spin has arbitrarily been assigned the values as $+1/2$ and $-1/2$ respectively.

To sum up, let us take an example of an electron belonging to the third shell ($n = 3$). This electron can be in an s-subshell ($l = 0$) or a p-subshell ($l = 1$) or a d-subshell ($l = 2$). If it happens to be in a p-subshell it may be in any of the three possible p orbitals (corresponding to $m_l = -1, 0 + 1$ directed along x , y or z - axis. And within the orbital it may have clockwise ($m_s = +1/2$) or anti-clockwise ($m_s = -1/2$) direction of electron spin. The possible

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values of different quantum numbers for an electron belonging to the third shell are given in Table 3.3.

Table 3.3 : The quantum numbers for an electron belonging to the third shell

Principal quantum number, n	Azimuthal quantum number, l	Magnetic quantum number, m_l	Magnetic spin quantum number, m_s
3	0	0	+1/2
			-1/2
		1	-1
	-1/2		
	0		+1/2
			-1/2
	+1		+1/2
			-1/2
	2	-2	+1/2
			-1/2
			+1/2
		-1	-1/2
			+1/2
			-1/2
		0	+1/2
			-1/2
			+1/2
	+1	+1/2	
-1/2			
+1/2			
+2	+1/2		
	-1/2		
	-1/2		

You may note here that the third shell can contain a maximum of 18 electrons and each of them, has a distinct set of four quantum numbers.



Intext Question 3.6

- What do you understand by a Wave Function?
.....
- What is the difference between an orbit and an orbital?
.....
- What are quantum numbers? List different quantum numbers obtained from Schrödinger Wave Equation?
.....
- Give the significance of the Principal, azimuthal and magnetic quantum numbers?
.....



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3.8.2 Shapes of Orbitals

We have defined an orbital as “*the three dimensional region of space around the nucleus where there is maximum probability of finding the electron*”. Let us try to understand the meaning of an orbital by taking the example of $1s$ orbital ($n = 1 ; l = 0$). This can be understood in terms of a radial probability curve. Such a curve gives the variation of the probability of finding the electron as a function of distance from the nucleus. For $1s$ orbital the radial probability curve (Fig. 3.14 (a)) shows that the probability of finding the electron in $1s$ orbital increases as we move away from the nucleus and reaches a maximum at a certain distance ($= 0.0529$ nm or 52.9 pm for hydrogen atom) and then decreases as we go further away from it and at a certain distance it becomes close to zero. The curve shows the radial probability for a given direction. The

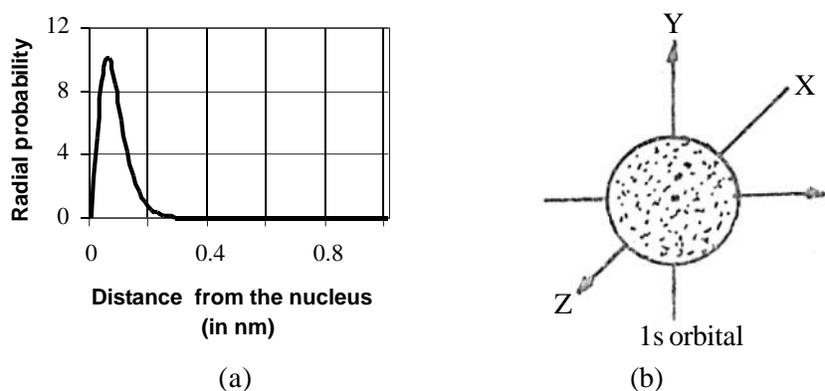


Fig.3.14: (a) Radial probability curve for $1s$ orbital (b) Boundary surface diagram for $1s$ orbital

probability would be same for all possible directions. If we put all such curves together it would give a spherical distribution of the electron probability. Since the radial probability does not become zero at any distance, we cannot specify the size of the sphere. Therefore, the orbital is represented as a boundary surface diagram, which may be thought as a region of space, which contains 95 % of the probability of finding the electron, as indicated in Fig.3.14(b). Thus the $1s$ orbital is represented as a sphere.

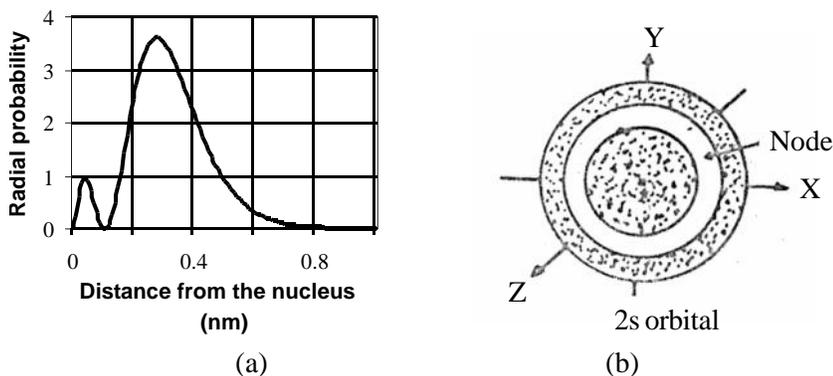


Fig.3.15: (a) Radial probability curve for $2s$ orbital (b) Boundary surface diagram for $2s$ orbital

Similarly, the Fig 3.15 (a) gives the radial probability curve for a $2s$ orbital while the Fig 3.15 (b) shows the boundary surface diagram for the same. You can note two things here. First you may note that for a $2s$ orbital the boundary surface diagram is bigger as compared to a $1s$ orbital. Secondly, the radial probability curve shows two maxima. The probability

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initially increases, reaches a maxima then it decreases and comes close to zero. It increases again and decreases as we move further away from the nucleus. The region where the probability comes close to zero (before increasing again) is called a **spherical node**. There are $n-l-1$ spherical nodes in an orbital.

A node is a region in space where the probability of finding the electron is close to zero.

p-orbital : Now when we draw the shape of a p orbital ($n=1 ; l=1$) we get a shape as shown in the Fig. 3.16. This picture shows the shape of one of the three possible p orbitals which is directed towards the z-axis; p_z . You may note that the probability picture for a p_z orbital consists of two lobes ; one along the positive z-axis and the other along the negative z-axis. Another important feature of a p-orbital is the absence of the electron probability in the XY- plane. Such a plane is called a **nodal plane**. The shapes of the three p-orbitals are given in Fig.3.17.

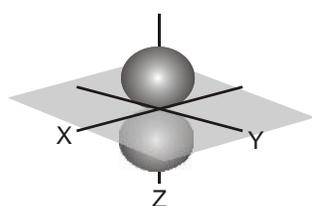


Fig.3.16 : A p orbital surface diagrams (Shapes)

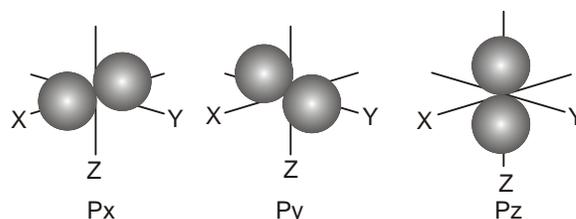


Fig.3.17: The boundary showing a nodal plane of the p-orbitals

The Fig.3.18 gives the shapes of five possible d-orbitals. The d-orbitals also contain nodal planes. The five d-orbitals have different shapes but they all have same energies i.e., these are degenerate.

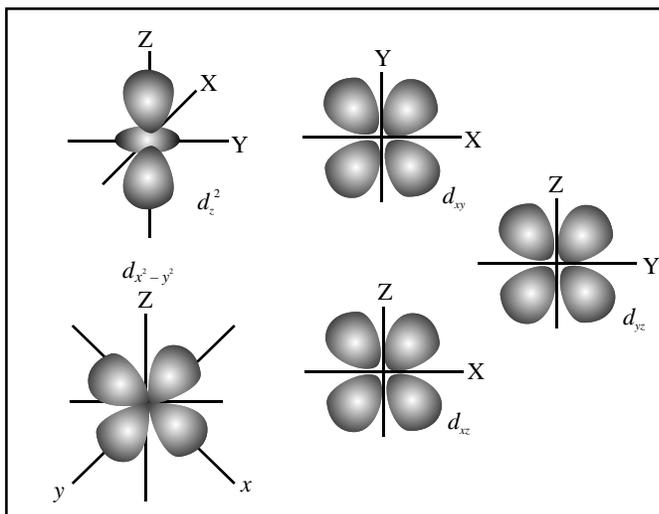


Fig.3.18: The boundary surface diagrams (shapes) of the five d-orbitals



Intext Questions 3.7

1. What are the shapes of s,p and d orbitals?



2. Describe the shape of a $2s$ orbital. How is it different from that of a $1s$ orbital?

.....

3. What do you understand by

i) a spherical node?

ii) a nodal plane?

.....

4. How many spherical nodes will be there in $3s$ orbital ?

.....

3.9 Electronic Configuration of Elements

You have so far learnt that an atom consists of a positively charged nucleus surrounded by electrons present in orbitals of different shapes and sizes. These orbitals are part of different shells and sub-shells and are characterized by the three quantum numbers viz. n, l and m_l . Let us now take up the distribution of electrons in these shells and sub-shells. Such a distribution of electrons is called **Electronic Configuration** and is governed by three basic rules or principles.

3.9.1 Aufbau (or building up) Principle

This principle is concerned with the energy of the atom and states that the electrons should occupy the orbitals in such a way that the energy of atom is minimum. In other words **the electrons in an atom are filled in the increasing order of their energies**. Now, how does one know the increasing order of the orbital energies? You have learnt above that the principal quantum number determines the energy of the orbitals. Higher the value of n higher the energy. This is true only for hydrogen atom. For other atoms, we need to consider both n and l . This means that **different sub-shells in a given shell have different energies**. The order of orbital energies can be determined by the following $(n + l)$ rules.

Rule 1: An orbital with a lower value for $(n + l)$ has lower energy. For example, the $4s$ orbital ($n + l = 4 + 0 = 4$) will fill before a $3d$ orbital ($n + l = 3 + 2 = 5$).

Rule 2: If the value of $(n + l)$ is same for two orbitals then the orbital with lower value of n will be filled first. For example, the $3d$ orbital ($n + l = 3 + 2 = 5$) will fill before a $4p$ orbital ($n + l = 4 + 1 = 5$).

Following these rules the increasing order of the orbital energies comes out to be

$$1s < 2s < 2p < 3s < 3p < 4s < 3d < 4p < 5s < 4d < 5p < 6s$$

3.9.2 Pauli's Exclusion Principle

This principle concerns the spin of electrons present in an orbital. According to the Pauli's principle, **no two electrons can have all the four quantum numbers to be same**. For example, if a given electron in an atom has the set of four quantum numbers as $n = 2, l = 1, m_l = 1$ and $m_s = +\frac{1}{2}$ then no other electron in the atom can have the same set of quantum numbers.

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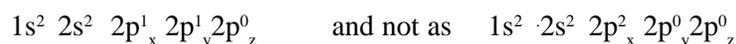


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As you know that an orbital is characterized by three quantum numbers so the electrons occupying a given orbital would have same values of these three quantum numbers. These electrons are distinguished in terms of their spin quantum number, m_s . Since the spin quantum number can have only two values so **only two electrons can occupy a given orbital**. In fact this fourth quantum number was introduced through Pauli's principle only.

3.9.3 Hund's Rule

This rule concerns the distribution of electrons in a set of orbitals of the same energy, *i.e.* constituents of a subshell. According to this rule if a number of orbitals of the same subshell are available then the electrons distribute in such a way that each orbital is first singly occupied with same spin. For example, the six electrons in carbon distribute as

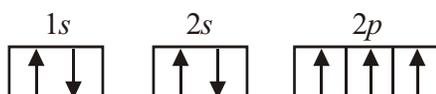


Since electrons repel each other, they remain as far as possible from one another by occupying different orbitals.

The rules discussed above can be used to write the electronic configuration of different elements. There are two common ways of representing the electronic configurations. These are

a) Orbital notation method: In this method the filled orbitals are written in the order of increasing energies. The respective electrons in them are indicated as superscripts as shown in the example given below. For example, the electronic configuration of nitrogen atom (atomic number 7) is written as $1s^2 2s^2 2p_x^1 2p_y^1 2p_z^1$.

b) Orbital diagram method: In this method the filled orbitals are represented by circles or boxes and are written in the order of increasing energies. The respective electrons are indicated as arrows whose direction represents their spin. For example, the electronic configuration of nitrogen in the orbital diagram notation can be written as



Electronic configurations can also be written in a short hand form. In this method the **last completed orbital shell** is represented in terms of a noble gas. For example, the electronic configuration of lithium and sodium can be written as



The electrons in the noble gas configuration are termed as **core electrons** while the ones in the outer shell are called **valence electrons**.



Intext Question 3.8

1. What do you understand by the electronic configuration of an atom?
.....
2. What is Pauli's exclusion principle?
.....



3. What is Aufbau principle? What are ($n+l$) rules?
.....

4. Which of the following orbitals will be filled first?
.....

i) $2p$ or $3s$

ii) $3d$ or $4s$
.....



What You Have Learnt

- Atoms are made up of three fundamental particles namely, electrons, protons and neutrons.
- J.J Thomson made the first attempt to describe the structure of an atom in terms of a model called **plum pudding model**. According to this atoms can be considered as a large positively charged body (pudding) in which a number of small negatively charged electrons (plums) are scattered..
- According to the Rutherford's model, the positive charge of the atom and most of its mass is contained in the nucleus and the rest of the atom is empty space which contains the much smaller and negatively charged electrons.
- Electromagnetic radiation is a kind of energy, which is transmitted through space in the form of electric and magnetic fields. It travels with the speed of light and does not need any medium to travel.
- The electromagnetic radiations are characterized by a number of parameters like, amplitude, wavelength, frequency, wave number and velocity.
- Hydrogen gas gives a line spectrum consisting of distinct lines suggesting the quantisation of energy in hydrogen atom.
- In 1913, Niels Bohr proposed 'Planetary Model' for atom. According to the model the electrons move in definite circular paths of fixed energy around a central stationary nucleus. The electrons can change their orbits by absorbing or emitting a photon of energy (= $h\nu$) equal to the difference of the energies of the orbits.
- Bohr's model did explain for the stability of atom and the line spectrum of hydrogen. The model however was unable to explain the spectra of atoms other than hydrogen.
- Louis de Broglie, argued for the dual nature of electron and proposed that matter particles should have a wave nature. The associated wavelength, λ is given by the formula; $\lambda = \frac{h}{mv}$ or $\lambda = \frac{h}{p}$ • This was experimentally verified by Thomson and Davisson by diffraction of electron waves by the crystal lattice of nickel.
- The wave-particle duality of matter led Werner Heisenberg to propose the **uncertainty**

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principle. According to which it is not possible to measure simultaneously both the *position* and *momentum* of a particle with a infinite precision.

- The dual nature of electron and Heisenberg's uncertainty principle led to the development of wave mechanical model.
- According to the Wave Mechanical Model, the motion of electron inside the atom can be described in terms of a mathematical function called, wave function, ψ . This wave function contains all the information about the system and can be found by solving a wave equation called Schrodinger wave equation.
- The square of the wave function, ψ^2 is a measure of the probability of finding the electron in a certain three dimensional space around the nucleus. This region is called as **atomic orbital** or simply **orbital**.
- These wavefunctions are characterized by three quantum numbers. These quantum numbers describe the size, shape, and orientation of the atomic orbitals in space. Every electron in an atom has a unique set of quantum numbers.
- The principal quantum number n concerns the quantisation of the energy of the electron while the Azimuthal quantum number, l is related to the shape of the orbital. The magnetic quantum number m_l describes the direction or orientation of the orbital in space.
- An additional quantum number, m_s is introduced to account for electron spin. This quantum number does not follow from the wave mechanical model and describes the spin of the electron.
- Different orbitals have different shapes. An s orbital is spherical; p orbitals are dumb-bell shaped ; d orbitals have cloverleaf shape while f orbitals have a eight lobed shape.
- The distribution of electrons in the shells and subshells is called **Electronic Configuration**. It is governed by three rules which are Aufbau principle ; Pauli's exclusion principle and Hund's Rule of maximum multiplicity.
- According to Aufbau principle the electrons in an atom are filled in the increasing order of their energies which is determined by $(n + l)$ rules.
- According to the Pauli's exclusion principle, no two electrons can have all the four quantum numbers to be same.
- While filling electrons in the orbitals of same subshell, according to Hund's rule, each orbital is first singly occupied with same spin then the pairing up takes place.



Terminal Exercise

1. a) What are the three fundamental particles that constitute an atom?
b) Compare the charge and mass of an electron and of a proton.
2. What do you think is the most significant contribution of Rutherford to the development of atomic structure?



3. What experimental evidence shows the dual nature of light?
 - a) Compute the energy of a FM radio signal transmitted at a frequency of 100 MHz.
 - b) What is the energy of a wave of red light with $\lambda = 670 \text{ nm}$?
4. In what way was the Bohr's model better than the Rutherford's model?
5. What are the drawbacks of Bohr's Model?
6. What led to the development of Wave Mechanical Model of the atom?
7. What do you understand by an orbital? Draw the shapes of s and p orbitals.
8. Explain the Hund's rule of maximum multiplicity with the help of an example.



Answers to Intext Questions

3.1

- 1 Proton is heavier than electron. The ratio of their masses is

$$= m_p/m_e = \frac{1.672\ 623 \times 10^{-27} \text{ kg}}{9.109\ 389 \times 10^{-31} \text{ kg}}$$

$$= 1836$$

- 2 Main constituent particles like proton, neutron and electron etc. present in the atom come in the category of fundamental particles.
3. Neutron

3.2

- 1 Electron, proton and neutron
- 2 The aim of Rutherford's experiment was to test the Thomson's plum-pudding model.
- 3 According to Rutherford's model for atom, the positive charge of the atom and most of its mass is contained in the nucleus. The rest of the atom is empty space which contains the much smaller and negatively charged electrons.
- 4 Rutherford's model was rejected because it could not explain the stability of the atom.

3.3

1. Electromagnetic radiation is a kind of energy which is transmitted through space in the form of electric and magnetic fields. It travels with the speed of light and does not need any medium to travel.
2. The different characteristics of electromagnetic radiation are
 - i) Amplitude,
 - ii) Wavelength,
 - iii) Frequency,

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iv) Wave number and

v) Velocity

3. The wave number is defined as the number of waves per centimeter. It is equal to the reciprocal of the wavelength.
4. A quantum of visible light is called photon. The energy of the quantum (or photon) is proportional to the frequency of radiation.

3.4

1. A line spectrum consists of a series of discrete lines of characteristic wavelengths while a continuous spectrum contains a broad band of radiations containing all possible wavelengths in the range i.e., the wavelengths of the radiation varies continuously.
2. The main postulates of Bohr's model are
 - i) The electrons move in a definite circular paths called as **stationary orbits** or **stationary states** around a central stationary nucleus.
 - ii) The electrons can change their orbits by absorbing or emitting a photon of energy ($= h \nu$) equal to the difference of the energies of the orbits.
 - iii) The angular momentum of the electron is quantised.
3. The energy of a Bohr's orbit increases with an increase in the value of the principal quantum number, n . In fact it becomes lesser and lesser negative.

3.5

1. The wave-particle duality refers to the fact that light and the material particles like electrons could sometimes behave as a particle and as a wave at other times.
2. The wave nature of electron was established by the diffraction of electron waves by the crystal lattice of nickel.
3. Mass of the electron = 9.1×10^{-31} kg

$$\text{Speed or Velocity} = 100 \text{ km s}^{-1} = 10^5 \text{ m s}^{-1}$$

Using equation , the wavelength associated with the electron will be

$$\lambda = \frac{h}{mv} = \frac{6.626 \times 10^{-34} \text{ J s}}{(9.1 \times 10^{-31} \text{ kg})(10^5 \text{ m s}^{-1})} = 7.28 \times 10^{-9} \text{ m}$$

4. According to Heisenberg's Uncertainty Principle it is not possible to measure both the *position* and *momentum* of a particle with any degree of certainty. More accurately we measure a particle's position, the less accurately we are able to measure its momentum, and vice versa.

3.6

1. It is a mathematical function that describes the motion of an electron inside the atom. It contains all the information about the system and can be found by solving a wave equation called Schrödinger wave equation.



- An orbit refers to definite circular paths of fixed energy around a central stationary nucleus while an orbital refers to the three dimensional region of space around the nucleus where there is a probability of finding the electron.
- The quantum numbers are integers that characterize the wavefunctions. These are obtained in the process of solving Schrödinger wave equation and every electron in an atom has a different set of quantum numbers. The three quantum numbers obtained from Schrödinger Wave Equation are
 - The principal quantum number, n
 - Azimuthal quantum number, l and
 - The magnetic quantum number m_l
- The principal quantum number, n is concerned with the energy of the electron in a shell. The quantum number l is related to the geometrical shape of the orbital and the quantum, number, m_l describes the orientation of the orbital in space.

3.7

- s orbital : spherical;
 p orbitals : dumb-bell shaped ;
 d orbitals : cloverleaf shaped.
- The $2s$ orbital is spherical in shape similar to the $1s$ orbital . However there are two differences. Firstly, the size of a $2s$ orbital is bigger as compared to a $1s$ orbital and secondly, it contains a spherical node.
- It is a spherical region of zero probability in an s orbital (other than $1s$).
 - It is a planar region in an orbital (other than s orbitals)where the probability of finding the electron is zero.
- The $3s$ orbital will have **two** spherical nodes.

3.8

- The distribution of electrons in the shells and subshells of an atom is called *Electronic Configuration*.
- Pauli's principle states that in an atom no two electrons can have same set of the four quantum numbers.
- Aufbau principle states that the electrons in an atom are filled in the increasing order of their energies which is determined by $(n + l)$ rules.

There are two $(n + l)$ rules. These are

An orbital with a lower value for $(n + l)$ is filled first.

If the value of $(n + l)$ is same for two orbitals then the orbital with lower value of n will be filled first

- $2p$: $(n + l)$ for $2p = 2 + 1 = 3$; for $3s (n + l) = 3 + 0 = 3$; Rule 2
 - $4s$: $(n + l)$ for $4s = 4 + 0 = 4$; for $3d (n + l) = 3 + 2 = 5$; Rule 1