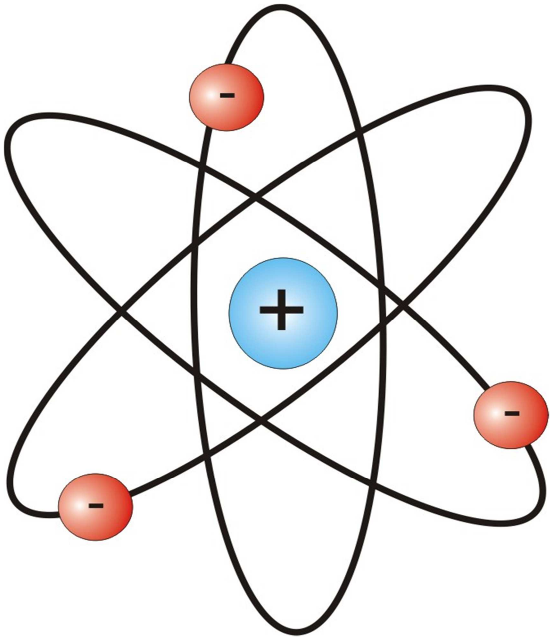
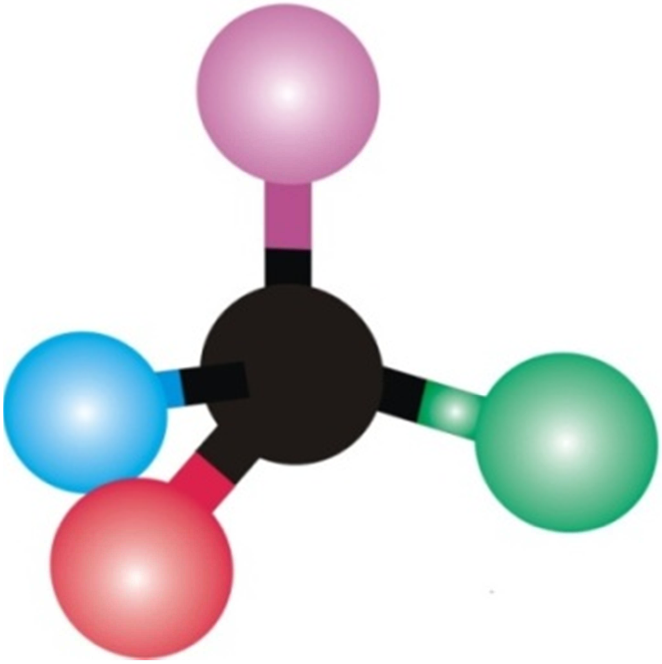
Indira Gandhi National
Open University
School of Sciences

BCHCT-131

ATOMIC STRUCTURE, BONDING, GENERAL ORGANIC CHEMISTRY AND ALIPHATIC HYDROCARBONS





ATOMIC STRUCTURE

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ATOMIC STRUCTURE, BONDING, GENERAL ORGANIC CHEMISTRY AND ALIPHATIC HYDROCARBONS

Block

1

ATOMIC STRUCTURE

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Course Design Committee

Prof. H. B. Singh (Retd.)
Dept. of Chemistry,
University of Delhi,
Delhi

Prof. A.K. Bakhshi
Dept. of Chemistry,
University of Delhi,
Delhi

Prof. Amir Azam
Dept. of Chemistry,
Jamia Millia Islamia,
New Delhi

Prof. Tabrez Alam
Dept. of Chemistry,
Jamia Milia Islamia,
New Delhi

Prof. J.M. Khurana
Dept. of Chemistry,
University of Delhi,
Delhi

School of Sciences,
IGNOU

Prof. Vijayshri

Prof. Sunita Malhotra

Prof. Javed A. Farooqi

Dr. Lalita S. Kumar

Block Preparation Team

Prof. Sunita Malhotra (Unts 1-5)
School of Sciences, IGNOU

Prof. B. S. Saraswat (Retd.) (Editor)
School of Sciences, IGNOU

Course Coordinators: Prof. Sunita Malhotra and Prof. Javed A. Farooqi

Production

Mr. Sunil Kumar
Assistant Registrar (Pub.)

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ATOMIC STRUCTURE, BONDING, GENERAL ORGANIC CHEMISTRY AND ALIPHATIC HYDROCARBONS: INTRODUCTION

This is the first core course of Chemistry in the B.Sc. programme being offered under CBCS Scheme. The theory course (BCHCT-131) has a credit-weightage worth 4 credits and there is a separate lab course (BCHCL-132) worth 2 credits alongwith this course.

This theory course consists of four blocks which contain nineteen Units. The first two blocks, i.e. Block 1 and Block 2 are devoted to the basic concepts related to atomic structure, chemical bonding and molecular structure. The other two blocks, i.e., Block 3 and Block 4 focus on the fundamental aspects of organic chemistry and hydrocarbons.

Block 1 on ‘Atomic Structure’ contains five units which discuss the important concepts related to the structure of atom in Units 1 to 3. The structure of Hydrogen Atom is described in detail in Unit 4. This block also explains the Electronic Configurations of Multi-electron Atoms in Unit 5.

Block 2 on ‘Chemical Bonding and Molecular Structure’ comprises four units. Unit 6 is devoted to Ionic Bonding while Covalent Bonding is discussed in detail in Unit 7 whereas Valence Bond Theory is described in Unit 8. The last unit of this Block, i.e. Unit 9 explains the important aspects of Molecular Orbital Theory.

Block 3 on ‘Fundamentals of Organic Chemistry’ contains five units. The first three units of this block, i.e. Units 10 to 12 cover the important concepts of Stereochemistry. Unit 10 describes the general aspects as well as Geometrical and Optical Isomerisms. However, the Configurational Isomers are discussed in Unit 11. Unit 12 explains Conformational Isomerism. In Unit 13, the Structure Reactivity Relationships are discussed in detail. The last unit of this Block, i.e. Unit 14 explains the basic concepts related to Organic Reactions and Reactive Intermediates.

Block 4 on ‘Hydrocarbons’ comprises five units. The important aspects of the structure and chemical reactions of Alkanes are discussed in Unit 15. Units 16 and 17 describe the chemistry of Alkenes while Unit 18 explains the structure and reactions of Alkynes. The last unit of this block and the course, i.e. Unit 19 on Aromacity highlights the important features and nomenclature of aromatic compounds.

This course is being offered at the first Semester and will build up foundation for the other courses which you will study in the other semesters.

You are expected to spend a total of about 120 hours for completing this course. This is the average time which is to be spent by a learner on studying the course material, doing self-assessment questions given in the blocks and the assignment, attending counselling sessions, watching the audio-video programmes and participating in IRC/tele conferencing sessions related to this course.

We hope you will find this course quite interesting to study.

Our best wishes.

Expected Learning Outcomes

After studying this course, you should be able to:

- discuss the important features of various models of structure of atom;
- describe the dual nature of radiation and matter;

- highlight the need for the quantum-mechanical approach to explain the structure of atom;
- explain Schrodinger equation and discuss the origin of various quantum numbers;
- write the electronic configurations of various elements and explain the anomalous electronic configurations;
- discuss the important aspects of ionic bonding and explain the characteristics of covalent compounds;
- describe VSEPR theory and predict the shapes of molecules and ions;
- discuss the principles of Valence-bond theory and explain the concepts of resonance and hybridisation;
- explain molecular orbital theory and predict the molecular orbital configuration of simple diatomic molecules;
- describe important characteristics of geometrical isomers and optical isomers;
- write configurational isomers and assign them *R*/*S* configuration;
- draw conformational isomers of simple alkanes such as ethane, butane and cyclic alkanes such as cyclohexane;
- define acids and bases and explain various factors which affect the acidity and basicity of a compound;
- discuss various types of reactions and explain the reactive intermediates involved in them;
- describe the preparation, properties and important reactions of alkanes, alkenes and alkynes; and
- explain aromaticity and name aromatic compounds.

BLOCK 1 : ATOMIC STRUCTURE

This is the first Block of the Core Course ‘Atomic Structure, Bonding, General Organic Chemistry and Aliphatic Hydrocarbons’ (BCHCT-131). It describes the important aspects of atomic structure in detail and also deals with the electronic configurations of multi-electron atoms.

There are five units in this Block.

The first unit of this block, i.e., Unit 1 deals with ‘Bohr’s Theory’. The Unit touches very briefly on the important features of earlier atomic models given by Dalton, Thomson and Rutherford. Then, Bohr’s model of atomic structure is discussed in detail. You will also learn here about the calculation of radii of various orbits and energy of the electron when present in these orbits. You will then learn how Bohr’s theory has been helpful in explaining some of the features hydrogen atom spectrum. The Unit ends with a discussion on the limitations of the Bohr’s theory and a brief idea about the Sommerfeld modification to Bohr’s theory.

Unit 2 on ‘Dual Behaviour of Radiation and Matter’ begins with a description of the nature of radiation. Both the wave nature and the particle nature of radiation have been explained. This is followed by a discussion on the nature of matter where both the particle nature and wave nature of matter have been described. Lastly, Heisenberg uncertainty principle has been discussed.

Unit 3 on ‘Quantum Mechanical Approach’ begins with a brief introduction to the need of a new approach to explain atomic structure. This is followed by a discussion of important aspects and general terminology of quantum mechanics. The time-independent Schrodinger equation has been discussed and its application to yield the energy states of hydrogen like atoms has been explained.

Unit 4 on ‘Hydrogen Atom’ discusses in detail about the Schrodinger equation for hydrogen atom and origin of three quantum numbers. The radial distribution functions and angular dependence of wave functions have been explained. The shapes of various orbitals have been illustrated. Finally, the origin of spin quantum number has been explained.

Unit 5 on ‘Electronic Configuration of Multi-electron Atoms’ begins with a discussion on the energy levels of multi-electron atoms. Then, the rules for filling of electrons in various orbitals have been explained. The electronic configurations of the elements have been illustrated and the stability of half-filled and completely filled orbitals have been discussed. After that, the anomalous configurations of elements have been explained. At the end of this unit, on the basis of their electronic configurations, the arrangement of elements into the periodic table has been illustrated.

Expected Learning Outcomes

After studying this Block, you should be able to:

- explain the important features of earlier models of the structure of atom;
- discuss Bohr model of atom giving its success and limitations in explaining the atomic structure;
- describe the wave nature and particle nature of radiation and matter;
- explain Heisenberg uncertainty principle;
- discuss the importance and the need of quantum mechanical approach in explaining the atomic structure;

- write time-independent Schrodinger equation and arrive at the energy states of the hydrogen atom;
- discuss the origin of quantum numbers and draw the shapes of various atomic orbitals;
- explain the filling of electrons in various atomic orbitals of elements;
- highlight the stability of elements having half-filled and completely filled orbitals; and
- write the electronic configuration of an element and find its placement in the appropriate position in the periodic table.

UNIT 1

BOHR'S THEORY

Structure

1.1 Introduction
    Expected Learning Outcomes
1.2 Earlier Atomic Models: Dalton, Thomson and Rutherford Models
1.3 Bohr Atom Model
    Calculation of Radius of Orbits
    Energy of an Electron in an Orbit
1.4 Hydrogen Atom Spectrum and Bohr's Theory
1.5 Critical Analysis and Limitations of Bohr's Theory
    Sommerfeld Modification
1.6 Summary
1.7 Terminal Questions
1.8 Answers

1.1 INTRODUCTION

This is the first Unit of the first Block on Atomic Structure. Here, we will mainly focus on earlier developments and models proposed for the structure of the atom. We will begin this unit with a brief discussion on the atomic models proposed by Dalton, Thomson and Rutherford to refresh your knowledge as you might have studied about these models in earlier classes also.

Then, the model proposed by Bohr would be described in detail. Here, we will also be calculating the radius of orbits and energy of an electron in a particular orbit. You will then be given an elementary idea about the atomic spectrum to help you understand how hydrogen atom spectrum could be explained on the basis of Bohr's theory. We will then present a critical analysis of Bohr's theory in terms of its success and limitations. Finally, the modification in Bohr's theory proposed by Sommerfeld will be discussed.

Expected Learning Outcomes

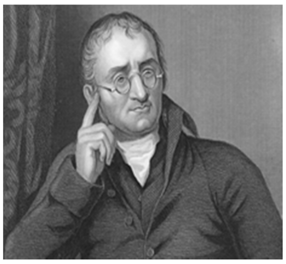
After studying this unit, you should be able to:

- briefly explain earlier models for the structure of atom proposed by Dalton, Thomson and Rutherford;

- state the postulates of Bohr's Theory;
- derive an expression useful in calculating the radius of the hydrogen atom;
- calculate the energy of an electron in an orbit;
- describe the general features of atomic spectrum;
- explain the atomic spectrum of hydrogen in the light of Bohr's theory;
- analyse critically the advantages and limitations of Bohr's theory; and
- state the refinements in the Bohr's theory to explain atomic spectrum.

1.2 EARLIER ATOMIC MODELS: DALTON, THOMSON AND RUTHERFORD MODELS

The atomic theory of the Greek philosophers Leucippus and Democretus (400 B.C.) held that continued subdivision of matter would ultimately yield **atoms** which would not be further divided. The word 'atom' is derived from the Greek word, *atomos*, which means "uncut" or indivisible. Here, we would present the models proposed by Dalton, Thomson and Rutherford.



John Dalton
(6th Sept.1766-27th July 1844)

He was an English Chemist and Physicist and did pioneering work in the development of modern atomic theory.

Dalton (1808) based his atomic theory on the ideas of Democretus and was able to explain the laws of chemical combination.

The postulates of Dalton's atomic theory are as follows:

1. Matter is composed of small indivisible particles called atoms.
2. All the atoms of a given element are identical.
3. The atoms of different elements have different masses.
4. A compound is a specific combination of more than one element.
5. In a chemical reaction, atoms are neither created nor destroyed but exchange partners to give new substances.

Sir J.J. Thomson
(18th Dec. 1856 – 30th Aug. 1940)

He was an English Physicist andwas awarded the Nobel Prize in 1906.

Thus, Dalton's atomic theory suggested that atom is indivisible. But the discovery of sub-atomic particles like electron, led to a revision of this theory.

Thomson (1904) proposed a model for the atomic structure, known as "plum pudding" model, which is shown in Fig. 1.1.

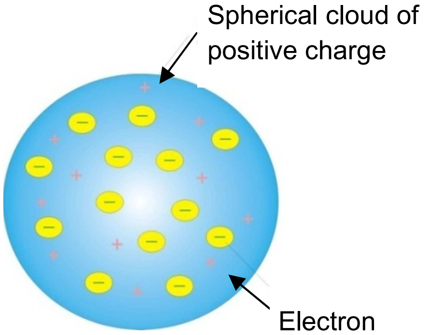


Fig. 1.1: Thomson plum pudding model.

He considered an atom to be a uniform sphere of positive electricity of about 10^{-8} cm radius, with the electrons embedded in such a way as to give the most stable electrostatic arrangement. This model considered negatively charged electrons embedded in a sphere of positive charge just like plum pieces are present in a pudding. Therefore, it is also known as *plum pudding model*.

Thomson compared atom to be a pudding having electrons as partially dried grapes in it.

This model was not able to explain the observation of Geiger and Marsden (1909) regarding the scattering of the α-particles directed towards thin gold foil, see Fig.1.2.

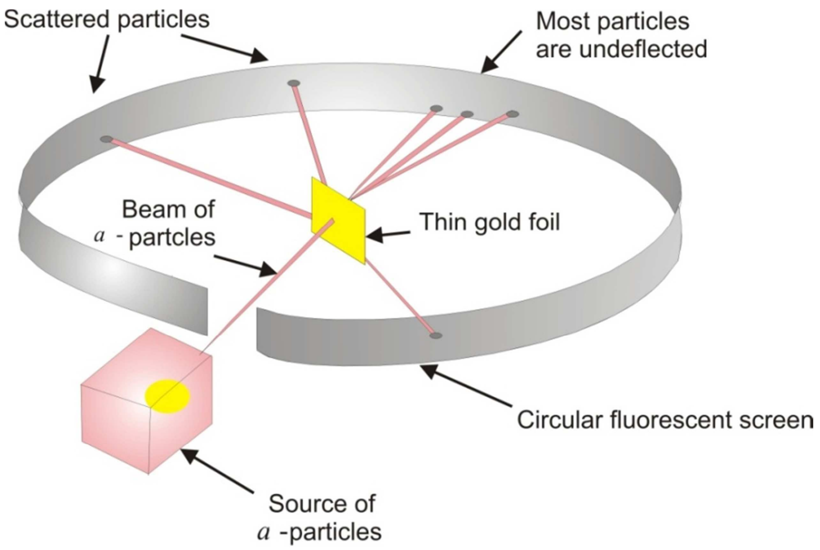
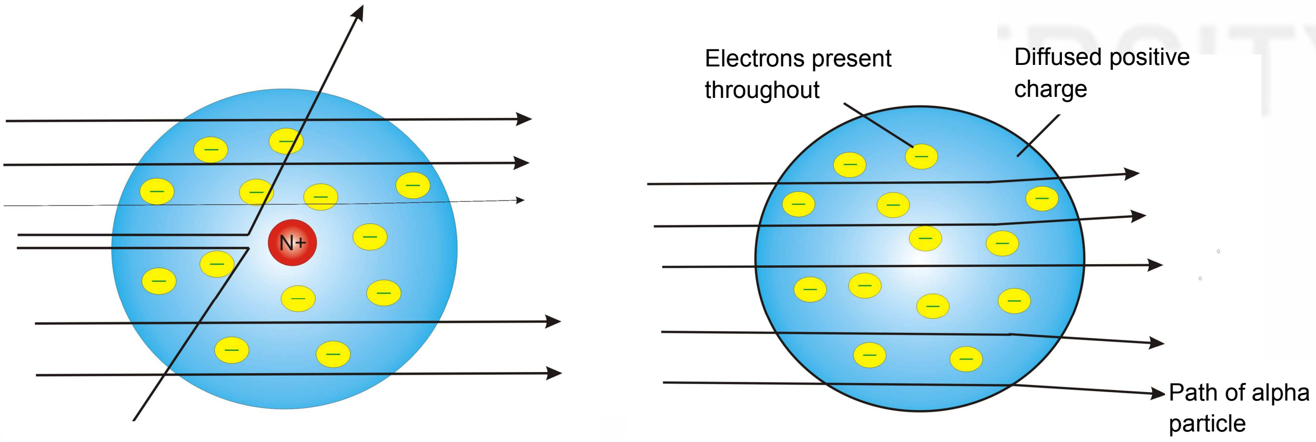


Fig. 1.2: Geiger and Marsden’s α-particle experiment.

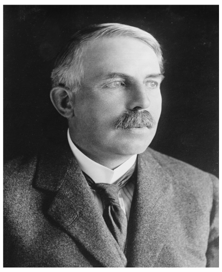
Some α-particles were deflected from their straight-line path and a few recoiled back toward their source, Fig. 1.3 a). A uniform sphere of positive charge, would mean only a gradual deflection of the α-particles, but not scattering as it progressed through the foil, see Fig.1.3 b).



a) **b)**

Fig. 1.3: Deflection of α-particles by nuclei of metal foil: a) Observed results and b) Expected outcome of the experiment. Curved lines shows the path of α-rays deflected while straight lines indicate the path of those not deflected.

Rutherford (1911), on the basis of the α-ray scattering experiment, suggested that positive charge and mass of the atom are concentrated in a space which



Earnest Rutherford
(30th Aug. 1871 – 19th Oct. 1937)

is very much smaller than that occupied by the atom as a whole. He suggested an atomic model, known as *nuclear model* which consisted of a nucleus at the centre and negative particles surrounding it. The nucleus accounted for mass and positive charge. This could explain the actual results of the α-particle experiment shown in Fig. 1.3 a). Thus, those α-particles which passed very close to the nucleus, were deflected by large angles while others showed small deflections, see Fig. 1.4.

Rutherford, on observing the recoil of some α-particles from thin gold foil, exclaimed "It was quite the most incredible event that has ever happened to me in my life. It was almost as if you fired a 15 inch shell into a piece of tissue paper and it came back and hit you"

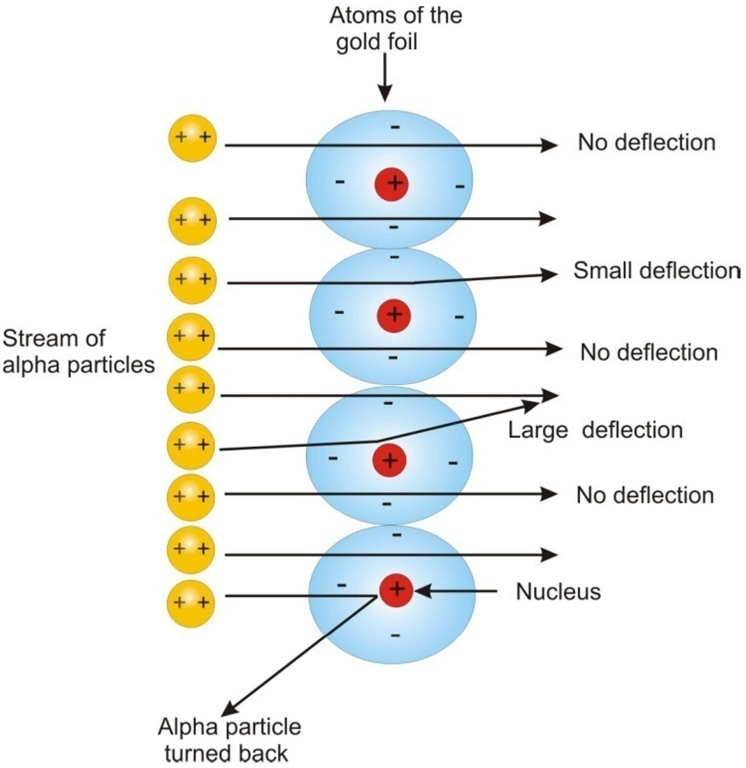


Fig. 1.4: Larger deflection of α-particle which passed very close to the nuclei as compared to those which passed at a distance from the nuclei.

If a nucleus of an atom were the size of a tennis ball, the atom would have a diameter of over one mile.

To support the fact that the electrons did not fall into a nucleus as a result of electrostatic attraction, Rutherford found it necessary to postulate rapid rotation of the electrons about the nucleus just as planets go around the sun, see Fig. 1.5.

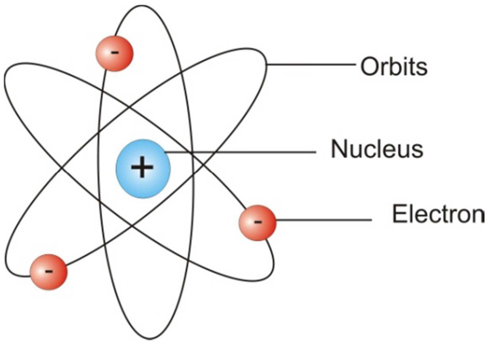


Fig.1.5: Rutherford Nuclear model of atom.

This analogy is misleading since according to classical electromagnetic theory, an electron in orbit is subject to continual acceleration towards the centre and the accelerated electric charge must emit radiation. This consequent loss of energy, should bring the electron down in a spiral path to the nucleus – that is the collapse of the atom, as shown in Fig. 1.6.

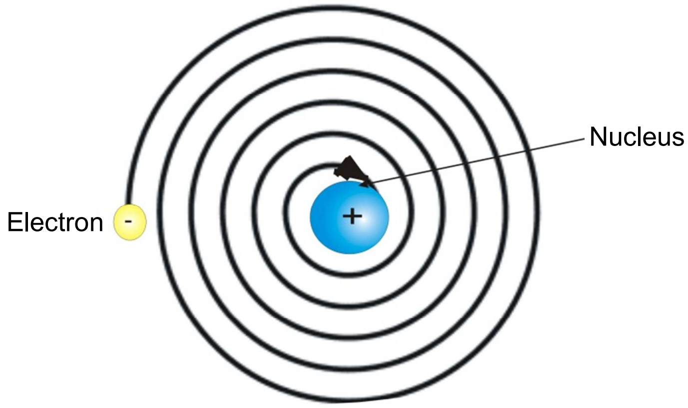


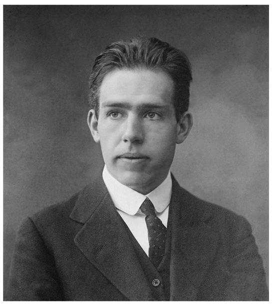
Fig.1.6: Spiral path of electron.

SAQ 1

What is the essential difference between the atomic models proposed by Thomson and Rutherford?

1.3 BOHR ATOM MODEL

To explain the stability of hydrogen atom and the spectrum of the hydrogen atom, the Danish physicist, Niels Bohr (1913) suggested an atom model which was an improvement over Rutherford model described in Sec.1.2.



Niels Bohr
(7th Oct. 1885 – 18th Nov. 1962)

The quantum theory proposed by Max Planck in 1900 was applied by Niels Bohr in suggesting the model of the atom.

Bohr based his theory on the following postulates:

i) An electron can exist only in orbits of definite angular momentum and energy. Each orbit is known as a **stationary state**.

ii) The electron does not radiate energy when it is in an allowed orbit.

iii) While in an orbit, the angular momentum of the electron, $m\,v\,r$, is an integral multiple of $h\,/\,2\pi$ units.

$$m\,v\,r = \frac{nh}{2\pi} \qquad ...(1.1)$$

Where m and v stand for the mass and velocity of the electron, r is the radius of the orbit and n is an **integer called principal quantum number**. The orbits are called K, L, M, N … depending on the values of n, viz., 1, 2, 3, 4,… Here, h is Planck's constant. At the time this view was proposed, there was no reason for the quantisation of angular momentum. But you will study later in Unit 2 that h has the units of angular momentum.

iv) Each spectral line is produced by a single electron. When an electron jumps from one orbit to another, radiation of a definite frequency is emitted or absorbed giving rise to a definite spectral line. The frequency of the spectral line is related to the difference in energy, ΔE, between initial and final levels, as per the following equation:

$$\Delta E = h\,\upsilon = hc\,\overline{\upsilon} \qquad …(1.2)$$

Using the above postulates, Bohr was able to calculate the radii of different orbits in hydrogen atom, the energy of the electron in various orbits and the frequency of the spectral lines. These are discussed below in detail.

1.3.1 Calculation of Radius of Orbits

Bohr atom model considers an electron of charge -*e* and mass *m* revolving around the nucleus of charge $+Ze$ with velocity v in a stationary orbit of radius *r* (Fig. 1.7). The nuclear charge is taken as $+Ze$ since the nucleus is assumed to contain Z protons and each proton has charge $+e$.

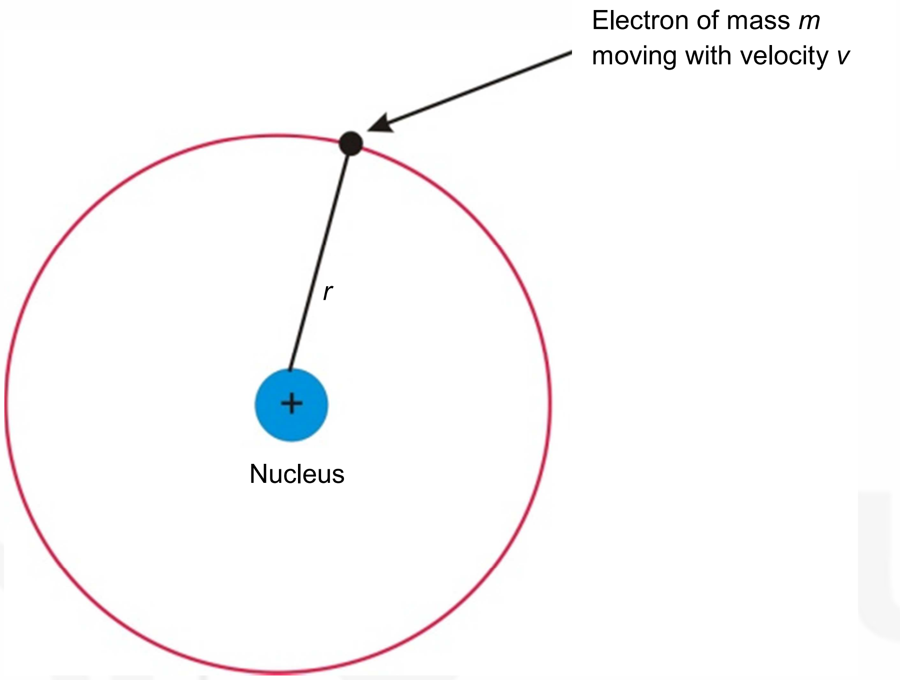


Fig 1.7: Bohr model for the hydrogen atom. An electron of mass *m* moves with the velocity *v* in an orbit with radius *r* from the nucleus.

For attaining mechanical stability, the electrostatic force of attraction, f_a between the electron and the nucleus must be equal to the centrifugal force, f_c, which is operating in the opposite direction.

ϵ_0 is pronounced as "epsilon zero".

i.e., $f_a = -f_c$ …(1.3)

Note the negative sign in Eq. 1.3 which indicates that one type of force opposes the other. The electrical force of attraction, f_a is directly proportional to the product of charges, $-e$ and Ze, and inversely proportional to the square of the distance of separation, r^2, between the nucleus and the electron.

Unit of f_a = Unit of $\frac{-Ze^2}{4\pi \epsilon_0 r^2}$; π and Z are unitless.

Unit of f_a = $\frac{\mathrm{C}^2}{\mathrm{C}^2\,\mathrm{N}^{-1}\mathrm{m}^{-2}\,\mathrm{m}^2} = \mathrm{N}$

$$f_a \propto \frac{(-e)(+Ze)}{r^2}$$

i.e., $$f_a = \frac{-Ze^2}{(4\pi \epsilon_0) r^2} \quad \text{…(1.4)}$$

Here, $(4\pi \epsilon_0)^{-1}$ is proportionality constant in SI units. The term, ϵ_0, is the *permittivity in vacuum*, and it is equal to $8.854 \times 10^{-12}\,\mathrm{C}^2\,\mathrm{N}^{-1}\,\mathrm{m}^{-2}$. The terms *e* and *r* have coulomb (C) and metre (m) units, respectively while *Z* is unitless.

The centrifugal force, $f_c = \frac{mv^2}{r}$ …(1.5)

Substituting Eq. 1.4 and Eq. 1.5 in Eq.1.3,

$$\frac{-Ze^2}{4\pi \epsilon_0 r^2} = \frac{-mv^2}{r}$$

$$mv^2 = \frac{Ze^2}{4\pi \epsilon_0 r} \quad \text{…(1.6)}$$

Rearranging Eq. 1.1, we can write,

$$v = \frac{nh}{2\pi mr}$$

Squaring both sides, we get

$$v^2 = \frac{n^2h^2}{4\pi^2 m^2 r^2}$$

Then, after multiplying both sides by m, we get

$$mv^2 = \frac{n^2h^2}{4\pi^2 mr^2} \quad \text{…(1.7)}$$

Substituting Eq. 1.6 in Eq. 1.7, we get

$$\frac{Ze^2}{4\pi \epsilon_0 r} = \frac{n^2h^2}{4\pi^2 mr^2}$$

$$r = \frac{n^2 \epsilon_0 h^2}{\pi mZe^2} \quad \text{…(1.8)}$$

For Units
$\frac{1\,\text{N}^{-1}\text{m}^{-2}\text{J}^2\,\text{s}^2}{\text{kg}}$
Using
$1\,\text{N} = 1\,\text{kg m s}^{-2}$
and
$1\,\text{J} = 1\,\text{kg m}^2\,\text{s}^{-2}$
in above equation expression, we get
$= \frac{\text{m}^{-2}\,(\text{kg m}^2\,\text{s}^{-2}).\text{s}^2}{\text{kg m s}^{-2}.\text{kg}}$
$= \frac{\text{m}^{-2}\,\text{kg}^2\,\text{m}^4\,\text{s}^{-4}.\text{s}^2}{\text{kg m s}^{-2}.\text{kg}}$
$= 1\,\text{m}$

Eq. 1.8 is useful in calculating the radius of the orbits with different n values. As an illustration, we calculate the radius of the first Bohr orbit (r_1) for hydrogen atom $(n = 1, Z = 1)$.

$$r_1 = \frac{1^2 \times 8.854 \times 10^{-12}\text{C}^2\,\text{N}^{-1}\,\text{m}^{-2} \times \left(6.636 \times 10^{-34}\,\text{J s}\right)^2}{3.142 \times 9.109 \times 10^{-31}\text{kg} \times 1 \times \left(1.602 \times 10^{-19}\,\text{C}\right)^2}$$

$$= 53 \times 10^{-12}\,\text{m} = 53\,\text{pm (rounded to whole number)}$$

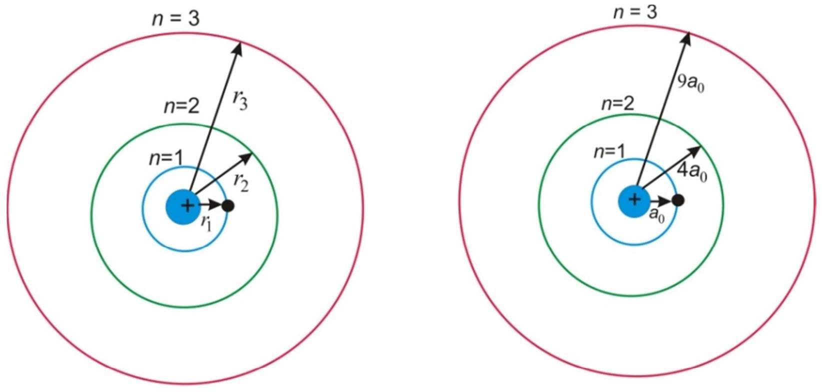
The Unit, picometre (pm), is quite convenient in describing the radius of the orbits in atoms.

Using this value in Eq. 1.8, a general expression for this radius of the different obits of hydrogen atom is given below:

$$r = 53\,n^2\,\text{pm} \quad \text{…(1.9)}$$

The radius of the first orbit in hydrogen atom is called **Bohr radius**, a_0.

From Eq. 1.8, you can infer that **radius of a particular orbit in hydrogen atom is proportional to the square of its principal quantum number value**. This is illustrated in Fig. 1.8.



$$r_n = n^2 a_0$$

where $n=1, 2, 3,\ldots$

Fig. 1.8: The radii of the orbits in hydrogen atom are proportional to n^2 values. Here, only first three orbits are shown and $r_1 : r_2 : r_3 = 1:4:9$.

SAQ 2

Calculate the radius of the second orbit in hydrogen atom.

1.3.2 Energy of an Electron in an Orbit

The total energy, E_n, of an electron in n^{th} orbit, is given by the sum of its potential energy (P.E.) and kinetic energy (K.E.), i.e.,

$$E_n = \text{P.E.} + \text{K.E.} \qquad \ldots(1.10)$$

The potential energy of the electron is defined as the work necessary to take the electron to infinity from its equilibrium distance *r*, with respect to the nucleus. Since the columbic force (f_a) between the electron and nucleus is $-Ze^2/4\pi \epsilon_0 r^2$ as per Eq. 1.4, potential energy is calculated as follows:

$$\text{P.E.} = \int_r^\infty f_a.dr$$

$$= \int_r^\infty \frac{-Ze^2}{4\pi \epsilon_0 r^2}.dr$$

$$= \frac{-Ze^2}{4\pi \epsilon_0} \int_r^\infty \frac{dr}{r^2}$$

$$= \frac{-Ze^2}{4\pi \epsilon_0} \left[\frac{1}{r} \right]_r^\infty$$

$$\text{P.E.} == \frac{-Ze^2}{4\pi \epsilon_0 r};$$

Also, $\text{K.E.} = \dfrac{mv^2}{2}$

The negative sign indicates that work must be done on the electron to remove it to infinity.

So substituting the values of K.E. and P.E. in Eq. 1.10, we get,

$$E_n = \frac{mv^2}{2} - \frac{Ze^2}{4\pi \epsilon_0 r} \qquad \ldots (1.11)$$

From Eq. 1.6, $\dfrac{mv^2}{2} = \dfrac{Ze^2}{8\pi \epsilon_0 r}$ … (1.12)

Substituting Eq. 1.12 in Eq. 1.11,

$$E_n = \frac{Ze^2}{8\pi \epsilon_0 r} - \frac{Ze^2}{4\pi \epsilon_0 r}$$

$$= \frac{-Ze^2}{8\pi \epsilon_0 r} \qquad \ldots (1.13)$$

Substituting for r from Eq. 1.8,

$$E_n = \frac{-Ze^2}{8\pi \epsilon_0} \cdot \frac{\pi m Ze^2}{n^2 \epsilon_0 h^2}$$

$$= \frac{-Z^2 e^4 m}{8 \epsilon_0^2 h^2 n^2} \qquad \ldots (1.14)$$

For units of E_n

$$\frac{C^4\,kg}{(C^2\,N^{-1}\,m^{-2})^2.(J\,s)^2}$$
$$= \frac{kg}{N^{-2} m^{-4}.J^2\,s^2}$$
$$= \frac{kg}{(kg\,m\,s^{-2})^{-2}\,m^{-4}\,J^2\,s^2}$$
$$= \frac{kg.(kg\,m\,s^{-2})^2.m^4}{J^2\,s^2}$$
$$= \frac{kg.kg^2\,m^2\,s^{-4}.m^4}{J^2\,s^2}$$
$$= \frac{kg.kg^2\,m^6\,s^{-6}}{J^2}$$
$$= \frac{kg^3\,m^6\,s^{-6}}{J^2}$$
$$= \frac{J^3}{J^2}$$
$$= J$$

The negative sign in Eq. 1.14 denotes that there is attraction between the nucleus and the electron; so work must be done to move it to a distance greater than the equilibrium distance r from the nucleus.

Substituting the values of e, m, ϵ_0 and h in Eq. 1.14, the energy of the electron in the nth orbit of hydrogen atom is obtained as,

$$E_n = \frac{-1^2 \times \left(1.602 \times 10^{-19} C\right)^4 \times 9.109 \times 10^{-31} kg}{8 \times \left(8.854 \times 10^{-12} C^2\,N^{-1}\,m^{-2}\right)^2 \times \left(6.626 \times 10^{-34}\,J\,s\right)^2 \times n^2}$$

$$E_n = \frac{-2.178 \times 10^{-18}}{n^2} J \qquad \ldots (1.15)$$

You must remember that $Z = 1$ for hydrogen atom. In the first orbit, when $n = 1$, the energy of the electron is equal to -2.178×10^{-18} J. Since E_n is related to n^2 in Eq. 1.14, the increase in energy with the value of n is as shown in Table 1.1.

Table 1.1: Energy variation with *n* values

n	$\frac{E_n}{J} = \frac{-2.178 \times 10^{-18}}{n^2}$	$\frac{E_n - E_{n-1}}{J}$
1	-2.178×10^{-18}	–
2	-5.445×10^{-19}	1.634×10^{-18}
3	-2.42×10^{-19}	3.025×10^{-19}
4	-1.361×10^{-19}	1.059×10^{-19}
5	-8.712×10^{-20}	4.898×10^{-20}

The successive differences in energy values in Table 1.1 are obtained to show how successive energy levels become closer. So energy levels are distinctly discrete at lower n values. As n becomes sufficiently large, the energy levels differ only slightly. This is called *convergence of the energy levels*. This principle will be helpful to you in understanding the atomic spectrum of hydrogen described in the next section.

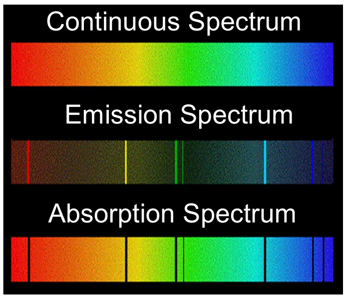
But before proceeding to the next section, why don't you try the following SAQ?

SAQ 3

What is the energy value of an electron if $n = \infty$?

1.4 HYDROGEN ATOM SPECTRUM AND BOHR'S THEORY

Let us first understand what atomic spectrum is. When gases or vapours of a chemical substance are heated in an electric arc or bunsen flame, light is emitted. If a ray of this light is passed through a prism, a **line spectrum** is produced (Fig.1.9).



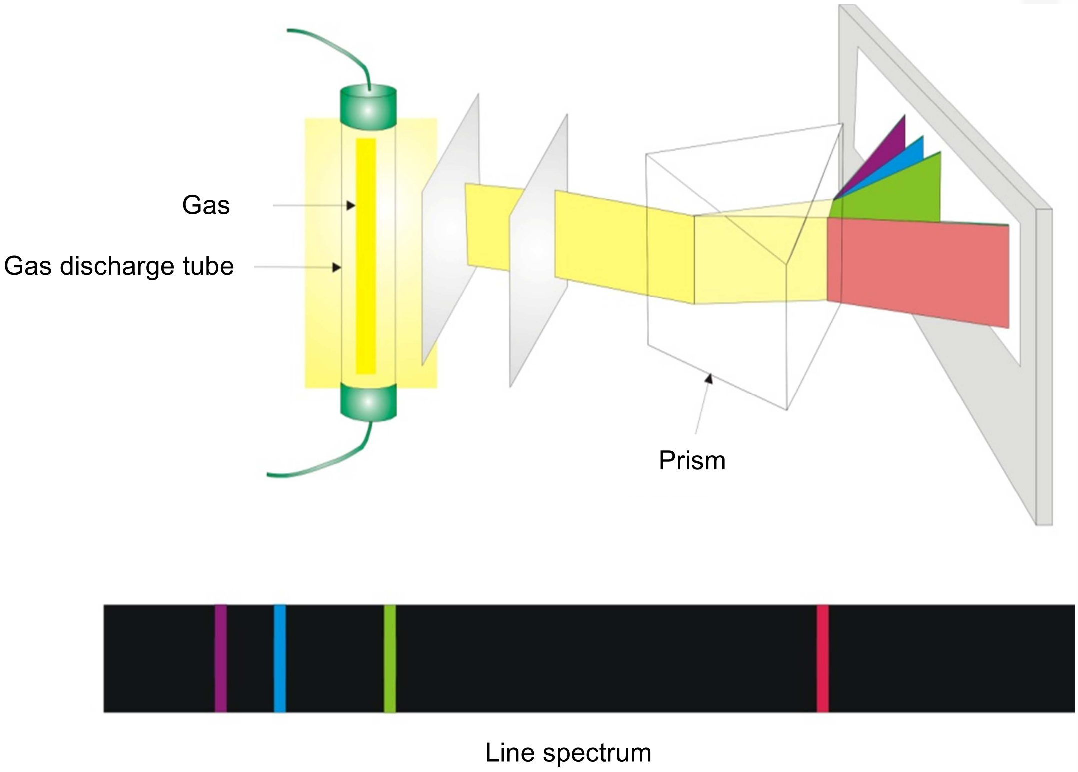


Fig.1.9: Line Spectrum.

This spectrum consists of a limited number of coloured lines, each of which corresponds to different wavelength of light. The line spectrum of each element is unique. On careful examination, it was found that in the atomic spectra of elements, spectral lines occur discretely at lower frequencies followed by a continuous spectrum at very high frequencies.

An examination of a part of the spectrum of hydrogen as in Fig. 1.10, indicates the presence of three groups of lines.

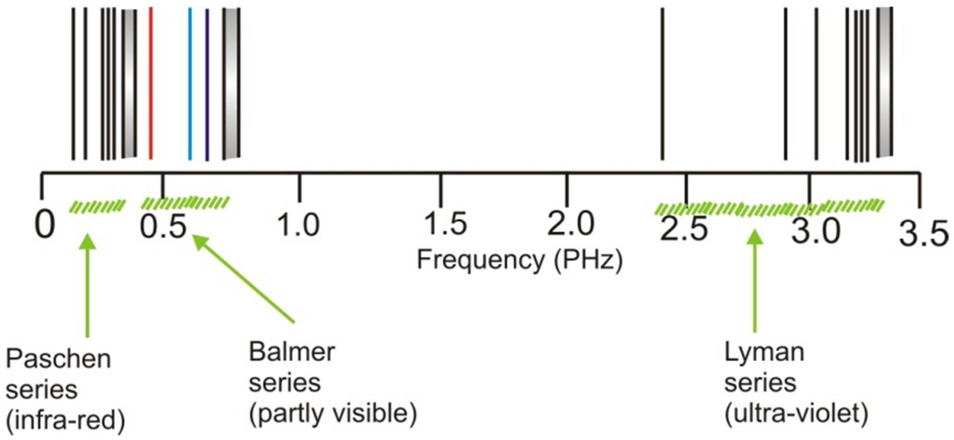


Fig. 1.10: Discrete lines followed by continuum in the atomic spectrum of hydrogen.

In the case of atoms, only electronic transitions are possible and therefore, the spectrum is very simple consisting of electronic spectral lines. However, in molecules, on the other hand, besides electronic transitions, transitions between rotational and vibrational energy levels are also possible and therefore, molecular spectrum is relatively complex and has a large number of closely spaced line and looks like a band (called band spectra).

One of them is in the visible region, and it was discovered by Balmer in 1885 (Fig. 1.10). This series known as Balmerseries, has a mathematical relationship as shown by Eq. 1.16.

$$\bar{\upsilon} = \frac{1}{\lambda} = R(\frac{1}{2^2} - \frac{1}{n^2}) \quad \text{... (1.16)}$$

In this equation, R is a constant, now known as Rydberg constant, having a value of $1.097 \times 10^7 \text{ m}^{-1}$ and n is a whole number having values 3, 4,…etc.

Later, Rydberg showed that the lines in the atomic spectra of the alkali metals could be classified into a number of spectral series, each of which could be described by a relationship of the following type:

$$\bar{\upsilon} = \bar{\upsilon}_\infty - \frac{R}{(n-d)^2} \quad \text{...(1.17)}$$

Here, n is an integer and d is a constant. The Rydberg constant, R, was shown to have the same value as mentioned above for all the elements and for the first time, indicated a common link between the spectra of different elements.

You can see in Fig.1.10 that the Balmer series consists of a series of spectral lines in which the distance of separation or spacing between the lines decreases, as the frequency increases. At very high frequencies or lower wavelengths, the spectral lines, converge to give a continuous spectrum or continuum. The other two series known as Lyman and Paschen series, with a similar pattern, occur in the far ultraviolet and infrared regions, respectively.

Ritz (1908) showed experimentally that in any spectrum, such that the wave numbers of the observed spectral lines could be written as the difference of two terms (having dimensions of cm^{-1}). This is known as *Ritz combination principle* and in case of hydrogen, new spectral series were predicted for which the frequencies were given by:

$$\bar{\upsilon} = R(\frac{1}{m^2} - \frac{1}{n^2}) \quad \text{... (1.18)}$$

Here, m and n are integers and m is constant for a given series. This principle applies to two other series as well, namely, Lyman series and Paschen series.

Classical physics failed in its attempts to account for the appearance of various spectral series, each of which has discrete spectral lines at lower frequencies and continuous spectra at higher frequencies. On the basis of classical physics, the atomic spectra was assumed to be consisting of a continuous band throughout. We shall now see how Bohr was partly successful in explaining the above observations.

Bohr's theory is useful in calculating the frequencies of spectral lines in the atomic spectrum of hydrogen. Let us assume that E_1 and E_2 represent the energies of the inner and outer orbits having quantum number values n_1 and n_2, respectively. Using Eq. 1.14 we can write,

$$E_1 = \frac{-Z^2e^4m}{8\in_0^2 h^2}\cdot\frac{1}{n_1^2} \qquad \ldots(1.19)$$

$$E_2 = \frac{-Z^2e^4m}{8\in_0^2 h^2}\cdot\frac{1}{n_2^2} \qquad \ldots(1.20)$$

The amount of energy emitted when an electron jumps from an outer level n_2 to an inner level n_1 is given by,

$$E_2 - E_1 = \frac{-Z^2e^4m}{8\in_0^2 h^2}\left(\frac{1}{n_2^2} - \frac{1}{n_1^2}\right)$$

Representing this quantity as ΔE, we get

$$\Delta E = \frac{Z^2e^2m}{8\in_0^2 h^2}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \qquad \ldots(1.21)$$

Substituting Eq. 1.12 in Eq. 1.21, it is possible to get the wave numbers of spectral lines as given by the expression,

$$\bar{\upsilon} = \frac{\Delta E}{hc}$$

$$= \frac{Z^2e^4m}{8\in_0^2 h^3c}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \qquad \ldots(1.22)$$

The term $\frac{Z^2e^4m}{8\in_0^2 h^3c}$ is called **Rydberg constant** for hydrogen atom. It is equal to $1.097\times10^7\,\mathrm{m}^{-1}$ and is denoted by the symbol R_H. Hence, the above equation for hydrogen atom can be written as follows:

$$\bar{\upsilon} = R_\mathrm{H}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \qquad \ldots(1.23)$$

You can see that Eq. 1.23 is similar in form to Eqs. 1.16, 1.17 or 1.18 mentioned earlier. In the above derivation, it has been assumed that the nucleus is fixed at the centre of the orbits. In fact, the nucleus and the electrons are both rotating about the common centre of mass.

Anyhow, by using Eq. 1.23, we can calculate the frequencies of the spectral lines in Lyman, Balmer, Paschen, Brackett and Pfund series although at the time Bohr formulated his theory, only Balmer and Paschen series were known. For these five series in the atomic hydrogen spectra, the values of n_1 and n_2 are given in Table 1.2.

Table 1.2: Series of spectral lines in the atomic spectrum of hydrogen

Name of the series	n_1	n_2	Region
Lyman	1	2,3,4,…	Ultraviolet
Balmer	2	3,4,5,…	Visible
Paschen	3	4,5,6,…	Infrared
Brackett	4	5,6,7,…	Infrared
Pfund	5	6,7,8,…	Infrared

A diagrammatic representation of spectral transitions among the different energy levels responsible for presence of above series of spectral lines in the atomic spectrum of hydrogen is given in Fig. 1.11.

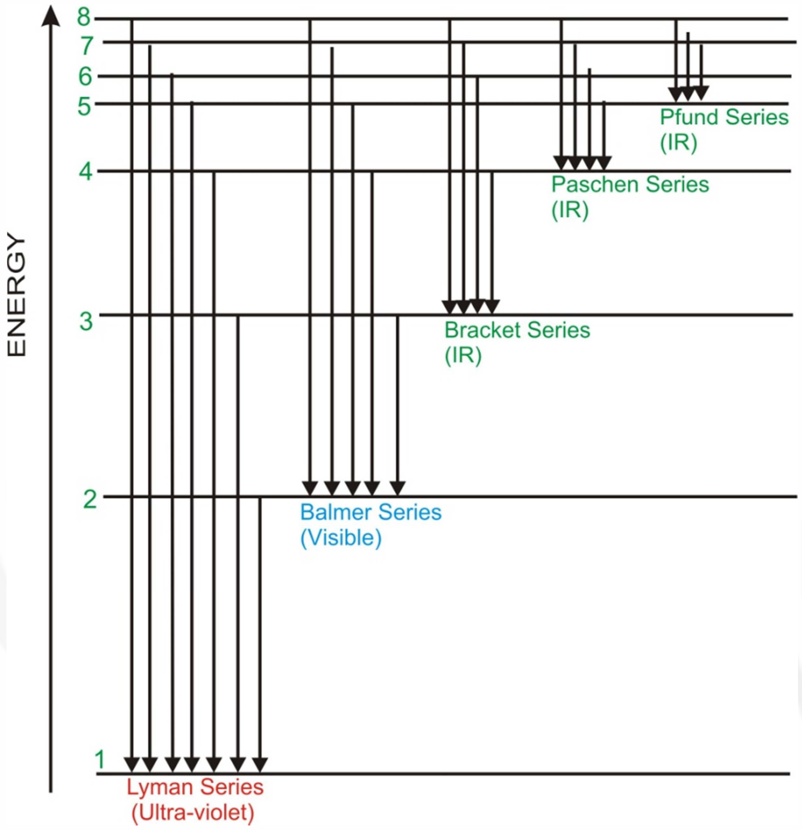


Fig. 1.11: Spectral transitions between different energy levels of hydrogen atom responsible for various spectral lines in the atomic spectrum of hydrogen.

You can see in the figure above that the spacing between two successive levels becomes smaller, as *n* increases. We have mentioned about the converging nature of energy levels in the above discussion also. Experimentally, it has been found that within a particular series, for example, Lyman series, the lines in the spectrum of atomic hydrogen are discrete at lower frequencies and they converge as the frequency increases. Each successive line becomes closer to the previous one. This is quite evident from the spacings of the first four lines in Lyman series, as given in the last column of Table 1.3.

Table 1.3: Wave Number Values of spectral lines in Lyman Series

Number of the spectral line (n)	n_1	n_2	$\frac{\bar{\upsilon}_n}{\text{m}^{-1}} = 1.097 \times 10^7 \left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$	Spacing $(\bar{\upsilon}_n - \bar{\upsilon}_{n-1})/\text{m}^{-1}$
1	1	2	8.228×10^6	1.523×10^6
2	1	3	9.751×10^6	5.29×10^5
3	1	4	1.028×10^7	2.5×10^5
4	1	5	1.053×10^7	

As Eq. 1.21 predicts, each series of lines converges towards a limit beyond which the spectrum is continuous. At this point, electron responsible for the spectral line has been excited into an orbit of such high energy $(n_2 = \infty)$ that it has effectively escaped from the influence of the nucleus. In other words, the atom has lost its electron and formed a positive ion:

$$\text{H (g)} \longrightarrow \text{H}^+\text{(g)} + e^-$$

The energy difference between the ground state of hydrogen atom, and the excited state that corresponds to convergence limit of the spectral lines, $n_2 = \infty$ is called the **Ionisation energy of hydrogen atom**. Note that ionisation energies refer to the removal of an electron in the gas phase. You will study more about ionisation energies later in another course of chemistry.

Thus, Bohr's theory can explain the appearance of discrete spectral lines at lower frequencies and a continuous spectra at higher frequencies in the atomic spectrum of hydrogen. In the light of what you have studied above, answer the following SAQ.

SAQ 4

What is the reason for the increase in the spectral frequency as $n_2$increases?

From spectral studies, Bohr constructed a theoretical periodic chart which agreed with Mendeleev's chart. On the basis of atomic spectrum, Bohr was able to predict that the element with Z = 72, has properties similar to titanium (Z = 22) and zirconium (Z = 40), and this element was later discovered and named hafnium.

1.5 CRITICAL ANALYSIS AND LIMITATIONS OF BOHR'S THEORY

Let us examine how the theoretical model of Bohr is able to explain some of the features given below:

- Atomic spectrum of hydrogen
- Rydberg constant value
- Ionisation energy of hydrogen

Bohr's theory is successful as an atom model to the extent that its findings are consistent with atomic spectrum of hydrogen. The agreement between the theoretical and experimental values of spectral frequencies is a testimony to the validity of this theory.

Again, the value of Rydberg constant, calculated according to Bohr's theory, is in agreement with the experimental value.

The ionisation energy of hydrogen atom is defined as the minimum energy required to remove the electron from $n = 1$state to infinite distance $(n_2 = \infty)$ leaving it without any kinetic energy and it can be calculated using Eq. 1.23. For hydrogen atom, the ionisation energy in the wave number unit can be calculated as follows:

$$\bar{\upsilon} = R_H\left(\frac{1}{1^2} - \frac{1}{\infty^2}\right) = R_H = 1.097 \times 10^7 \,\text{m}^{-1}$$

For the purposes of chemical calculation, ionisation energy of hydrogen may be defined as the energy required to remove one mole of electrons, i.e., 6.022×10^{23}electrons from one mole hydrogen atoms in the ground state, Hence, ionisation energy:

$$= 6.022 \times 10^{23} h c \bar{\upsilon} \text{ J mol}^{-1}$$

$$= 6.022 \times 10^{23} \times 6.626 \times 10^{-34} \times 2.998 \times 10^8 \times 1.097 \times 10^7 \text{ J mol}^{-1}$$

$$= 1.312 \times 10^6 \text{ J mol}^{-1}$$

$$= 1312 \times 10^3 \text{ J mol}^{-1}$$

$$= 1312 \text{ kJ mol}^{-1}$$

Thus, Bohr's theory offers a method of calculating ionisation energy of hydrogen and this principle has been extended to other elements in calculating their ionisation energies.

In spite of the success of Bohr's theory as mentioned above, it has certain limitations as discussed below.

Limitations of Bohr's Theory

1) According to Bohr's theory, the angular momentum of the electron can never be zero. However, later in Unit2you will study that in $n = 1$state, electron has zero angular momentum.

2) The hyperfine structure in the atomic spectrum of hydrogen is not well explained by Bohr's theory.

3) Also, Bohr's theory is not able to explain the spectra of multi-electron atoms.

4) Further, this theory does not explain how molecules are formed from atoms.

5) It does not recognise the wave properties of electrons.

The splitting of spectral lines in the atomic spectrum is called *hyperfine structure*. It is caused by the spin angular momentum of the electrons and the coupling of the spin to the orbital angular momentum.

Just like electromagnetic radiation, the electron also has both particle and wave aspects. Using the crystal spacings in a nickel crystal as a diffraction grating, it is possible to obtain diffraction patterns that could be understood in terms of wave motion of the electron. But Bohr's theory has not provided any explanation for this phenomenon.

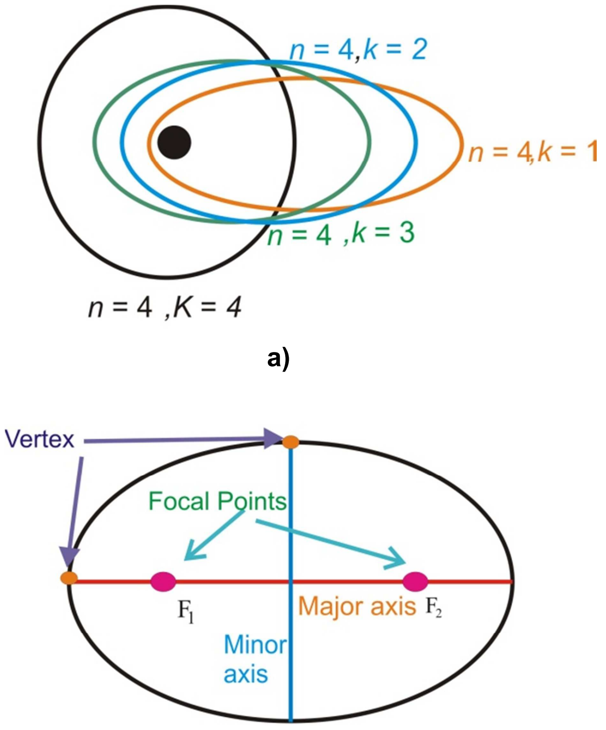
6) According to Bohr's theory, electron moves in orbits known as stationary states. The path of this orbit (or its trajectory) can be known only if we know simultaneously both the position and the velocity of electron. It, therefore, assumes the accurate and simultaneous determination of both position and velocity of the electron.

But this assumption is not in conformity with the wave nature of electron. In the forthcoming units, we shall see, how theories were developed by Heisenberg and Schrodinger to explain the wave characteristics of electrons.

In order to further explain the fine structure of spectral lines in the atomic spectrum of hydrogen, Sommerfeld proposed the following modification in the Bohr’s model.

1.5.1 Sommerfeld Modification

Sommerfeld (1916) modified Bohr's theory and tried to interpret the fine structure in the *atomic spectrum* of hydrogen as due to elliptical path of the electron in the orbits shown below in the Fig. 1.12 a). In the elliptical orbits, the nucleus was assumed to be present at one of the focii of the ellipse, see Fig. 1.12 b).



a)

b)

Fig.1.12: a) Elliptical orbits proposed by Sommerfeld, and b) Major and Minor axes and focal points of an ellipse.

You can see in the Fig. 1.12 b) above that in contrast to a circle where the radius is constant and the angle is changing; in an ellipse both the radius and the angle may change. Such a change in angle is shown in the Fig.1.13 below.

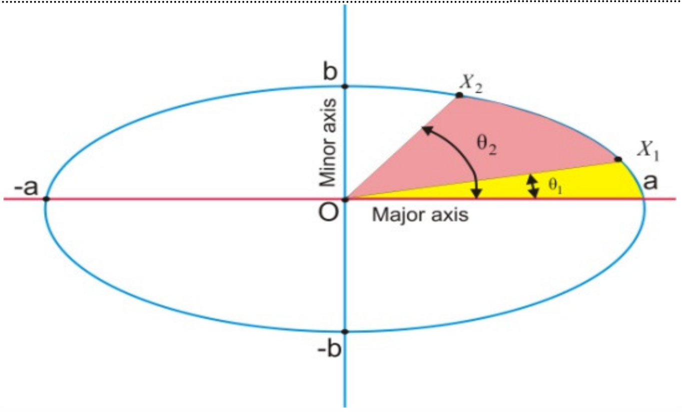


Fig. 1.13: Variation of the angle in an ellipse.

In an elliptical orbit, the motion of an electron could be describe by considering radial quantum number, n_r and azimuthal quantum number, *k.* These quantum numbers are related to the Bohr's quantum number, *n* as follows:

$$n = n_r + k$$

These quantum numbers are related to the geometry of the ellipse as follows:

$$\frac{n}{k} = \frac{\text{Length of the major axis}}{\text{Length of the min or axis}}$$

Also, for a given value of n, k can have values from 1 to n.

Let us now consider various possible values of $\frac{n}{k}$ for a given value of *n*.

If we take $n = 4, k$ can be 1, 2, 3 or 4. This will lead to the following $\frac{n}{k}$ values:

i) $\frac{4}{1}$,

ii) $\frac{4}{2}$,

iii) $\frac{4}{3}$, and

iv) $\frac{4}{4}$

You can see that the orbits represented in i), ii), iii) are elliptical orbits whereas the orbit mentioned in iv) is a circular orbit, see Fig.1.12 a). Thus,the circular orbit is a special case of elliptical orbits having *n* = *k*.

Sommerfeld give the following expression for energy of the electron in hydrogen atom.

$$E_n = \frac{2\pi^2 e^4 m}{(k + n_r)^2 h^2} \qquad \text{.... (1.24)}$$

Thus, it was shown by the above expression that energy depends not only on the principal quantum number, *n* but on the azimuthal quantum number, *k* also to some extent. Therefore, according to Sommerfeld modification, the existence of sub-energy levels in each principal energy level was possible.

The presence of these extra elliptical orbits which differ slightly from each other in energy can account for the extra lines in the spectra of atoms.

Thus, the azimuthal quantum number represented by Sommerfeld by ***k* was later modified as** 'l' ***and was shown to have values*** **(0, 1, …, (*n* – 1)** ***where n is the principal quantum number.*** Thus, if n = 2, then l can have values 0 and 1.Similarly, for n = 4, l can have values 0,1, 2 and 3.

The splitting of spectral lines when atoms are placed in a strong magnetic field, known as **Zeeman effect**, could also be partially explained by introducing **magnetic quantum number** (m_l) describing the allowed orientations of electron orbits in space. It was shown that for each value of l, m_l can have $(2l + 1)$ values namely from $+l$ to $-l$. Hence, if $l = 1, m_l$ can have three values, $+1, 0$ and -1. You will see in Unit 4, an alternate way of arriving at the quantum numbers n, l and m_l.

SAQ 5

a) If $n = 3$, what are the possible values of l?

b) If $l = 2$, what are the value of m_l?

1.6 SUMMARY

In this Unit, earlier models of the structure of atom proposed by Dalton, Thomson and Rutherford were briefly explained. Then, Bohr atom model was discussed in detail. The postulates of Bohr's theory were listed. The general expression for calculation of radius of various orbits of hydrogen atom was arrived at. Using this expression, the calculation of radii of various orbits was illustrated. Here, you also learnt about the diagrammatic representation of these orbits.

The expression of energy of these orbits was then derived and energies of various orbits of hydrogen atom were calculated. It was then explained that Bohr's theory was useful in calculation of the frequencies of spectral lines in the atomic spectrum of hydrogen.

Then, an analysis of Bohr's theory was presented giving its achievements and limitations. Finally, the modification proposed by Sommerfeld was described which was helpful in explaining the fine structure of the atomic *spectrum* of hydrogen.

1.7 TERMINAL QUESTIONS

1. Explain the significance of α-ray scattering experiment.
2. In what way is the analogy between an atom and solar system contradicting classical electromagnetic theory?
3. What do you think is the most novel idea among Bohr's postulates?

4. Derive an expression relating radius of the atom to the mass, charge and orbit number of the electron.

5. Calculate the radius of the third orbit in hydrogen atom using Bohr's theory.

6. Derive an expression useful in calculating the energy of an electron in n th orbit of hydrogen atom.

7. What are the energy values of the electron in the third and fourth orbits of hydrogen atom?

8. a) From the expression, $R_H = \dfrac{Z^2 e^4 m}{8 \epsilon_0^2 h^3 c}$, find the value of R_H .

   b) What is the value of R_H in cm^{-1}?

9. Calculate the wave numbers of the first two lines in Balmer series.

10. Explain the limitations of Bohr's theory.

1.8 ANSWERS

Self-Assessment Questions

1. Thomson proposed that electrons are distributed within a sphere of positive electricity whereas Rutherford thought that the electrons move around a central positively charged nucleus.

2. $r_2 = 53\,n^2 \text{pm} = 53 \times 2^2 \text{pm} = 212\,\text{pm}$

3. $E_\infty = 0$

4. The electron in an outer orbit has higher energy than that in an inner orbit, i.e., as n_2 increases, E_2 also increases. Since E_1 remains constant, the spectral frequency increases with increase of n_2 .

5. a) $l = 0, 1$ and 2.

   b) $m_l = +2, +1, 0, -1, -2$.

Terminal Questions

1. This experiment was utilised by Rutherford to formulate nuclear atom model.

2. According to classical theory, an electron being a charged particle, as it moves, must gradually lose its energy and fall into the nucleus.

3. Quantisation of angular momentum

4. By balancing the force of attraction with centrifugal force, the equation can be derived. The final expression is,

$$r = \frac{n^2 \epsilon_o h^2}{\pi m Z e^2}$$

5. $r_3 = 9\ r_1 = 477\,\text{pm}$

6. Total energy of the electron is calculated by adding its kinetic energy and potential energy terms. The final expression is

$$E_n = \frac{-Z^2 e^4 m}{8 \in_0^2 n^2 h^2}$$

7. $-2.42 \times 10^{-19}\,\text{J}; -1.361 \times 10^{-19}\,\text{J}$

8. a) Substitution of the values of the various parameters gives

   $R_\text{H} = 1.097 \times 10^7\,\text{m}^{-1}$,

   b) $1.097 \times 10^5\,\text{cm}^{-1}$

9. $1.524 \times 10^6\,\text{m}^{-1}; 2.057 \times 10^6\,\text{m}^{-1}$.

10. Bohr's theory cannot explain the hyperfine structure in the atomic spectrum of hydrogen and the atomic spectra of multi-electron elements. It cannot explain the formation of molecules from atoms. It does not take into account the wave property of the electron.

UNIT 2

DUAL BEHAVIOUR OF RADIATION AND MATTER

Structure

2.1 Introduction

Expected Learning Outcomes

2.2 The Nature of Radiation

Light as an Electromagnetic Wave

Particle Nature of Radiation

2.3 Nature of Matter

de-Broglie's Relation

Matter Waves

Davisson and Germer Experiment

2.4 Heisenberg Uncertainty Principle

2.5 Summary

2.6 Terminal Questions

2.7 Answers

2.1 INTRODUCTION

In Unit 1, you have studied about the Bohr model of atom. Bohr model was successful in explaining the atomic spectrum of one-electron atom, namely, hydrogen. But, it failed in case of multi-electron atoms, even for the simplest case of helium atom. In the case of hydrogen atom also, Bohr's theory could not explain the finer details of the atomic spectrum such as the intensities of spectral lines and the spectrum that arises when magnetic field is applied to the system.

In this unit, we will study about the nature of radiation and matter. We will begin this unit with a discussion on how light behaves as an electromagnetic wave. Here, the characteristics of a wave such as *wavelength*, *frequency* and *wave number* will be explained. Then, particle nature of radiation will be discussed based on the explanation of black body radiation and photoelectric effect.

We will then focus our attention on the nature of matter. The concept of dual behaviour of matter, i.e. particle as well as wave will be explained. Here, de Broglie relation will be discussed and illustrated. We will also explain matter waves. Then, the Davisson and Germer experiment will be described which provided the experimental verification of de Broglie's idea of wave nature of matter. Finally, Heisenberg uncertainty principle will be discussed.

Expected Learning Outcomes

After studying this unit, you should be able to:

- explain the wave parameters of light such as *wavelength*, *frequency* and *wave number;*
- discuss the wave and the particle nature of radiation;
- describe the dual nature of matter;
- state and illustrate de Broglie relationship;
- compute de Broglie wavelength of a given system;
- discuss matter waves; and
- state Heisenberg uncertainty principle.

2.2 NATURE OF RADIATION

The radiation is the emission or transmission of energy in the formof waves or particles through space or through a material medium. You are familiar from your previous classes that energy can be transmitted in the form of heat, light, sound etc. You will now study how light behaves as an electromagnetic wave and what are the parameters associated with a wave.

2.2.1 Light as an Electromagnetic Wave

A wave is a travelling disturbance that transports energy.

Electromagnetic theory of light depicts propagation of light through space, as oscillating electric and magnetic fields.These fields are mutually perpendicular and are also perpendicular to the direction of propagation of light. Further, the energy of a wave depends on the square of its amplitude.

A beam of light has oscillating electric and magnetic fields associated with it. It is characterised by the properties such as frequency, wavelength and wave number. We can understand all these properties by considering, in general, a wave propagating in one dimension only, see Fig. 2.1.

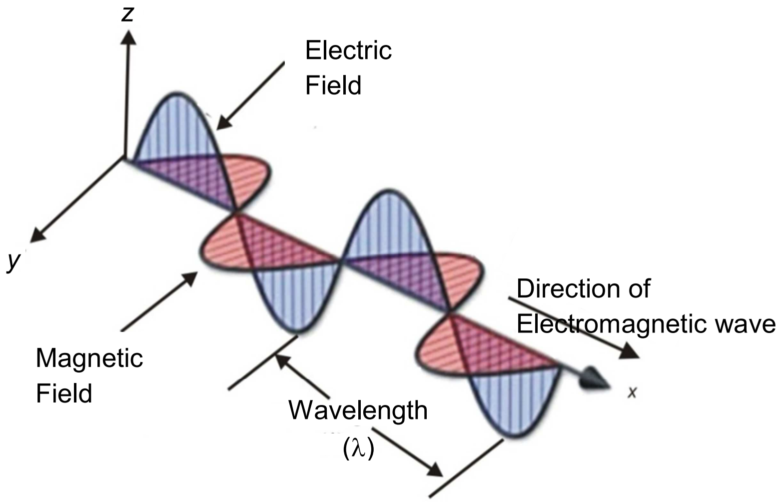


Fig. 2.1: Wave Propagation.

The Wavelength, λ(Greek: *lambda*) is the distance between two successive crests or troughs. It is expressed in the unit, metre (m).

The **frequency** is the number of waves per second. It is represented by the Greek letter υ (*nu*). Its unit is hertz (Hz). In fact, one hertz is equal to $\text{second}^{-1}(s^{-1})$. Wavelength and frequency are related by Eq. 2.1 where *c* is the velocity of the light wave in the medium.

$$\lambda = \frac{c}{\upsilon} \qquad \ldots (2.1)$$

In vacuum, $c = 2.998 \times 10^{8}\ \mathrm{m\,s^{-1}}$, and we will use this value for c in our calculations. From the above expression, we understand that wavelength is *inversely proportional* to frequency.

The reciprocal of frequency is the *period of oscillation*, $T = \frac{1}{\upsilon}$. It indicates the time for one oscillation. Similarly, the reciprocal of wavelength is the **wave number** ($\bar{\upsilon}$, *nu tilde* or *nubar*).

Wave number is related to frequency and wavelength as given in Eq. 2.2.

$$\bar{\upsilon} = \frac{1}{\lambda} = \frac{\upsilon}{c} \qquad \ldots (2.2)$$

$\bar{\upsilon}$ is pronounced as "nu bar" $1\ \mathrm{m^{-1}} = 10^{-2}\ \mathrm{cm^{-1}}$

The SI unit of $\bar{\upsilon}$ is $\mathrm{m^{-1}}$ although most of the literature values are reported in $\mathrm{cm^{-1}}$. The peak height or trough depth is called the *amplitude*of the wave.

The maximum displacement of a medium from its equilibrium position is the amplitude of the wave.

We shall see later how energy of a light wave is related to its frequency and wavelength.

The electromagnetic spectrum describes the range of values of frequency and wavelength of the electromagnetic radiation, see Fig.2.2.

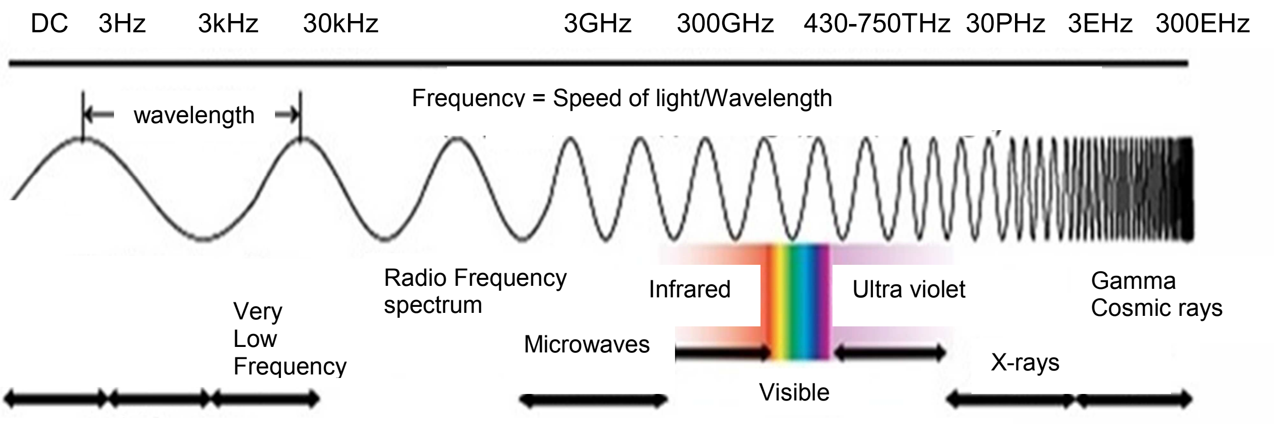


Fig. 2.2: The range of electromagnetic radiation.

The characteristics of electromagnetic spectrum are given in Table 2.1. At one end of the spectrum, there are X-rays and gamma-rays with low wavelength and high frequency; at the other end, we find radio waves and microwaves with high wavelength and low frequency.

1 millimetre

$= 1\,\text{mm} = 10^{-3}\,\text{m}$

1 micrometre

$= 1\,\mu\text{m} = 10^{-6}\,\text{m}$

1 nanometre

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

1 picometre

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

1 Angstrom unit

$= 1\,\text{A}^0 = 10^{-10}\,\text{m}$

The energy values given in Table 2.1 are calculated using the following equation:

$E = nh\upsilon$

where *n* is numerically equal to Avogadro number (6.022×10^{23}).

Table 2.1:Characteristics of Electromagnetic Spectrum

Description	Wavelength, λRange	Wave number, $\bar{\upsilon}$/cm^{-1}	Frequency, υ/Hz	Energy/kJ mol^{-1}
Radio wave	3×10^3 m	3.33×10^{-6}	10^5	3.98×10^{-8}
	0.30 m	0.0333	10^9	3.98×10^{-9}
Microwave	0.0006 m	16.6	4398×10^{11}	0.191
	(600 μm)			
Far infrared				
	30 μm	333	10^{13}	3.98
Near infrared	0.8 μm	1.25×10^4	3.75×10^{14}	149.8
	(800 nm)			
Visible	400 nm	2.5×10^4	7.5×10^{14}	299.2
Ultraviolet	150 nm	6.66×10^4	19.98×10^{14}	795
Vacuum ultraviolet	5 nm	2×10^6	6×10^{16}	2.39×10^4
X-rays and gamma-rays	10^4 nm	10^{11}	3×10^{21}	1.19×10^9

At one end of the spectrum, there are X-rays and gamma-rays with low wavelength and high frequency; at the other end, we find radio waves and microwaves with high wavelength and low frequency.

In Table 2.2, you can find the wavelength values of ultraviolet and visible light of different colours.

Table 2.2: Expanded Ultraviolet – Visible Region

Colour	Wavelength/nm
Ultraviolet	200
Violet	410
Indigo	430
Blue	470
Green	520
Yellow	570
Orange	620
Red	710

It is seen that violet light has lower wavelength than the light of the red colour.

Let us calculate λ and $\bar{\upsilon}$ values for a light having $\upsilon = 10^{15}$ Hz . According to the Eq. 2.1, $\lambda = \frac{c}{\upsilon}$

$$= \frac{2.998 \times 10^8}{10^{15}}$$

$$= 2.998 \times 10^{-7}\,\text{m}$$

$$= 299.8\,\text{nm}$$

Using Eq. 2.2, $\bar{\upsilon} = \frac{\upsilon}{c}$

$$= \frac{10^{15}}{2.998 \times 10^{8}}$$

$$= 3.336 \times 10^{6}\ \text{m}^{-1}$$

$$= 3.336 \times 10^{4}\ \text{cm}^{-1}$$

You can verify Eqs. 2.1 and 2.2 by substituting λ, υ and $\bar{\upsilon}$ values for various regions, given in Table 2.2.

The phenomena of *diffraction* and *interference* can be understood on the basis of wave nature of radiation. You must have read about these phenomena in your earlier classes. However, the *black body radiation* and the *photoelectric effect* are explainable only in terms of the *particle nature* of radiation. We will now discuss the particle nature of radiation but before that attempt the following SAQs.

SAQ 1

Calculate the frequency of yellow light having, $\lambda = 560\,\text{nm}$.

SAQ 2

In **VIBGYOR**, relate the frequencies of different colours.

2.2.2 Particle Nature of Radiation

A number of experiments done in the latter half of nineteenth century and the first two decades of the twentieth century gave results totally at variance with the predictions of classical physics. Some such specific cases are given below, which indicated the inadequacy of classical physics:

- Black body radiation
- Photoelectric effect
- Atomic spectra

The laws of motion put forward by Newton formed the basis of classical mechanics. Till 1900, it was thought that these classical concepts and laws hold good both for celestial bodies like planets and sub-atomic entities like electrons. Is this assumption quite acceptable? Before trying to see whether classical mechanics is applicable to sub-atomic system, we have to be familiar with important assumptions of classical mechanics, viz.,

i) No restriction on the value that a dynamic variable (e.g. energy, momentum etc.) can have.

ii) No limit to the accuracy with which one or more of the dynamic variables of a system can be measured except the limit imposed by the precision of the measuring instruments.

iii) No restriction on the number of dynamic variables that can be accurately measured at the same time.

You have got the general idea of atomic spectra and some features of the atomic spectrum of hydrogen as dealt in Unit 1. Let us know understand the phenomena of black body radiation and the photoelectric effect.

- **Black Body Radiation**

A perfect black body is one which absorbs all the radiation falling on it, (Fig.2.3).Black body radiation is the radiation emitted by the black body.

A black body is both a good absorber and radiator of energy. Experimentally, a hollow body, blackened on the inside and with a small opening, is considered a typical black body. Any radiation that enters through the small opening is reflected repeatedly from the walls until all of the energy eventually becomes absorbed.

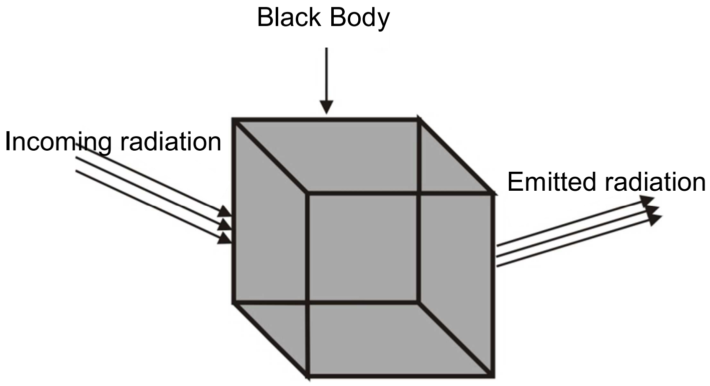


Fig. 2.3: A black body.

Of the various types of bodies heated to a particular temperature, only black body, radiates the maximum amount of energy. It radiates the same amount of energy as it absorbs.

The main aspects of black body radiation which emerge from experimental observations, are shown below in Fig. 2.4.

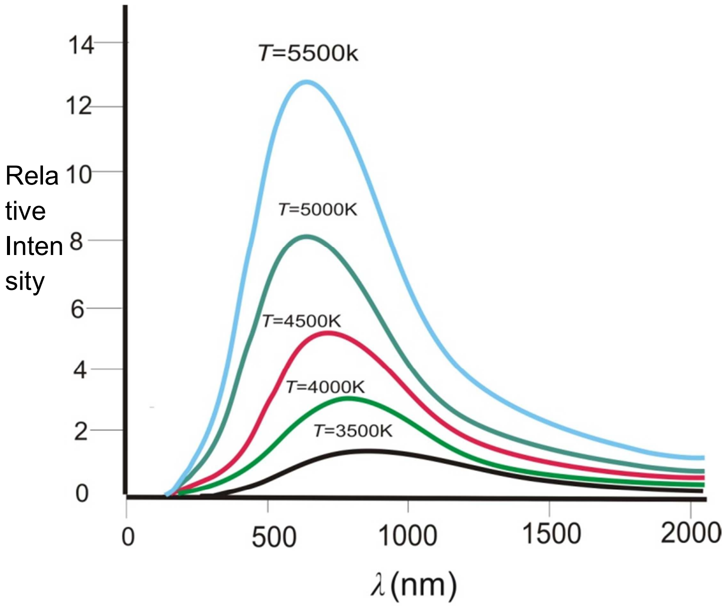


Fig. 2.4: Observed results of the black body radiation.

You can see in Fig. 2.4 that

i) At every temperature, there is a wavelength at which energy radiated is maximum. This wavelength is called λ_{max} value of that temperature.

ii) At shorter wavelength region, i.e., at higher frequency region, intensity of radiation is low.

iii) In the shorter wavelength region, there is increased intensity of radiation at higher temperatures.

In general, as temperature is increased, the radiation emitted, contains more of shorter wavelength region, whether it is from black body or a simple iron piece.

In contrast to the above experimental fact, the classical theory predicts that the black body ought to radiate over the whole wavelength region including visible region even at room temperature. As temperature is increased, the radiation emitted should get uniformly more intense. In other words, an iron piece even at room temperature should radiate a little in the visible range. These results are shown below in Fig. 2.5.

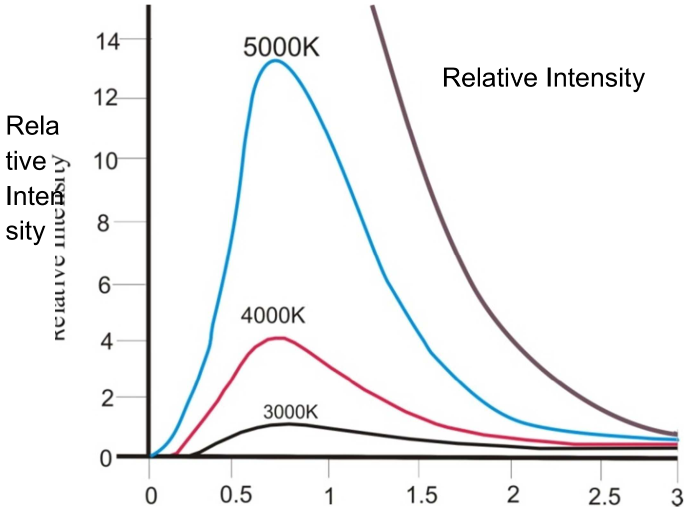


Fig. 2.5: The expected result according to the classical theory for black body radiation is shown as a continuously rising curve in the right portion of the figure *viz*-a-*viz* the actual observed results shown by left hand side curves.

When the evidence of eyes and fingers does not fit the predictions of the classical theory, it is time for this theory to be modified. We shall now see how quantum theory successfully explains the experimental facts regarding black body radiation.

In 1900, Max Planck proposed the quantum theory and explained the observed results of the black body radiation. He argued that the assumption of the classical theory that the energy of the system may take any arbitrary value, is wrong.

He suggested a detailed model for the processes taking place at the cavity walls. He considered the black body to consist of oscillators of molecular dimensions, each with a fundamental vibration frequency υ, and that each oscillator could emit energy only by a specified amount, known as **quanta**, but not continuously. His assumptions are given below:

$\in$ epsilon, stands for one quantum of energy, $h\upsilon$.

Unit of h = J s

= kg $m^2 s^{-2}$.s

= kg $m^2 s^{-1}$ = (kg m s^{-1}) m

= (Unit of mass×unit of velocity)× unit of length =(unit of linear momentum)×unit of length =Unit of angular momentum

h is also known as action constant; later, we shall see in Sec. 2.3 how h relates wave and particle aspects of sub-atomic particles.

i) An oscillator cannot have any energy, but only energies given by Eq. 2.3 given below.

$$E = nh\upsilon = n\in \qquad \ldots (2.3)$$

In this expression, υ is the frequency of emitted radiation, while h is a constant and n is an integer. Presently, h is called Planck's constant and n is known as quantum number. One quantum of energy, $\in$, is equal to the product $h\upsilon$. Planck evaluated the value of the constant h as 6.626×10^{-34} J s. So Eq. 2.3 asserts that the oscillator energy is **quantised.** It is interesting to know that h is related to angular momentum, which is equal to linear momentum (mass × velocity) multiplied by length.

ii) The oscillators do not radiate energy continuously but only in quanta. These quanta of energy are emitted when an oscillator changes from one qauntised energy state to another. Thus, if the oscillator goes from the level $n+1$ to level n, we get from Eq. 2.3, the amount of energy radiated as,

$$\Delta E = E_2 - E_1 = (n+1)h\upsilon - nh\upsilon = h\upsilon \qquad \ldots (2.4)$$

Also, an oscillator neither absorbs nor emits energy as long as it remains in the same quantised state.

Planck gave the following equation for the energy density (p_υ) which is energy per unit volume per unit frequency.

$$p_\upsilon = \frac{8\pi h(\upsilon/c)^3}{e^{h\upsilon/kT} - 1} \qquad \ldots (2.5)$$

Using the above equation, Planck was able to show that there was a good agreement between the experimental results of the black body radiation with the theoretical prediction on the basis of the quantum nature of the oscillators provided h has the value 6.626×10^{-34} J s.

Let us now see in a qualitative way how Planck's theory is useful in explaining black body radiation. The number of oscillators possessing sufficient energy $\in$, known as *oscillator population* at that energy level, is proportional to the exponential term, $e^{-\in/kT}$, known as Boltzmann factor. Here, T is the temperature and k, the Boltzmann constant.

The intensity of radiation is proportional to the oscillator population at a particular energy level. Hence, the intensity of radiation is proportional to $e^{-\in/kT}$.

Using Eq. 2.3, we can say that the intensity of radiation is proportional to the quantity, $e^{-h\upsilon/kT}$.

The term $e^{-h\upsilon/kT}$ is in fact equal to $\dfrac{1}{e^{h\upsilon/kT}}$ and hence, is a fraction.

As υ *increases, the value of the fraction* $e^{-h\upsilon/kT}$ *and also the population of the oscillators, decrease*. This means, the **intensity of radiation of higher frequency region or shorter wavelength region is low,** (Fig. 2.4).

The intensity of radiation is increased, once the temperature is increased. Since, T is in the denominator of the exponential term, an increase in temperature decreases $e^{h\upsilon/kT}$ and increases the value of $1/e^{h\upsilon/kT}$, and the intensity of radiation. That is, *more radiation of shorter wavelengths will be emitted at higher temperatures,*(Fig. 2.4).

Planck, using a mathematical approach, was able to explain the λ_{max} value at each temperature.

Apart from explaining the black body radiation, Planck's theory is useful in calculating the energy of oscillators from the frequency values. The values of energy are given in Table 2.1 in kJ mol^{-1} as per Eq. 2.3 for each constituent of electromagnetic radiation, assuming that n is numerically equal to Avogadro number.

A ray of light having frequency υ can be considered as a stream of particles, each one having energy $h\upsilon$. These particles are now known as *photons*. This means that if a ray carries an energy E into some region, then the number of photons n, arriving is $E/h\upsilon$.

i.e. $n = \dfrac{E}{h\upsilon}$.

Let us now study the photoelectric effect.

- **Photoelectric Effect**

Another major setback to classical theory was explanation of photoelectric effect. The emission of electrons when metals are irradiated with ultraviolet light is known as **photoelectric effect**, see Fig. 2.6.This was observed by Hertz in 1887.

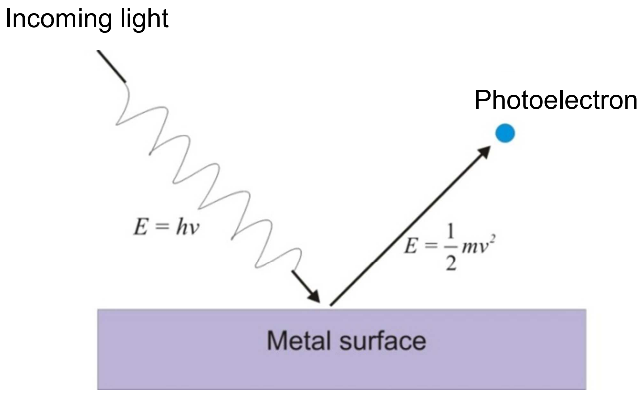
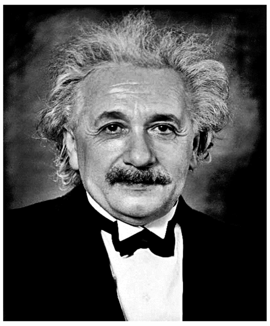


Fig. 2.6: Photoelectric effect.

The electrons, so emitted, are known as **photoelectrons**, to differentiate them from the electrons remaining inside the metal atoms. The main feature of this phenomenon is that a minimum frequency of light, known as **threshold frequency** (υ_o)**,** is required to emit photoelectrons. If the frequency of the incident light is less than this value, then photoelectrons are not emitted. The value of (υ_o) is a characteristic of the metallic surface used. Increasing the frequency of the light beyond threshold frequency value only increases the velocity of the photoelectrons. These observations could not be explained by the nineteenth century view of light as wave phenomenon. We will now discuss how Einstein's theory explained the photoelectric effect.



Albert Einstein

(14th March 1879-18th April 1955)

Einstein was awarded the Nobel Prize of Physics in 1921 for explanation of the Photoelectric Effect.

Einstein's Explanation of Photoelectric Effect

Applying the *photon* concept to the photoelectric effect, Einstein proposed that an electron at the surface of the metal gains as energy $h\upsilon$ by the absorption of a *photon* from the electromagnetic radiation. If the frequency υ of the photon is greater than the minimum value υ_0, called **threshold frequency** which is characteristic of a particular metal, then the emission of photoelectron occurs. The difference, $h\upsilon - h\upsilon_0$, is transformed as the kinetic energy of the photoelectron which is equal to $mv^2/2$. In conformity with the principle of conservation of energy, Einstein's theory can be stated as:

$$h\upsilon - h\upsilon_o = mv^2/2 \quad \ldots (2.6)$$

In this expression, υ and υ_0 are the frequency of photon and the threshold frequency, respectively while *m* and *v* are the mass and velocity of the photoelectron. If $\upsilon < \upsilon_0$, then $mv^2/2$ is negative which is meaningless. That is, **photoelectron emission does not take place when υ is less than υ_0.**

After studying the above discussion on photoelectric effect, you can appreciate how particle nature of radiation was able to successfully explain the observation of this phenomenon.

You have seen above that radiation can behave both as a particle and as a wave. The phenomena of *diffraction* and *interference* can be understood if the *wave nature of radiation* is assumed. However, the *black body radiation* and the *photoelectric effect* are explainable only in terms of the *particle nature* of radiation. Thus, it was concluded that radiation has dual nature.

Using Eq. 2.6, you try the following SAQs.

SAQ 3

A yellow bulb generates 2.80×10^{20} photons with $\lambda = 560$ nm. Calculate the total energy generated.

SAQ 4

Calculate the frequency of the radiation required to eject photoelectrons at a velocity of 9×10^5 m s^{-1} from sodium metal surface, having a threshold frequency of 4.61×10^{14} Hz (mass of the photoelectron $= 9.109 \times 10^{-31}$ kg).

2.3 THE NATURE OF MATTER

Having understood the dual nature of radiation let us now study the nature of matter in more detail. It had been assumed that matter is composed of particles like atoms and molecules or more correctly, electrons and nuclei. Thus, matter is distinct from radiation which is the transmission of energy by wave motion. However, the experiments conducted during the years 1887-1927 demonstrated that the boundary between matter with its particle-like behaviour and radiation with its wave-like behaviour, is not as rigid as it was supposed to be. These observations implied that matter and radiation can posses both particle and wave aspects. In 1924, de Broglie proposed the following regarding the nature of matter.

2.3.1 de-Broglie Relation

de Broglie reasoned that similar to the dual behaviour of radiation, material particles also should behave both as particle as well as wave. Thus, every particle is associated with a wave whose wavelength, λ, is given by the equation

$$\lambda = \frac{h}{p} \qquad \dots (2.7)$$

where h is Planck's constant and p is the momentum of the particle. For a particle of mass m, and velocity v, momentum p can be expressed as

$$p = mv \qquad \dots (2.8)$$

Substituting the value of p from Eq. 2.8 into Eq. 2.7, we get

$$\lambda = \frac{h}{mv} \qquad \dots (2.9)$$

Note that Eq. 2.9 relates the wavelike property such as wavelength in the left hand side to the particle like property such as mass on the right hand side in the equation.

Let us now study more about waves associated with matter or material particles.

Louis Victor Pierre Raymond Duc de Broglie(15th Aug.1892-19th March 1977)

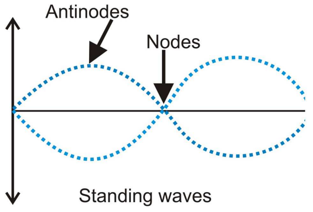
He was a French physicist. He proposed in his doctoral dissertation that matter and radiation have the properties of both wave and particle. He was awarded Nobel Prize in Physics in 1929.

2.3.2 Matter Waves

Waves, which are associated with material particles and which obey Eq. 2.9, are called **matter waves**. Since, electron is also a material particle, let us apply the above ideas to electron. When an electron moves in a circular orbit round the nucleus, the circumference of the orbit is given by $2\pi r$. Now, if the wave associated with it is extended round the circle as shown in Fig. 2.7 a), it can be continually **in phase** only when the circumference of the circle is equal to integral multiple of the wavelength,

i.e., $n\lambda = 2\pi r$

where $n = 1, 2, 3, \dots$ … (2.10)



Note that the *nodes* are points of zero amplitude and show no displacement while *antinodes* are points of maximum displacement.

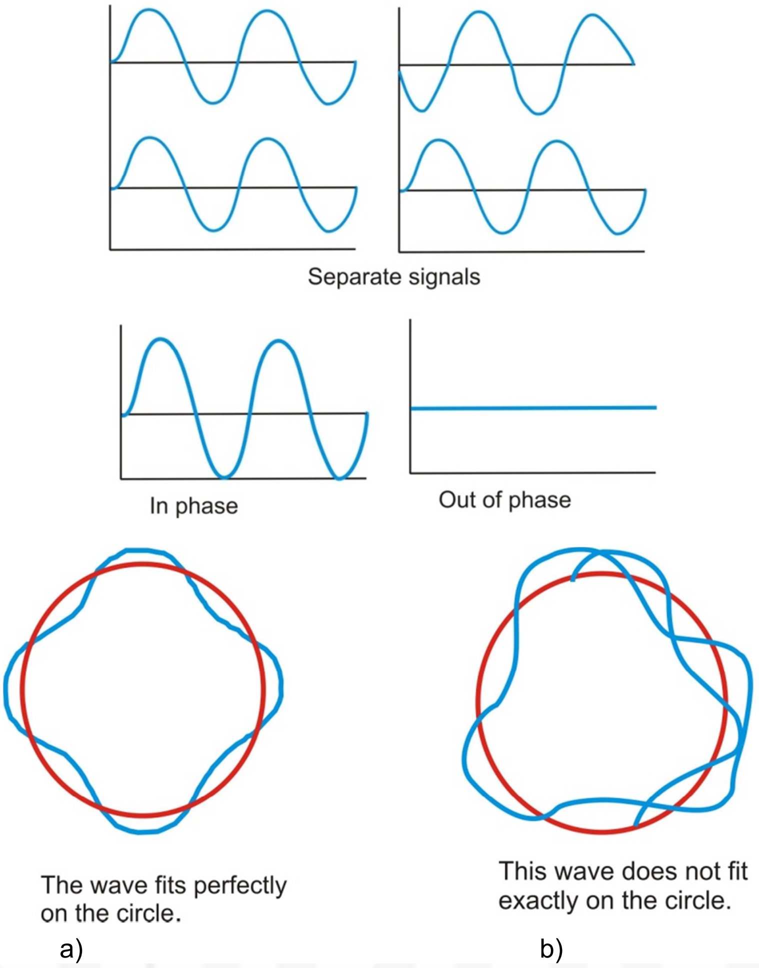
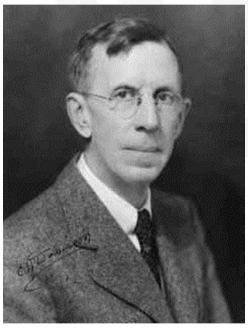


Fig. 2.7: a) In-phase wave and b) out of phase waves. The in phase wave represents an allowed orbits whereas out of phase indicates that the orbit is not allowed.



Clinton Joseph Davisson
(1881-1958)

He was an American physicist. He shared Nobel Prize in Physics in 1937 with G.P. Thomson for demonstrating the wave properties of electrons.

Substituting the value of λ from Eq. 2.9 into Eq. 2.10, we obtain

$$\frac{n.h}{mv} = 2\pi r \qquad \dots (2.11)$$

After rearranging Eq. 2.11, we get,

$$\frac{nh}{2\pi} = mvr \qquad \dots (2.12)$$

Since mvr is the angular momentum, it can be concluded that only those circular orbits are permitted for which the angular momentum is an integral multiple of $h/2\pi$ units. This is the same idea which Bohr postulated earlier intuitively (Unit 1, Sec. 1.4).

We will now discuss how de Broglie's idea of wave nature of particle was experimentally supported by Davisson and Germer.

2.3.3 Davisson and Germer Experiment

The de Broglie's idea was experimentally verified by Davisson and Germer in 1927 who observed the reflection of an electron beam from the metal surface, supporting its wave nature. In 1925, Davisson and Germer were, in fact, studying the surface of nickel by measuring the energies of electrons scattered from the metal surface. They conducted the experiment in vacuum by accelerating the electrons and then allowing them to strike the surface of the nickel metal. The number of scattered electrons was determined using a detector. The experimental set up for this experiment is shown in Fig. 2.8 below.

It was expected from the experiment that the smoothest metal surface would be rough enough to reflect the electron beam diffusely with a smooth distribution of the intensity with the angle of diffraction.

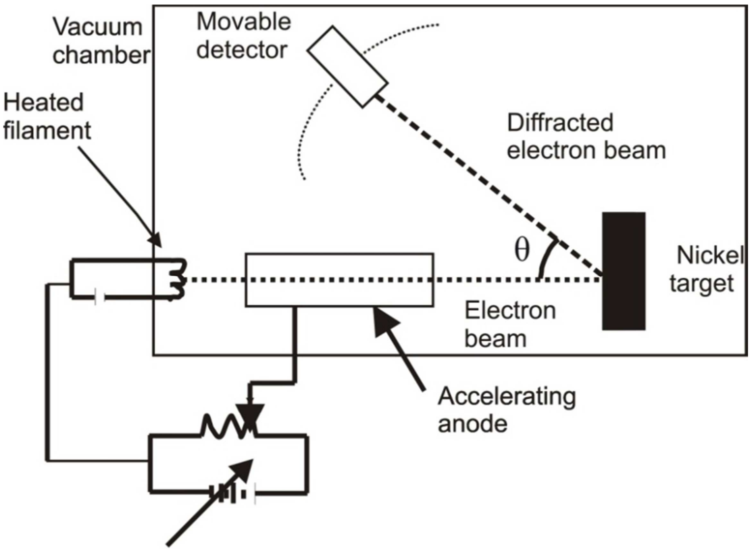


Fig. 2.8: Experimental setup for Davisson and Germer experiment.

But, while the experiment was conducted, accidently air entered into the chamber and nickel oxide was formed on the surface of nickel metal. To remove the oxide film, Davisson and Germer heated the metal piece at a high temperature which led to the formation of single crystal areas having crystal planes in the metal. When the experiment was done, the electrons got scattered from these planes and a diffraction pattern with unexpected peaks resulted.

The experiment was again repeated by Davisson and Germer in 1927 and calculations were done for intensities of electrons diffracted at different angles. The highest intensity was observed at $\theta = 50^{o}$ when kinetic energy of electrons was 54 eV.

Using de Broglie relation, the electrons having 54 eV energy have a wave length of 0.167 nm. The experimental results using Bragg's Law gave $\lambda = 0.165\,\text{nm}$ which was in agreement with the value predicted by de-Broglie relation. Thus, wave nature of electrons was proved.

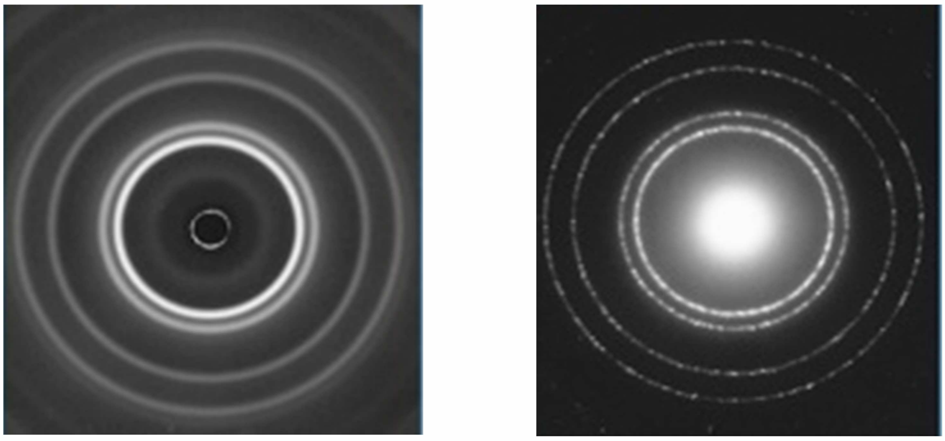
Similar support was provided by Thomson and Reid in 1928 when they photographed the diffraction rings produced when the electrons passed through a very thin metal (aluminum) foil, (Fig. 2.9).

The similarity of these two patterns is a strong evidence for the wave properties of particles.

George Paget Thomson
(1892-1975)

He was an English Physicist and was son of J.J. Thomson. He received the Nobel Prize in Physics in 1937 alongwith Davisson for demonstrating the wave properties of electrons.

Diffraction appears as a light and dark pattern when waves encounter an obstacle while they travel by towards a screen or a detector.



X-rays

a)

Electrons

b)

Fig. 2.9: Diffraction of waves by aluminium foil a) X-rays of wavelength 71 pm and b) Electrons of wavelength 50 pm. The similarity in the two patterns shows the wave nature of particles.

Electron microscope operates on the principle of electron diffraction; using this instrument, particles of molecular size can be observed.

In both the experiments referred above, the experimental results were in agreement with Eq. 2.7.

The above experiment confirmed the de Broglie's proposition that particles can behave as waves also. Thus, the dual nature of matter was also established.

Having understood that the electron can behave as a wave, let us now calculate the de Broglie wavelength associated with an electron having a velocity of $2.19 \times 10^{6}\,\mathrm{m\,s^{-1}}$. Using Eq. 2.9

$$\lambda = \frac{h}{mv} = \frac{6.626 \times 10^{-34}\,\mathrm{J\,s}}{(9.109 \times 10^{-31}\,\mathrm{kg})(2.19 \times 10^{6}\,\mathrm{m\,s^{-1}})} = 3.32 \times 10^{-10}\,\mathrm{m}$$

Now, let us calculate the de Broglie wavelength associated with a bullet of mass $2.2 \times 10^{-3}\,\mathrm{kg}$ moving with a velocity of $30\,\mathrm{m\,s^{-1}}$.

$$\lambda = \frac{h}{mv} = \frac{6.626 \times 10^{-34}\,\mathrm{J\,s}}{(2.2 \times 10^{-3}\,\mathrm{kg})(30\,\mathrm{m\,s^{-1}})} = 1 \times 10^{-32}\,\mathrm{m}$$

You can compare the two wavelengths and see how the mass of the system affects the de Broglie wavelength associated with it.

You can also conclude from Eq. 2.9 that de Broglie wavelength at a given velocity is inversely related to its mass. That is, for particles of larger mass, λ becomes smaller and hence, macroscopic bodies of large m have too small a λ to be measured.

Experimentally, λ can be measured using diffraction phenomenon.

Before studying the next section on Heisenberg uncertainty principle, answer the following SAQ.

SAQ 5

Why is not the wave nature of matter apparent in our daily observations?

2.4 HEISENBERG UNCERTAINTY PRINCIPLE

Werner Karl Heisenberg
(1901-1976)

He was a German physicist. He received Nobel Prize in Physics in 1932.

In the last section, you have studied about the dual nature of electrons. Let us now see if we can say something on the location of an electron. We define the location of any particle of macroscopic size, by the terms **position** and **velocity**. When we try to determine the position of a moving electron by focusing light on it or perturbing it with photons, this will result in a change in its momentum. Thus, **increasing** certainty in its position would **decrease** the certainty in its momentum. Heisenberg, thus, stated that it is impossible to determine, *simultaneously*, the determination of the exact position of a particle and its momentum. The uncertainties in the determination of these two quantities vary inversely, so that if one is determined fairly accurately, the other must be correspondingly less accurate. In the case of an electron, the product of the uncertainty of position (Δx) and the uncertainty of momentum (Δp_x) is equal to h, i.e., the Planck's constant. Thus,

$$\Delta p_x \,.\, \Delta x = h \qquad \dots (2.13)$$

It needs to be noted that in above equation, both momentum and position are along the same axis and not along different axes. It means that it is impossible to measure simultaneously both the momentum p_x and position x along x-axis, although one can always measure p_y (momentum along y-axis) and x (position along x-axis), simultaneously and accurately.

This limitation applies equally well to other combinations of variables like velocity, energy, time, angular momentum etc. Thus, we can also say that

$$\Delta E \cdot \Delta t = h \qquad \dots (2.14)$$

It is interesting to note that for each pair of variables to which Heisenberg uncertainty principle applies, the product has the same dimensions as Planck's constant.

Thus, in view of the uncertainty principle, Bohr's model having definite orbits needs some modification because we are not able to locate the electron precisely. The best we can do is that only the probability of finding an electron in a particular region of space can be predicted at a given time. About these, you will study in Unit 4.

The difficulties in explaining certain facts with the help of classical mechanics as studied earlier in this unit, led Schrödinger to develop a new approach towards the atomic structure which is known as wave mechanics. You will study about this approach in detail in the next unit.

2.5 SUMMARY

In this unit, you have learnt about the wave nature of radiation. The wave parameters such as wavelength, frequency, wave number and energy of an electromagnetic wave were explained. The inter-relationships of these parameters were described. It was emphasised that the phenomena of black body radiation and photoelectric effect could be satisfactorily explained if the particle nature of the radiation is taken into account.

It was explained that the same argument was extended by de-Broglie and he suggested that material particles should also have wave nature. The waves originating from the matter are called matter waves and these are significant when we consider the particles of very - very small size. The Davisson and Germer experiment was explained which confirmed the wave nature of the electrons. Finally, Heisenberg uncertainty principle was described which stated that it is impossible to determine, simultaneously, the exact position of the particle and its momentum.

2.6 TERMINAL QUESTIONS

1. Calculate the de Broglie wavelength associated with a body of mass 1 kg moving with a velocity 1500 m s^{-1}.
2. An electron has a speed of 300 m s^{-1} measurable accurately upto 0.01%. With what maximum accuracy, can you determine its position? $(m = 9.109 \times 10^{-31} \text{kg})$.
3. For a light of wavelength 300 nm, calculate frequency, wave number, energy per quantum and energy per mole.
4. Explain the two main reasons for the failure of classical mechanics.
5. a) Explain the salient features of black body radiation.
   b) In what way, classical theory is inadequate in explaining black body radiation?
6. a) Define photoelectric effect.
   b) State the mathematical form of Einstein's theory of photoelectric effect.
7. Calculate the wavelength of the light required to eject a photoelectron from caesium metal with a kinetic energy of 2.0×10^{-19} J (υ_o for caesium is $4.55 \times 10^{14} \text{Hz}$).

2.7 ANSWERS

Self-Assessment Questions

1. $\upsilon = \dfrac{c}{\lambda} = \dfrac{2.338 \times 10^{8}}{560 \times 10^{-9}} \text{Hz} = 5.35 \times 10^{14} \text{Hz}$
2. $\upsilon_R < \upsilon_o < \upsilon_y < \upsilon_G < \upsilon_B < \upsilon_I < \upsilon_V$
3. $E = nh\upsilon = \dfrac{nhc}{\lambda}$

$$= \frac{2.80 \times 10^{20} \times 6.626 \times 10^{-34} \times 2.998 \times 10^{8}}{560 \times 10^{-9}} \text{J}$$

$= 99.3$ J

4. $$v = \frac{(h\upsilon_o + mv^2/2)}{h}$$

$$= \frac{(6.626\times10^{-34}\times4.61\times10^{14}) + (\frac{1}{2}\times9.109\times10^{-31}\times(9\times10^5)^2}{6.626\times10^{-34}}\text{Hz}$$

$$= 1.02\times10^{15}\ \text{Hz}$$

5. In our daily life, we come across the macroscopic objects having large mass; hence, λ associated with them is very small and cannot be measured. So, we do not recognise de Broglie waves in our daily life.

Terminal Questions

1. Use $\lambda = \frac{h}{mv}$

$$= \frac{6.626\times10^{-34}\ \text{J s}}{1\ \text{kg}\times1500\ \text{m s}^{-1}}$$

$$= 4.417\times10^{-37}\ \text{m}$$

2. Use $\Delta p\cdot\Delta x = h$

i.e. $\Delta p = m\cdot\Delta v$. Calculate first Δv.

Hence, $\Delta x = \frac{h}{m\cdot\Delta v} = 2.427\times10^{-2}\text{m}$

3. $\upsilon = 9.993\times10^{14}$ Hz; $\bar{\upsilon} = 3.333\times10^{6}\ \text{m}^{-1}$;

$\epsilon = 6.621\times10^{-19}$ J; $E = 398.8\,\text{kJ mol}^{-1}$

4. i) Energy can have any arbitrary value,

   ii) Simultaneous fixation of position and momentum is possible.

5. a) i) At shorter wavelength region, intensity of radiation is low.

   ii) As temperature increases, the intensity of radiation in the shorter wavelength region also increases.

   b) Classical theory suggested that black body must radiate over the whole wavelength region.

6. a) Emission of photoelectrons when a mental irradiated with ultraviolet light.

   b) $h\upsilon - h\upsilon_o = mv^2/2$.

7. $\frac{hc}{\lambda} = h\upsilon_o + mv^2/2$

$$= [(6.626\times10^{-34}\times4.55\times10^{14}) + 2.0\times10^{-19}]\ \text{J}$$

$\lambda = 396.1\ \text{nm}$.

UNIT 3

QUANTUM MECHANICAL APPROACH

Structure

3.1 Introduction

Expected Learning Outcomes

3.2 Need for a New Approach to Atomic Structure

3.3 What is Quantum Mechanics?

Postulates of Quantum Mechanics

Observables and Operators

Eigenfunctions

Eigenvalues

3.4 Time-independent Schrödinger Equation

3.5 Significance of ψ and ψ^2

3.6 Applications of Schrödinger Equation

Energy States of the Hydrogen-like Atoms

3.7 Summary

3.8 Terminal Questions

3.9 Answers

3.1 INTRODUCTION

In Unit 2, we discussed in detail about the dual behavior of radiation and matter. Therefore, at this stage, you very well appreciate the fact that both radiation and matter can exhibit the wave-like behavior or the particle-like behavior. Hence, a new approach is needed to describe the structure of the atom in which the wave as well as the particle nature of the electron is taken into account.

We will begin this unit with a discussion on need for such as an approach. Then, the details of this approach called quantum mechanics will be elaborated where in you will study about various postulates of quantum mechanics. While discussing these postulates we would keep the mathematical treatment at a level which is bare minimum for understanding the outcomes of these postulates.

Here, we will also be explaining various observables and their corresponding quantum-mechanical operators. The concepts of eigenfunctions and eigenvalues will be discussed. You will then be introduced to the time-independent Schrödinger equation. The significance of ψ and ψ^2 will be explained. Then, the energy states for the hydrogen-like atoms will be described. The understanding of these concepts in this unit will be useful in Unit 4 where we will apply them for the understanding of the structure of the hydrogen atom.

Expected Learning Outcomes

After studying this unit, you should be able to:

- explain the need of the new approach called quantum mechanical approach in describing the structure of the atoms;
- discuss the important aspects of the quantum mechanics;
- list various postulates of quantum mechanics;
- define an observable and write the operators corresponding to various observables;
- write time-independent Schrödinger equation and explain various terms appearing in it; and
- describe the significance of ψ and ψ^2.

3.2 NEED FOR A NEW APPROACH TO ATOMIC STRUCTURE

The developments in quantum theory from 1913 when Bohr gave his theory of atomic structure till 1925-26 when Schrödinger developed a new approach are called as ‘old quantum theory’. As discussed in Unit 2, when it was realised that electrons cannot be simply described as particles and they also exhibit wave like properties, then a need was felt to describe the electron in such a way that its wave nature is also taken into account. This wave-particle duality is not simply limited to electrons but is applicable to all matter.

Hence, to give a complete description of the behaviour of matter at subatomic level, both wave and particle characteristics are to be accommodated. Added to this was the problem of location of a subatomic particle like electron which is behaving like a wave also. And, according to Heisenberg uncertainty principle, its position and momentum could not be exactly determined simultaneously.

Thus, a new approach was needed to describe the structure of atom. The new approach to the structure of atom describing the behaviour of electron both as a particle and a wave is called *quantum mechanics* or *wave mechanics* and is discussed in the next section. It was founded simultaneously and independently by Schrödinger and Heisenberg. Schrödinger (1926), reasoning that electronic motions could be treated as waves, developed Wave Mechanics and the principle mathematical formulation of Schrödinger is a partial differential equation known as Schrödinger equation. Heisenberg (1925) independently used the properties of matrices to get the same results as Schrödinger obtained and his formulation is known as **Matrix Mechanics.**

However, henceforth we will be using Schrödinger's approach. We will be discussing Schrödinger equation in this unit and also in Unit 4 in the context of the hydrogen atom. But before that, let us understand the general principles of quantum mechanics.

3.3 WHAT IS QUANTUM MECHANICS?

You are aware from your earlier studies that in the late seventeenth century Newton discovered the laws of motion of macroscopic objects which formed the part of **classical mechanics**. However, a number of experiments done in the latter half of nineteenth century and the first two decades of the twentieth century gave results totally at variance with the predictions of classical physics.

The laws describing the behavior of very small particles is called quantum mechanics.

When quantum mechanics is applied to the problems in chemistry, it is called **quantum chemistry**. The study of quantum chemistry is important in determination of the thermodynamic properties of molecules as well as in understanding their structures and relative stabilities. It also helps in understanding the spectral properties of atoms and molecules and the reaction kinetics. Quantum-mechanical principles find applications in the area of biochemical studies and nano-materials. Therefore, the understanding of general principles of quantum-mechanics is important.

The development of quantum mechanics began in 1900 when Planck studied the light emitted by heated solids. You have seen in Unit 2 how it had been applied in explaining the observed results of black body radiation.

Later, in Unit 2, you also studied that according to Heisenberg uncertainty principle, the exact position and momentum of a particle cannot be determined simultaneously. For small particles like electron, such an uncertainty cannot be ignored. This leads us to the first postulate of Quantum mechanics as given below:

Postulate 1

In classical mechanics, the state of a system containing N particles can be given by specifying $3N$ positions and $3N$ velocities or momenta.

The state of a quantum-mechanical system is completely specified by a function $\psi(r,t)$ *that depends on the coordinates of the particle and on the time.*

This function, called the wave function or the state function, has the important property that $\psi^*(r,t)\psi(r,t)\,dx\,dy\,dz$ *is the probability that the particle lies in the volume element* $dx\,dy\,dz,$ *located at r, at the time t.*

A measurable dynamical variable is called an **observable.** Thus, the examples of common observables are position, momentum, angular momentum and energy. The second postulate deals with such observables and is stated below.

Postulate 2

To every observable in classical mechanics, there corresponds an operator in quantum mechanics.

An operator is a mathematical command that tells one to do something on what follows the command. Thus in the expression $\sqrt{2}$, the $\sqrt{2}$, is an operator telling one to take the square root of what follows, in this case 2.

Likewise, in the expression $\frac{d}{dx}(x^2+5x)$,

d/dx is an operator telling one to take the derivative with respect to x of what follows, that is x^2+5x.

The examples of some familiar observables and their corresponding operators are given below in Table 3.1.

Table 3.1: Some observables and their operators

	Observable	**Operator**	
Name	**Symbol**	**Symbol**	**Operation**
Position	x	$\hat{X}$	Multiply by x
	r	$\hat{R}$	Multiply by r
Momentum	P_x	$\hat{P}_x$	$-ih\frac{\partial}{\partial x}$
	P	$\hat{P}$	$-ih\left(i\frac{\partial}{\partial x}+j\frac{\partial}{\partial y}+k\frac{\partial}{\partial z}\right)$
Kinetic energy	K_x	$\hat{K}_x$	$-\frac{h^2}{2m}\frac{\partial^2}{\partial x^2}$
	K	$\hat{H}$	$-\frac{h^2}{2m}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)$
Potential energy	$U(x)$	$U(\hat{x})$	*Multiply by* $U(x)$
	$U(x,y,z)$	$U(\hat{x},\hat{y},\hat{z})$	*Multiply by* $U(x,y,z)$
Total energy	E	$\hat{H}$	$-\frac{h^2}{2m}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)$ $+U(x,y,z)$
Angular momentum	$l_x = yp_z - zp_y$	$\hat{L}_x$	$-ih\left(y\frac{\partial}{\partial z}-z\frac{\partial}{\partial y}\right)$
	$l_y = zp_x - xp_z$	$\hat{L}_y$	$-ih\left(z\frac{\partial}{\partial x}-x\frac{\partial}{\partial z}\right)$
	$l_z = xp_y - yp_x$	$\hat{L}_z$	$-ih\left(x\frac{\partial}{\partial y}-y\frac{\partial}{\partial x}\right)$

Operators can be imaginary or complex quantities also as in case of operator for x component of the momentum.

Source: Quantum Chemistry, Donald A. McQuarrie, Viva Books Private Limited.

Before proceeding to the next section, answer the following SAQ.

SAQ 1

Define an observable.

3.4 TIME-INDEPENDENT SCHRÖDINGER EQUATION

Schrödinger argued that if an electron (or any other particle) has wave-like properties, then it must be described by a wave function. This wave function is represented by the Greek letter, ψ (psi) and it denotes the amplitude of the wave at a given point. Schrödinger expressed the wave properties of an electron in the form of an equation which is known as *Schrödinger equation*. Schrödinger equation is the fundamental equation of wave mechanics and it may be obtained in the following way.

Consider the equation of wave motion in one direction, say x - direction only, which is written as

In Eq. 3.1, the term $\frac{\partial^2\psi}{\partial x^2}$ represents the second order partial derivative of ψ with respect to x.

$$\frac{\partial^2\psi}{\partial x^2} = \frac{-4\pi^2\psi}{\lambda^2} \quad \text{or} \quad \frac{\partial^2\psi}{\partial x^2} + \frac{4\pi^2\psi}{\lambda^2} = 0 \qquad \text{... (3.1)}$$

This equation is applicable to all particles including electrons and protons.

Total energy E of a moving particle may be considered as a sum of its potential energy, V and its kinetic energy. Thus,

$$E = \text{P.E.} + \text{K.E.} \ \text{ or } \ \text{K.E.} = E - \text{P.E.} = E - V \qquad \text{... (3.2)}$$

The kinetic energy of a particle of mass m moving with momentum p is given by

$$\text{K.E.} = \frac{p^2}{2m} \qquad \text{... (3.3)}$$

From Eq. 2.7, p can be written as $p = h/\lambda$; hence Eq. 3.3 can be written as

$$\text{K.E.} = \frac{h^2}{\lambda^2(2m)} = E - V \quad \text{or} \quad \lambda^2 = \frac{h^2}{2m(E-V)} \qquad \text{... (3.4)}$$

Substituting the above value of λ^2 in Eq.3.1, one gets

$$\frac{\partial^2\psi}{\partial x^2} + \frac{4\pi^2 2m}{h^2}(E-V)\psi = 0 \quad \text{or} \quad \frac{\partial^2\psi}{\partial x^2} + \frac{8\pi^2 m}{h^2}(E-V)\psi = 0 \qquad \text{... (3.5)}$$

$p = mv$

$p^2 = m^2v^2$

$$\frac{p^2}{2m} = \frac{m^2v^2}{2m}$$

$$= \frac{1}{2}mv^2$$

$= K.E.$

Eq. 3.5 is the well-known Schrödinger equation in one dimension. In three-dimensions, it may be written in the following way.

$$\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2} + \frac{8\pi^2 m}{h^2}(E-V)\psi = 0 \qquad \text{... (3.6)}$$

Alternatively, it can also be written as

$$\nabla^2\psi + \frac{8\pi^2 m}{h^2}(E - V)\psi = 0 \qquad \text{… (3.7)}$$

where ∇^2 is $\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$ and is known as **Laplacian operator**.

Eq. 3.7 is customarily written in the following form

$$\left[\frac{-h^2}{8\pi^2 m}\nabla^2 + V\right]\psi = E\psi \qquad \text{… (3.8)}$$

Defining the Hamiltonian operator *H* as,

$$\hat{H} = \frac{-h^2}{8\pi^2 m}\nabla^2 + V \qquad \text{… (3.9)}$$

Eq. 3.8 becomes

$$\hat{H}\psi = E\psi \qquad \text{… (3.10)}$$

which is the abbreviated form of Schrödinger equation.

Note that Eq. 3.10 is time-independent Schrödinger equation because the neither the Hamiltonian nor the wave function is dependent on time.

The Schrödinger equation as given above in Eq. 3.10 is the most general form. Thus, according to this equation, when we perform the mathematical operations given by Hamiltonian operator on ψ , it gives us back the unchanged wave function ψ, multiplied by a constant, *E* which is the energy of the electron.

The wave function which satisfies the Schrödinger equation is not easy to determine and it becomes necessary to try various wave functions to give the satisfactory solution of the Schrödinger equation.

Thus, the Schrödinger equation can be solved using various trial wave functions. The particular values of ψ which yield satisfactory solutions of the above equation are called **eigenfunctions** and the corresponding energy values are called **eigenvalues** for the system under consideration.

This is as per the postulate 3 of quantum mechanics given below:

Postulate 3

In any measurement of observable associated with the operator $\hat{A}$, the only values that will ever be observed are the eigenvalues a, which satisfy the eigenvalue equation.

$$\hat{A}\psi = a\psi$$

Having understood the above concepts, let us study what is meant by ψ and ψ^2.

SAQ 2

What is Laplacian operator?

SAQ 3

Explain the terms eigenfunctions and eigenvalues.

3.5 SIGNIFICANCE OF ψ AND ψ^2

The wave function ψ can be regarded as an amplitude function for a wave. Similar to the amplitude, the wave function can take positive values in some region of space and negative values in the other regions. You will see later in Unit 9 how the nature of ψ affects the formation of a bond between the atoms, e.g., only the wave functions of same phase will lead to the bonding combination.

For any particular physical situation under consideration, ψ must be *finite*, *single-valued* and *continuous*; then only the wave function is said to be well behaved. For example, in Fig. 3.1 a), the wave function shown is *not* well behaved because it is not finite. Similarly, the wave function shown in Fig. 3.1 b) is *not* single-valued for a particular value of x. It has three values of ψ at points p, q and r.

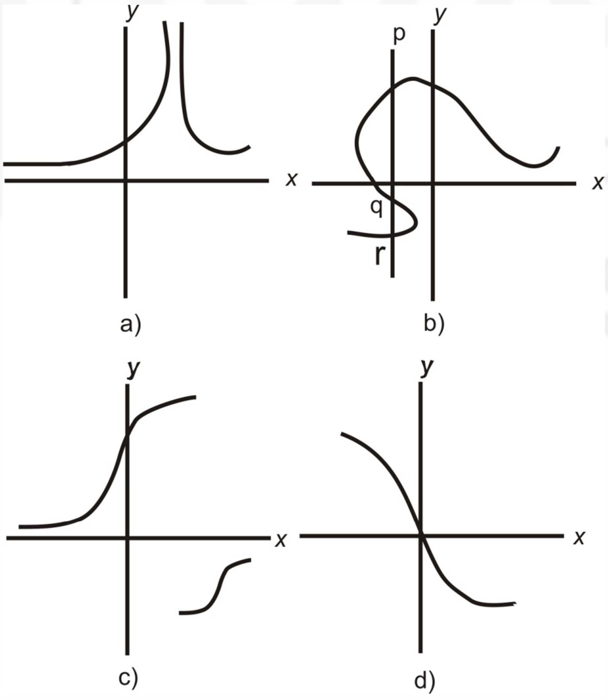


Fig. 3.1: Pictorial representation of wave functions; the curves a), b) and c) represent the functions which are not well behaved while d) shows the well behaved function.

Again, the wave function shown in Fig. 3.1 c) is *not* well behaved because it is not continuous. Now, you compare the above wave functions with the one shown in Fig. 3.1 d). You can see that this wave functions is single-valued, continuous and finite. So, it is a well behaved wave function. Similar to the wave theory of light in which the square of the amplitude represents the intensity of light, the square of the wave function ψ, i.e., ψ^2 is proportional to the probability of finding an electron in the given region of space.

Since we presume that ψ^2 is **proportional** to the probability of finding an electron in a given region of space and **not equal** to the probability; the wave function ψ has to be multiplied by a constant N so that its square becomes,

$$(N\psi)^2 = N^2\psi^2 \qquad \ldots (3.11)$$

When an electron is confined in a particular region of space $d\tau$, the probability of locating the electron in this region can be obtained by integration, as shown in the following expression. This integral quantity has to be equal to unity. Hence,

$$\int N^2\psi^2 d\tau = N^2\int \psi^2 d\tau = 1 \qquad \ldots (3.12)$$

Now this probability indicates the certainty of finding the electron in the given region. Here, N is called the **normalisation constant** and it ensures that the probability of finding the electron is equal to unity and not just proportional to it. Here onwards, we will deal with normalised functions only.

Concept of ψ^*

Sometimes ψ is a complex function. Since the probability of finding the particle has to be a real quantity, in such cases, the above normalisation condition represented by $N^2\int \psi \cdot \psi d\tau = 1$, does not yield real values. In these cases, normalisation condition is given by $N^2\int \psi \cdot \psi^* d\tau = 1$, where ψ^* is the complex conjugate of ψ and is obtained by replacing i (iota, square root of -1) in ψ by $-i$. This ensures that $\psi\psi^*$ is a real number.

For example, if

$\psi = e^{ix}$, then

$$\psi\psi = e^{ix} \cdot e^{ix} = e^{2ix} \qquad \ldots (3.13)$$

which is a complex quantity. But

$$\psi\psi^* = e^{ix} \cdot e^{-ix} = e^0 = 1 \qquad \ldots (3.14)$$

which is a real quantity.

Postulate 4

If a system is in a state described by a normalised wave function ψ, then the average value of the observable corresponding to $\hat{A}$ is given by

$$\langle a \rangle = \int_{-\infty}^{\infty} \psi^* \hat{A}\psi \, d\tau$$

It may be worth mentioning here that the more general form of Schrödinger equation is *time-dependent* Schrödinger equation. In time-dependent

Schrödinger equation the Hamiltonian and the wave function depend on time also. Such an equation is given below:

$$\hat{H}\Psi(x,t) = i\hbar\frac{\partial}{\partial t}\psi(x,t)$$

This is given as postulate 5 of quantum mechanics as shown below:

Postulate 5

The wave function or state function of a system evolves in time according to the time-dependent Schrödinger equation.

$$\hat{H}\Psi(x,t) = ih\frac{\partial\Psi(x,t)}{\partial t}$$

SAQ 4

Explain the meaning of ψ^2.

3.6 APPLICATIONS OF SCHRÖDINGER EQUATION

You are now familiar with Schrödinger equation. Let us now use Schrödinger equation and see what information can be derived from its solution. In general, the following steps are involved:

a) Since, the Hamiltonian operator is H for the system, the corresponding Schrödinger equation is

$$H\psi = E\psi$$

b) The Schrödinger equation is solved for the system. Its solution gives wave functions. As already mentioned, only those wave functions are acceptable which are well behaved, i.e., which are single-valued, continuous and finite. Such solutions are called eigenfunctions and the corresponding energy values are called eigenvalues.

c) According to quantum mechanics, all the information about the system is contained in its wave function ψ and it provides a recipe for calculating the values of dynamic variables (position, momentum, energy etc.) of a particle.

By using the above methodology, let us study the energy states obtained for hydrogen-like atoms.

3.6.1 Energy States of the Hydrogen-like Atoms

The solution of the Schrödinger equation for hydrogen atom, i.e. Eq. 3.8 or 3.10, yields the expression for energy E, as

$$E = \frac{-Z^2e^4\mu}{8\in_0 h^2n^2} \quad \text{... (3.15)}$$

where $n = 1, 2, 3, ...$

As M, the mass of the nucleus, is very large compared to that of an electron, μ can by replaced by m. Hence, the energy expression becomes,

$$E = \frac{-Z^2 e^4 m}{8 \in_0^2 h^2 n^2} \qquad \text{.... (3.16)}$$

which is identical to the energy expression (Eq. 1.14) obtained from the Bohr's theory. Since, this expression does not involve *l* and m_l, the levels given by a certain value of *n* are degenerate. The value of n^2 gives the degeneracy of the n^{th} energy level. For example, when $n = 1$, there is only one energy level and this corresponds to 1*s* level. When $n = 1$, degeneracy is $n^2 = 2^2 = 4$ and hence the 2*s* and three 2*p* orbitals are degenerate. Similarly $n = 3$ gives a n^2 value of 9. This corresponds to nine degenerate states which can be represented by 3*s*, three 3*p* and five 3*d* orbitals.

You are already aware that reduced mass is given as:

$$\mu = \frac{mM}{m + M}$$

3.7 SUMMARY

In this unit, we emphasised the need for a new approach to describe the structure of atom in the light of the dual behaviour of radiation and matter. We explained that the laws of classical mechanics could not be applied to the behaviour of objects having microscopic size.

The new ideas of quantum mechanics given by Schrödinger were discussed in detail. The terms observables and operators were described. The postulates of quantum mechanics were stated at appropriate places. We also discussed the time independent Schrödinger equation. It was explained that only certain wave functions give the satisfactory solution of the Schrödinger wave equation and these were called eigenfunctions. The energy values so obtained by using eigenfunctions in the Schrödinger equation were called eigenvalues.

We then discussed significance of ψ and ψ^2. Finally, the energy states of the hydrogen like atoms were given as obtained from the solution of the Schrödinger equation.

3.8 TERMINAL QUESTIONS

1. Explain the need for having a new approach to explain the structure of the atom.

2. Write Schrödinger equation and explain the terms appearing in it.

3. Write the operators for the following observables giving their symbols and the operation involved.

   i) Position (*x*)

   ii) Momentum (p_x)

4. What is Hamiltonian operator? Also give its significance.

5. Calculate the degeneracy of first three energy levels for hydrogen atom.

3.9 ANSWERS

Self-Assessment Questions

1. A measurable dynamical variable is called an observable.

2. The Laplacian operator is represented as ∇^2 and is given by

$$\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}.$$

3. The wave functions which give the satisfactory solution of the Schrödinger equation are called eigenfunctions. The energy values obtained from the Schrödinger equation by using the eigenfunctions in the equation are called eigenvalues.

4. ψ^2 gives the probability of finding an electron in a given region of space and when ψ^2 approaches unity, the probability approaches certainty of finding the electron in that particular region.

Terminal Questions

1. Please refer Sec. 3.2.

2. $\left[\frac{-h^2}{8\pi^2 m}\nabla^2+V\right]\psi = E\psi$ or $H\psi = E\psi$

   The terms appearing in the above equation have been explained in Sec. 3.4.

3. i) For position, the operator is $\hat{X}$, and the operation involved is multiplication by *x*.

   ii) For momentum, p_x the operator is represented by $\hat{P}_x$ and the operation is $-\hbar\frac{\partial}{\partial x}$.

4. Hamiltonian operator is represented by $\hat{H}$ is given as $\hat{H}=\frac{-h^2}{8\pi^2 m}\nabla^2+V$. It represents the total energy, *E*.

5. $n^2 = 1$ for first energy level,

   $n^2 = 2^2 = 4$ for the second energy level and

   $n^2 = 3^2 = 9$ for the third energy level.

   So, the degeneracies are 1, 4 and 9, respectively.

UNIT 4

HYDROGEN ATOM

Structure

4.1 Introduction
    Expected Learning Outcomes
4.2 Earlier Atomic Models: Dalton, Thomson and Rutherford Models
4.3 Bohr Atom Model
    Calculation of Radius of Orbits
    Energy of an Electron in an Orbit
4.4 Hydrogen Atom Spectrum and Bohr's Theory
4.5 Critical Analysis and Limitations of Bohr's Theory
    Sommerfeld Modification
4.6 Summary
4.7 Terminal Questions
4.8 Answer

4.1 INTRODUCTION

In the preceding unit, we described the general principles of quantum mechanics. Now, you will study about the application of these principles for the investigation of the structure of hydrogen atom. The arguments developed for hydrogen can be extended to hydrogen-like atoms also.

By hydrogen-like atoms, we mean any species having one electron. For example, He^+, Li^{2+}, Be^{3+}etc. are called hydrogen-like atoms. These species differ from hydrogen atom in their nuclear charge. Also, these have an overall charge +1,+2,+3etc., whereas hydrogen atom itself is neutral. We have seen in Unit 2 that the success of the old quantum theory of Bohr was due to its ability to explain the structure of hydrogen atom. Schrödinger equation also was first applied to hydrogen atom and its success provided a convincing proof of the theory of wave mechanics.

We will begin this Unit by writing the Schrödinger equation for hydrogen atom. You will learn that when this equation is written in polar coordinates, and its solution obtained, i.e. the wave function, can be separated into radial and angular components: then, the solution of the Schrödinger equation gave three quantum numbers-*principal quantum number*, *azimuthal quantum number* and *magnetic quantum number*.

Various energy levels of hydrogen atom called *orbitals* will be designated by using these quantum numbers. We will then explain the radial distribution functions for various orbitals. The significance of most probable distance will also be discussed.

The angular dependence of the wave function and shapes of various orbitals will be described. While explaining the shapes of orbitals, the significance of radial and angular nodes will be explained. Finally, a brief account for the discovery of spin of electron will be given and the origin of fourth quantum number, *spin quantum number* will be described.

Expected Learning Outcomes

After studying this unit, you should be able to:

- write Schrödinger equation for the hydrogen atom;
- explain various terms appearing in Schrödinger equation for hydrogen atom;
- list various quantum numbers and explain their significance;
- explain radial distribution functions for various orbitals;
- describe the importance of most probable distance;
- discuss angular dependence of wave functions and relate the shapes of various orbitals to the angular components of the wave function;
- explain the discovery of spin of an electron; and
- discuss the origin of spin quantum number.

In atom, the nucleus is very heavy as compared to an electron. If we have a single electron and a single proton (1836 times heavier than electron) exerting force on each other, then centre of gravity of whole system will move, with uniform velocity in a straight line with each particle rotating about the common centre of gravity. The centre of gravity divides the vector joining nucleus and electron in the ratio of 1:1836 (ratio of mass of electron to proton) so that the nucleus executes only a very slight motion and we can almost treat it as being fixed and the electron as moving about a fixed centre of attraction at the nucleus. This becomes an exact method of handling the problem of electronic rotation, provided we assign to the electron so called 'reduced mass', μ, slightly different from its true mass.

4.2 SCHRÖDINGER EQUATION FOR HYDROGEN ATOM

In hydrogen and hydrogen-like atoms, we have an electron moving in the force field of the nucleus. There is coulomb attraction between a fixed nucleus of charge *Ze* and mass *M* and a moving electron of charge *e* and mass *m*. The potential energy of this system is given by

$$V = \frac{-Ze^2}{4\pi \in_0 r} \qquad \text{... (4.1)}$$

and the reduced mass, μ, of the electron is given by Eq. 4.2.

$$\frac{1}{\mu} = \frac{1}{\text{m}} + \frac{1}{\text{M}} \text{ or } \qquad \mu = \frac{mM}{m+M} \qquad \text{... (4.2)}$$

The Schrödinger wave equation for hydrogen atom and hydrogen-like atoms thus becomes,

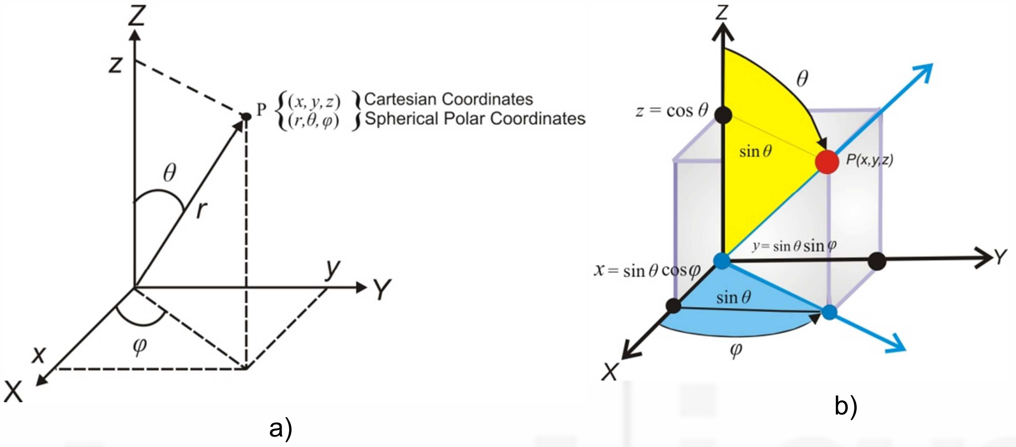
$$\nabla^2\psi + \frac{8\pi^2\mu}{h^2}(E + \frac{Ze^2}{4\pi \in_0 r})\psi = 0 \qquad \text{...(4.3)}$$

Please remember that for hydrogen, *Z* = 1.

The only successful attempts to find solutions of the wave equation have been those in which position of the electron is given in polar coordinates. The spherical polar coordinates, r, θ and ϕ are associated with rectangular cartesian coordinates x, y, z (see Fig 4.1 a)) by the following relations given in Eq. 4.4.

$$\left.\begin{aligned} x &= r\sin\theta\cos\phi \\ y &= r\sin\theta\sin\phi \\ z &= r\cos\theta \end{aligned}\right\} \qquad \dots (4.4)$$

These relations are shown below in Fig. 4.1 b).



a) b)

Fig 4.1: Transformation of Cartesian to spherical polar coordinates.

Schrödinger equation (Eq. 4.3) for hydrogen atom can be expressed in spherical polar coordinates r, θ and ϕ as follows:

$$\frac{1}{r^2}\cdot\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right)+\frac{1}{r^2\sin^2\theta}\cdot\frac{\partial^2\psi}{\partial\phi^2}+\frac{1}{r^2\sin\theta}\cdot\frac{\partial}{\partial\theta}(\sin\theta\frac{\partial\psi}{\partial\theta})$$

$$+\frac{8\pi^2\mu}{h^2}(E+\frac{Ze^2}{4\pi\in_0 r})=0 \qquad \dots (4.5)$$

Accordingly, the position of the electron in spherical polar coordinates is shown in Fig. 4.2.

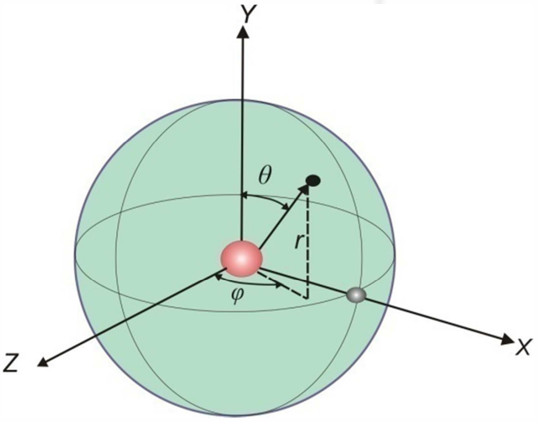


Fig. 4.2: Position coordinates of the electron.

We can write the solution of above Schrodinger equation (Eq. 4.5), i.e. thewave function as given below:

$$\Psi_{(r,\,\theta,\,\phi)} = R_{(r)}\theta_{(\theta)}\Phi_{(\Phi)} \qquad \dots (4.6)$$

where $R_{(r)}$ is the radial part of the wave functions and $\theta_{(\theta)}\Phi_{(\Phi)}$ is the angular part of the wave function.

Here, $R_{(r)}$ is a function of r only, $\theta_{(\theta)}$ is a function of θ only and $\Phi_{(\Phi)}$ is a function of ϕ only. Then, Eq. 4.5 can be separated into three differential equations with the separation of variables r, θ and ϕ . The solution of these equations gives three quantum numbers as discussed below.

Let us now understand what are these three quantum number and what is their significance.

4.2.1 Significance of Quantum Numbers

The solutions for the three differential equations obtained by separation of variables in polar coordinates are characterised by three quantum numbers; *n*, *l* and m_l. To be a well behaved wave function, a wave function must be *continuous*, *finite* and *single-valued*; these boundary conditions or the restrictions will not be met unless *n*, *l* and m_l are integers. Also, *l* is zero or any positive integer less than *n* whereas m_l can take the values from +*l* to–*l* through 0. Thus, various possible values of *n*, *l* and m_l are as follows:

n = 1,2,3,4…

l = 0,1,2,……(n – 1)

m_l = +*l*….., +2,+1,0,–1,–2,….–*l*.

You can realise that *n, l* and m_l are exactly the same as the *principal*, *azimuthal* and *magnetic quantum numbers*, respectively, mentioned earlier in Unit 1. Thus, the wave function, $\psi_{n\,l\,m_l}$, for any electron can be given by substituting the values of the three quantum numbers *n, l* and m_l. When $n = 1, l = 0, m_l = 0, \psi_{nl\,m_l}$ becomes ψ_{100} .Various combinations of *l* and m_l for values of *n* upto 4 are given in Table 4.1.

l has as many possible values as the value of *n*.

Table 4.1: Possible Values of *l* and m_l

n	*l*	m_l	orbital representation
1	0 One Value	0	1*s*
2	0 1 Two Values	0 +1,0,–1	2*s* 2*p*
3	0 1 2 Three Values	0 +1,0,–1 +2,+1,0,–1,–2	3*s* 3*p* 3*d*
4	0 1 2 3 Four Values	0 +1,0,–1 +2,+1,0,–1,–2 +3,+2,+1,0,–1,–2,–3	4*s* 4*p* 4*d* 4*f*

The various values of l are designated by the letters s, p, d, f, g......... as given below:

values of l	0	1	2	3	4
letters	s	p	d	f	g

The letters *s, p, d, f* denote the initial letters of the words *sharp, principal, diffuse* and *fundamental* which were originally used to describe the lines in spectra. After *f,* the alphabetical order follows.

Thus, we can summarise various energy levels with their notations as shown below:

values of *n*	1	2	3	4
values of *l*	0	01	0 1 2	0 1 2 3
Notation $(\mathbf{n}\boldsymbol{l})$	1*s*	2*s* 2*p*	3*s* 3*p* 3*d*	4*s* 4*p* 4*d* 4*f*

The notation in the last line denotes the combination of *n* and *l*.

Let us now summarise what information is available from various quantum numbers.

1) The ***principal quantum number***, *n,* denotes *the major energy level.*

2) The ***azimuthal quantum number***, *l,* denotes the *angular momentum* and *shape of the orbital*. It can also be understood as the sublevel of the major energy level, *n.* When $l = 0,$ the orbital is an *s* orbital and is spherical in shape. If $l = 1$, the orbital is designated as p orbital. Similarly, the orbitals having $l = 2$ and $l = 3$ are termed as d and *f* orbitals, respectively.

3) The ***magnetic quantum number***, m_l ,determines the possible *quantised orientations of the angular momentum* and *of the orbital, in space.*

4) There is a fourth quantum number, known as ***spin quantum number, s,*** which arises from the spectral evidence that any electron moving around the nucleus will *spin* or *rotate* about its own axis also. It will then behave like a small magnet. This spinning of the electron affects the angular momentum and hence, the energy. The spinning can be clockwise or anticlockwise.

   Later, in Sec. 4.6, you will study more about the discovery of spin and spin quantum number.

Let us now go back to Eq. 4.6 and see what information can be obtained by it for hydrogen atom. But before that answer the following SAQ.

SAQ 1

State the four quantum numbers and their significance.

4.3 RADIAL DISTRIBUTION FUNCTIONS

For a hydrogen-like atom, the total wave function is the product of the radial function, namely $\boldsymbol{R}_{(r)}$ and the two angular functions $\Theta_{(\theta)}$ and $\Phi_{(\Phi)}$. The expressions for the radial and angular components for $n=1$ to $n=3$ are given below in the Table 4.2.

The radial function $\boldsymbol{R}_{(r)}$ depends on the quantum numbers *n* and *l.*

The angular wave function depends on the quantum numbers *m* and *l.*

Table 4.2: The Hydrogen-Like Wave Functions

Orbital Desig-nation	***n***	***l***	m_l	$\boldsymbol{R}_{(\boldsymbol{r})}$	$\Theta_{(\theta)}\,\Phi_{(\phi)}$
1*s*	1	0	0	$2\left(\frac{Z}{a_0}\right)^{3/2} e^{-q}$	$\left(\frac{1}{4\pi}\right)^{1/2}$
2*s*	2	0	0	$\frac{1}{2\sqrt{2}}\left(\frac{Z}{a_0}\right)^{3/2}(2-q)e^{-q/2}$	$\left(\frac{1}{4\pi}\right)^{1/2}$
$2p_z$	2	1	0	$\frac{1}{2\sqrt{6}}\left(\frac{Z}{a_0}\right)^{3/2} qe^{-q/2}$	$\left(\frac{3}{4\pi}\right)^{1/2}\cos\theta$
$2p_x$	2	1	0	$\frac{1}{2\sqrt{6}}\left(\frac{Z}{a_0}\right)^{3/2} qe^{-q/2}$	$\left(\frac{3}{4\pi}\right)^{1/2}\sin\theta\cos\phi$
$2p_y$	2	1	-1	$\frac{1}{2\sqrt{6}}\left(\frac{Z}{a_0}\right)^{3/2} qe^{-q/2}$	$\left(\frac{3}{4\pi}\right)^{1/2}\sin\theta\sin\phi$
3*s*	3	0	0	$\frac{2}{81\sqrt{3}}\left(\frac{Z}{a_0}\right)^{3/2}(27-18q+2q^2)e^{-q/3}$	$\left(\frac{1}{4\pi}\right)^{1/2}$
$3p_z$	3	1	0	$\frac{4}{81\sqrt{6}}\left(\frac{Z}{a_0}\right)^{3/2}(6-q)qe^{-q/3}$	$\left(\frac{3}{4\pi}\right)^{1/2}\cos\theta$
$3p_x$	3	1	1	$\frac{4}{81\sqrt{6}}\left(\frac{Z}{a_0}\right)^{3/2}(6-q)qe^{-q/3}$	$\left(\frac{3}{4\pi}\right)^{1/2}\sin\theta\cos\phi$
$3p_y$	3	1	-1	$\frac{4}{81\sqrt{6}}\left(\frac{Z}{a_0}\right)^{3/2}(6-q)qe^{-q/3}$	$\left(\frac{3}{4\pi}\right)^{1/2}\sin\theta\sin\phi$
$3d_{z^2}$	3	2	0	$\frac{4}{81\sqrt{30}}\left(\frac{Z}{a_0}\right)^{3/2} q^2e^{-q/3}$	$\left(\frac{5}{16\pi}\right)^{1/2}(3\cos^2\theta-1)$
$3d_{xz}$	3	2	1	$\frac{4}{81\sqrt{30}}\left(\frac{Z}{a_0}\right)^{3/2} q^2e^{-q/3}$	$\left(\frac{15}{4\pi}\right)^{1/2}\sin\theta\cos\theta\cos\,\phi$
$3d_{yz}$	3	2	-1	$\frac{4}{81\sqrt{30}}\left(\frac{Z}{a_0}\right)^{3/2} q^2e^{-q/3}$	$\left(\frac{15}{4\pi}\right)^{1/2}\sin\theta\cos\theta\sin\,\phi$
$3d_{x^2-y^2}$	3	2	2	$\frac{4}{81\sqrt{30}}\left(\frac{Z}{a_0}\right)^{3/2} q^2e^{-q/3}$	$\left(\frac{15}{16\pi}\right)^{3/2}\sin^2\theta\cos2\phi$
$3d_{xy}$	3	2	-2	$\frac{4}{81\sqrt{30}}\left(\frac{Z}{a_0}\right)^{3/2} q^2e^{-q/3}$	$\left(\frac{15}{16\pi}\right)^{3/2}\sin^2\theta\sin2\phi$

Here, Z is nuclear charge and $q = Zr / a_0$; where a_0 is Bohr radius and r is the distance of the electron from the nucleus.

Also, $a_0 = \frac{\epsilon_0 h^2}{\pi \mu e^2} = 53\,\text{pm}$.

This is similar to Eq. 1.8 (Unit 1) but the only difference is that here m is replaced by μ and $Z = 1$ for hydrogen. The term a_0 was denoted as Bohr radius in Unit 1, sub-Sec. 1.3.1.

4.3.1 The Most Probable Distance

The *radial wave functions,* $\boldsymbol{R}_{(r)}$ are plotted in Fig. 4.3 a) for various combinations of *n and l.* The *radial distribution function,* $\boldsymbol{D}_{(r)}$ indicates the electron distribution or the probability of finding an electron in a spherical shell between the distance *r* and *r* + *dr*. If *r* is the distance of the electron from the nucleus, the volume between the two shells is given by $4\pi r^2$ and the probability of finding the electron between this volume element can be given by,

$$D_{(r)}dr = 4\pi r^2 \psi^2 dr \qquad \ldots (4.7)$$

The term 'radial probability density' is usually applied to the probability divided by 4π times the thickness of the shell.

Figure 4.3 b) shows the probability densities for finding an electron for various values of *n* and *l.*

The radial wave function has no physical meaning but $R^2_{(r^2)}$ gives the probability density.

Note that the probability density is 0 at nucleus when $r = 0$.

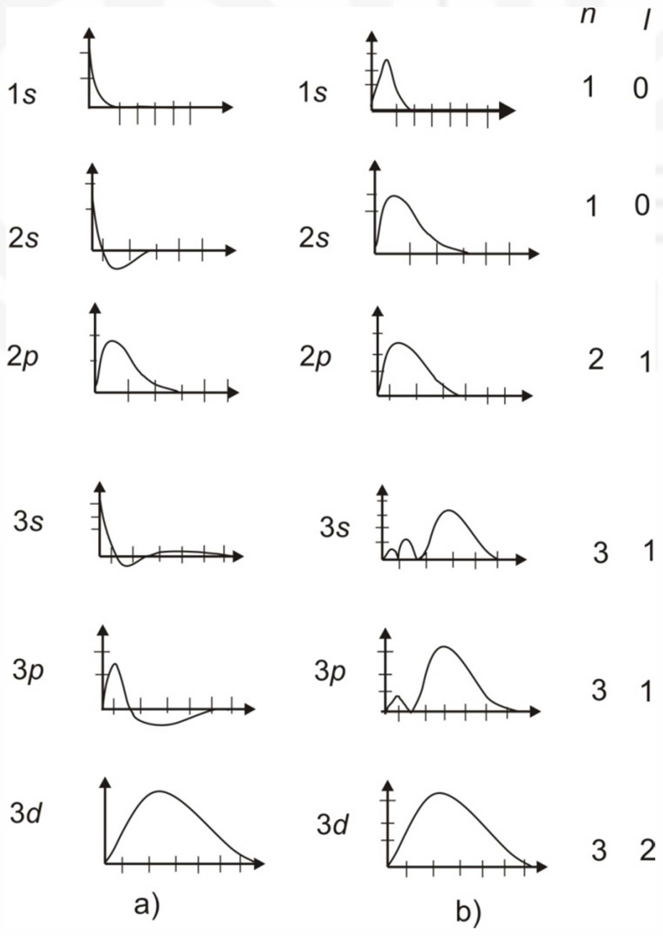


Fig.4.3: a) Electronic radial wave function $R_{(r)}$ for the hydrogen atom and + b) Radial probability density for finding an electron at a distance between *r* and *r* + *dr*.

Note that in case of 1*s* state, the probability of finding an electron is maximum in the spherical shell which has a radiusa_0, which in turn is the same as predicted by Bohr for the first orbit. Similarly, you can compare the probability density of the electron in 2*s* orbital. The maximum now is shifted away from the nucleus i.e., the electron in the 2*s* orbital will have its probable location farther away from the nucleus as compared to the 1*s* electron. But, you can see that the small hump indicates that although small, there is still finite probability of finding the 2*s* electron near the nucleus also.

SAQ 2

Calculate the reduced mass of an electron in hydrogen atom.

Mass of proton, $M = 1.673 \times 10^{-27}$ mass of electron, $m = 9.109 \times 10^{-31}$ Kg.

4.4 ANGULAR DEPENDENCE OF THE WAVE FUNCTION AND SHAPES OF ORBITALS

The wave functions for single electron as obtained in the previous section are often termed as **atomic orbitals**. The shapes of these atomic orbitals depend on the angles θ and ϕ , which in other words determine the *geometry* or the *spatial distribution of the orbitals*. This angular dependence is represented by spherical polar coordinates θ and ϕ and is given in the last column of Table 4.2 as $\Theta_{(\theta)}\,\Phi_{(\Phi)}$ term. You can see that for 1*s* orbital, it is just $\frac{1}{\sqrt{4\pi}}$; this means that the *s* orbital is independent of the angles θ and ϕ . Thus, whatever be the values of θ and ϕ, the **angular** portion of the wave function is *constant*. Hence, it is **spherically** symmetrical,(see Fig. 4.4).

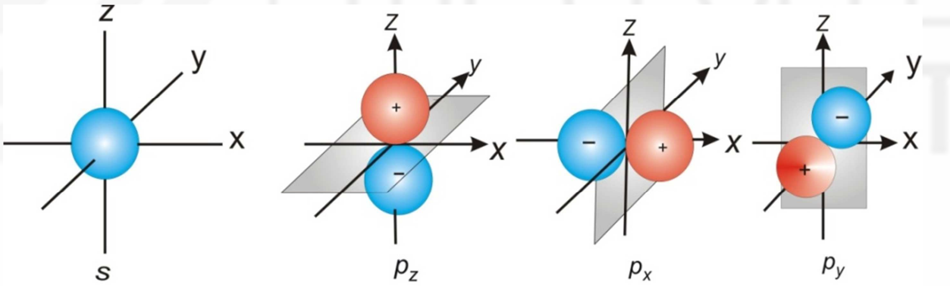


Fig.4.4: *s* and *p* orbitals.

The orientations of the *p* orbitals can be calculated by considering the magnitudes and signs of the trigonometric functions. Thus, for $2p_z$ orbital, as per Table 4.2, the $\Theta_{(\theta)}\Phi_{(\Phi)}$ term contains $\cos\theta$, which according to the relations given in Eq. 4.4 implies that this orbital is directed along the *z-direction*. Similarly, according to Eq. 4.4, the wave function for p_y orbital contains $\sin\theta\sin\phi$ term, and hence, it will correspond to the orbital having maximum electron density along *y-direction*. The wave function for p_x, containing $\sin\theta\cos\phi$ term, indicates that the orbital points to the *x-direction*.

Again, on the similar lines of discussion above, we can conclude that 2*s* and 3*s* orbitals are spherically symmetrical because they do not involve θ and ϕ

terms in their angular functions. Also, we can interpret the directional characteristics of 3*p* and 3*d* orbitals. In the absence of any electric or magnetic field, the electrons in the three *p* orbitals will have the same energy, which depends on the value of *n.* Hence, the three *p* orbitals are termed as **triply degenerate**. But, when the magnetic field is applied, the electrons in the *p* orbital in the direction of the field shows different energy and m_l, the *magnetic quantum number* comes into picture. The three *p* orbitals are shown in Fig. 4.4.

Similarly, the angular dependence of *d* orbitals can be visualised. There are five *d* orbitals and these are shown in Fig. 4.5. The + and–signs refer to the symmetry of wave function and you should not confuse them with the electrical charges.

If a crest of a wave is assumed to have positive amplitude, its trough can be considered to have negative amplitude. The positive and negative signs for ψ values are inherent in their solutioncontaining trigonometric functions like $\sin\theta, \sin\phi, \cos\theta$ and $\cos\phi$.

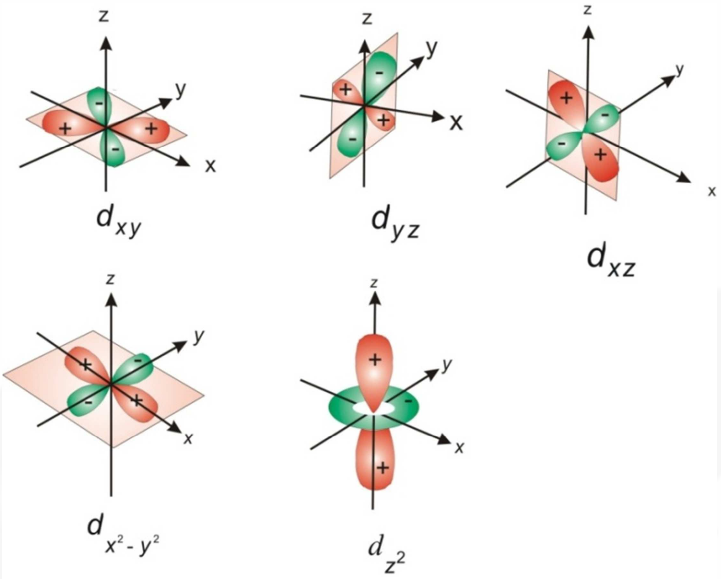


Fig. 4.5: Five *d* orbitals. The indicated signs are those of the wave functions. These signs are indicated because they will be of interest later when we discuss molecular orbitals in Unit 9. The probability density is, of course, always positive.

You will understand the importance of these signs in the bonding of orbitals during the formation of the molecules in Sec.9.2 of Unit 9 on Molecular Orbital Theory.

Diagrams of angular part of wave function exhibit the signs of the symmetry of the wave function and are used to show overlap of orbitals in bond formation.

The squaring of the total wave function does not change the shape of *s* orbital but elongates the lobes of *p* orbitals as shown below in Fig. 4.6.

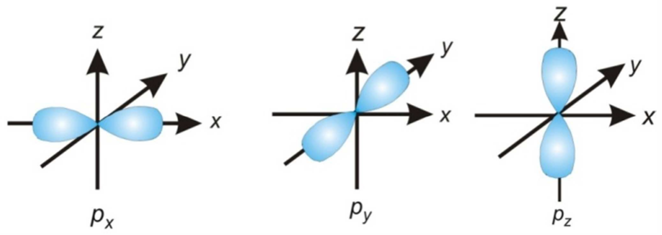
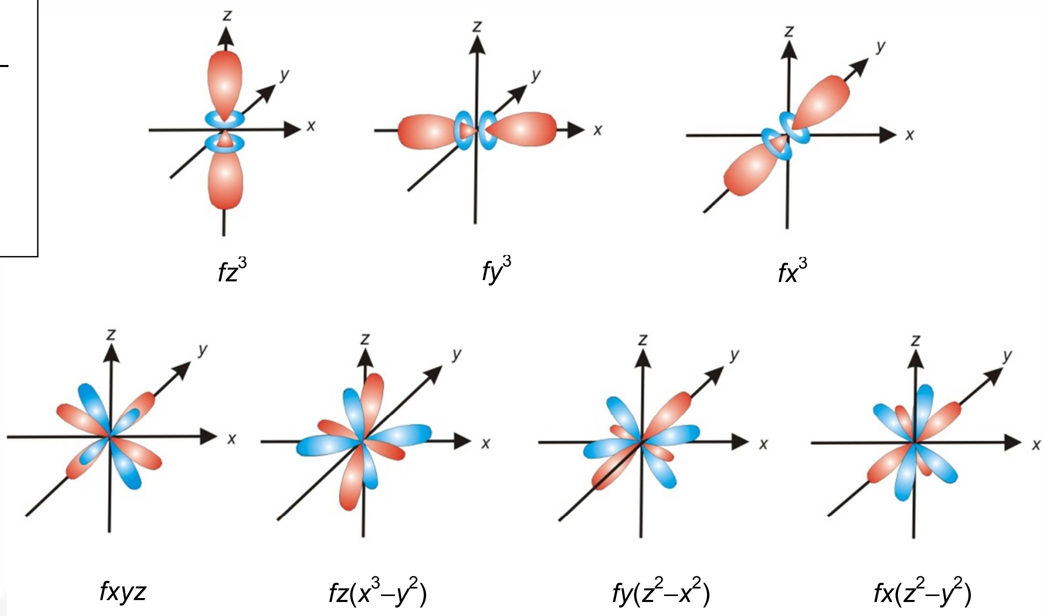


Fig. 4.6: The squared part of angular wave function for *p* orbitals showing their elongated shapes.

You can see in the figure above that + and – sign are not shown on the lobes of these orbitals because such diagrams represent the square of the wave function.

The above ideas can be further extended for *f* orbitals and the seven *f* orbitals can be represented as shown in Fig. 4.7.

When the squared wave functions are represented, the + and – signs shown in the angular wave functions are omitted in the lobes of the orbitals.



fz^3 fy^3 fx^3

$fxyz$ $fz(x^3–y^2)$ $fy(z^2–x^2)$ $fx(z^2–y^2)$

Fig. 4.7: Shapes of seven *f* orbitals.

Till now you were studying about the shapes of various orbitals. The degeneracy of these orbitals have already been explained in sub-Sec. 3.6.1

In the next section, you will study about the radial and angular nodes present in the above orbitals.

In the light of above discussion, answer the following SAQ.

SAQ 3

What do the + and – signs shown on the lobes of various orbitals indicate?

4.5 RADIAL AND ANGULAR NODES AND THEIR SIGNIFICANCE

You have studied about the shapes of various orbitals in the last section. There, while the shapes of orbitals were illustrated, we have shown the angular parts of the wave function showing the electron distribution density. However, the radial distribution functions representing the electron density as a function of the distance from the nucleus was discussed Sec. 4.3 before these shapes were described. Please note that the radial part of the wave function has not been shown while the shapes of orbitals were given in Figs. 4.4 to Fig. 4.7.

The shapes of orbitals described in last section show many areas which have zero electron density. Such area are called **nodes.** The nodes can be *radial* or *angular.* The general representation of radial and angular nodes is given in Fig. 4.8. The two radial nodes having $\psi = 0$ for 3*s*orbital are also indicated in its radial wave function curve. The curve shows two points where $\psi = 0$. The angular nodes shown on the right hand side is a plane having $\psi = 0$.

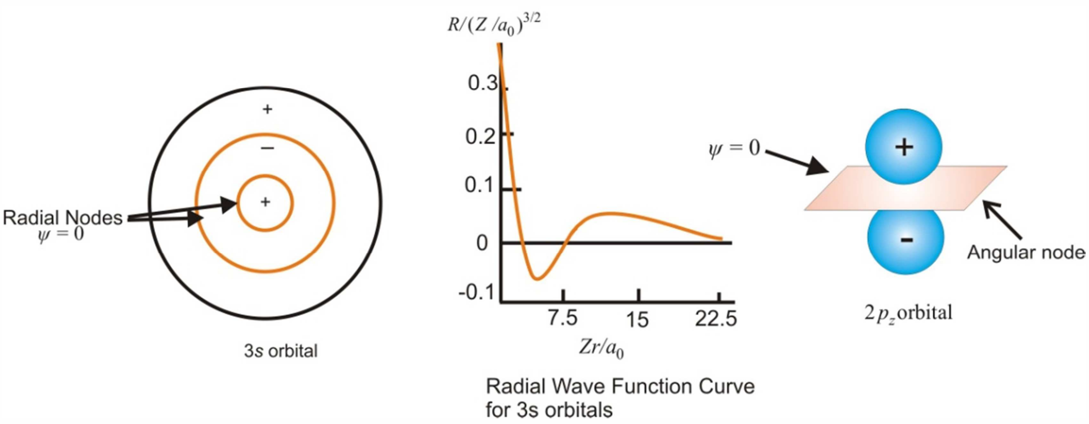


Fig. 4.8: Radial and angular nodes in wave function.

Let us first understand what are radial nodes. A *radial node* has a spherical surface with zero probability of having the electron in that area. Such radial nodes are shown below for various *s* orbitals in Fig. 4.9alongwith their radial probability density curves.

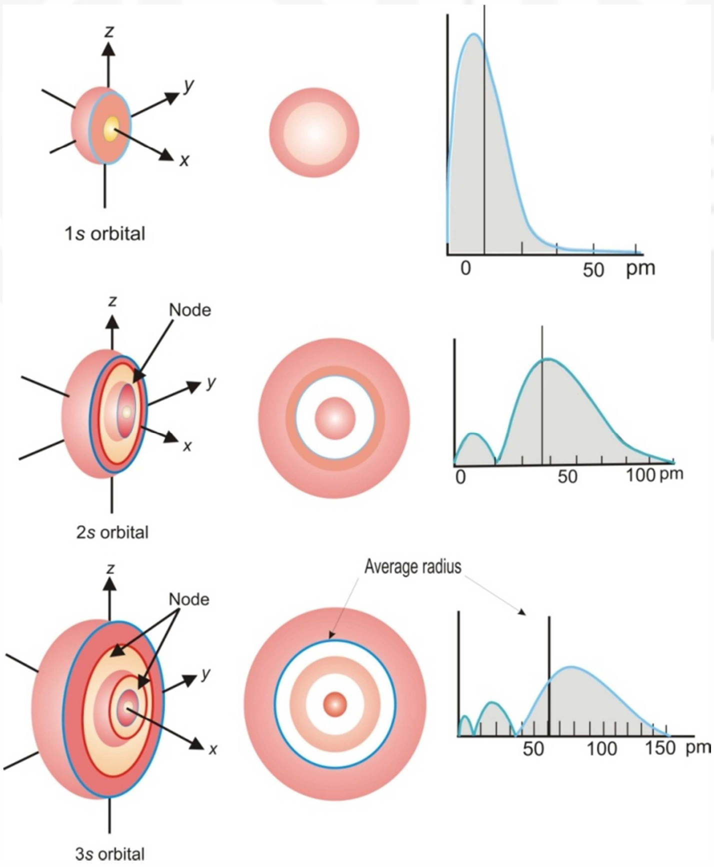


Fig 4.9: Radial nodes and radial probability density curves.

In Fig. 4.9 shown above, you can see that radial probability density curves also show 0, 1and 2 radial nodes in 1*s*, 2*s* and 3*s* orbitals, respectively. You can see that radial node is a nodal surface between the regions of positive and negative amplitude. This is shown below for the 2*s* orbital in Fig.4.10.

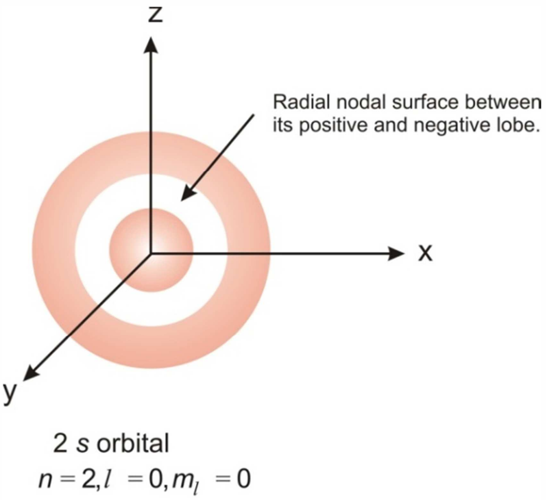


Fig. 4.10: Radial node in the 2*s* orbital.

On the other hand, the angular nodes are the nodal planes having zero electron density. Such nodal planes are shown in Fig. 4.11for *p* orbitals.

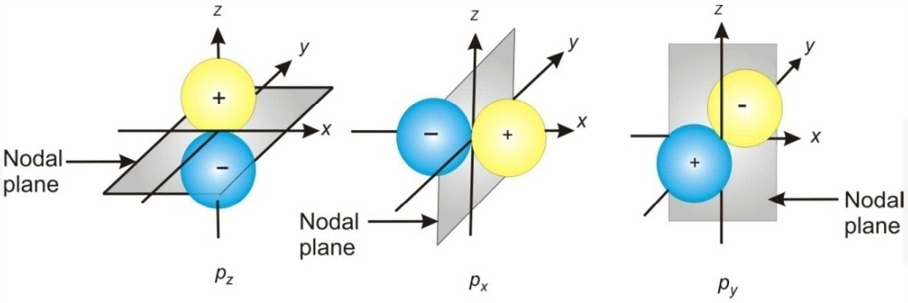
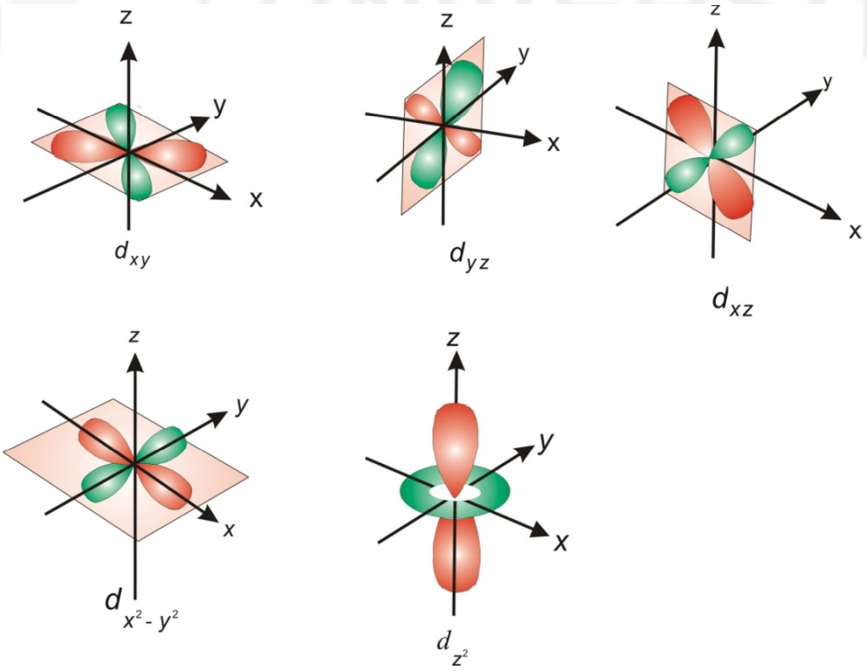


Fig. 4.11: Nodal planes in *p* orbitals.

You can see that the sign of the symmetry of the wave function changes whenwe move from one region to the other across the nodal plane. Such nodal planes are shown for *d* orbitals in Fig. 4.12 below.



4.12: Nodal planes in *d* orbitals showing change of sign of symmetry.

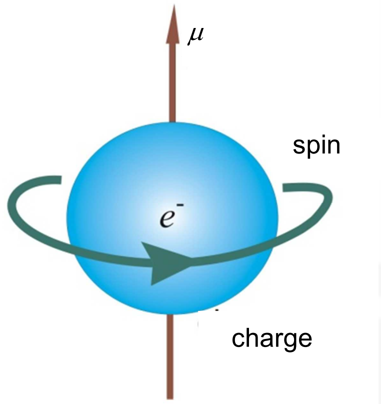
SAQ 4

What is a node?

4.6 DISCOVERY OF SPIN

The fine lines appearing in the atomic spectrum of hydrogen under the influence of magnetic field (*Zeeman effect*) could not be explained on the basis of the three quantum numbers mentioned earlier. In 1925, George Uhlenbeck and Samuel Goudsmit suggested the idea of self-rotation of the electron leading to the angular momentum vector, in addition the orbital angular momentum, see Fig. 4.13.

The magnetic moment, μ, of an electron caused by its intrinsic properties of spin and electric charge. The value of the electron magnetic moment is $-9284.764 \times 10^{-27}$ JT^{-1}.



4.13: The spin of an electron.

Such a spinning charge should generate a magnetic field and the electron should behave like a tiny magnet. The two orientations of the spin, one clockwise and another anticlockwise, would be possible as shown below in Fig. 4.14.

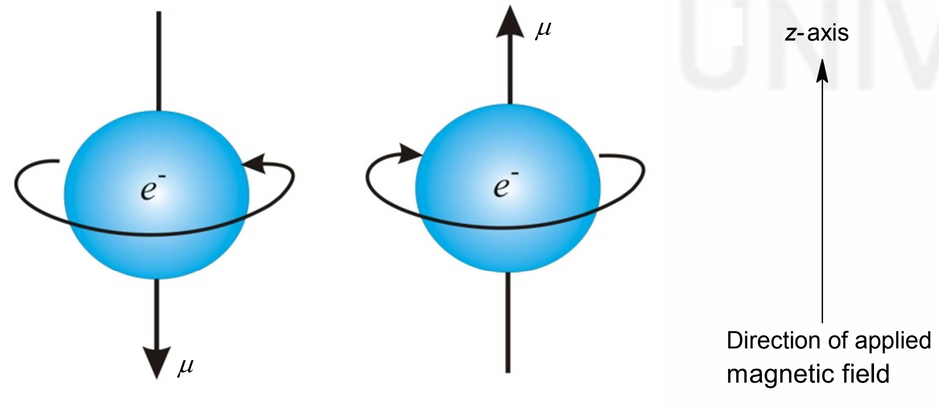


Fig. 4.14: Two possible orientations of spin.

The experimental evidence for the spin of the electron was provided by Stern-Gerlach Experiment which is discussed below:

Stern-Gerlach Experiment

Otto Stern and Walter Gerlach performed an experiment in 1924 in which they directed the beam of silver atoms form a hot oven through a region of non-uniform magnetic field, see Fig. 4.15.

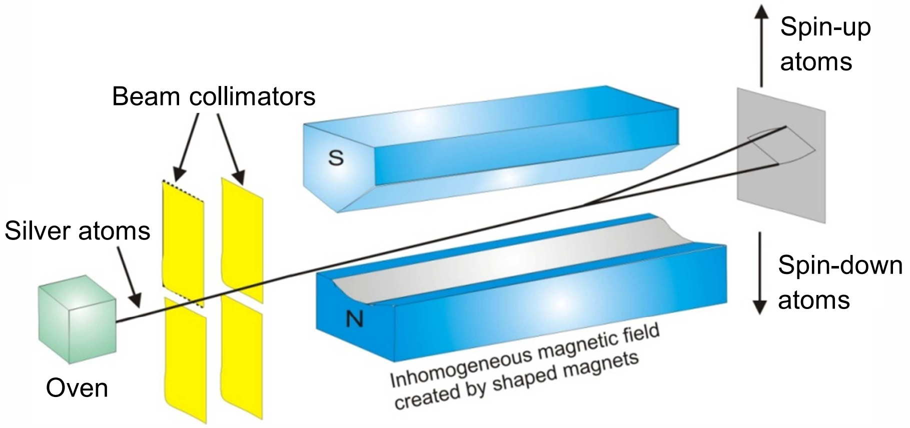


Fig. 4.15: Stern-Gerlach experiment.

On detection of these atoms using a photographic plate, it was found that the beam of silver atoms got separated into two parts and two spots resulted instead of a single continuous smear on the plate, as expected by the classical laws. The separation of beam into two parts indicated two possible orientations of the magnetic moment. But, the angular momentum of the electron in silver atom was zero, since $l = 0$ for $5s^1$ electron in silver. Thus, the proposal of Samuel A. Goudsmit and George E. Uhlenback that the electron has an intrinsic angular momentum, which is independent of orbital angular momentum, could be explained if the electron has *spin* which led to the origin of spin quantum number (s).

4.6.1 Spin Quantum Number(*s*)

The spin of the electron was represented by *s,* the spin quantum number. The spin quantum number has a value of $\frac{1}{2}$. The magnitude of the spin is given by

$$|\mathbf{s}| = \sqrt{s(s+1)}\,\hbar$$

For $$\mathbf{s} = \frac{1}{2}, \mathbf{s} = \frac{\sqrt{3}}{2}\hbar$$

In the presence of the magnetic field, the angular momentum vector could take two possible orientations that is one along the field and the other in the direction opposite to the magnetic field. These two orientations are represented by using the magnetic spin quantum number (m_s) see Fig. 4.16. This is explained below,

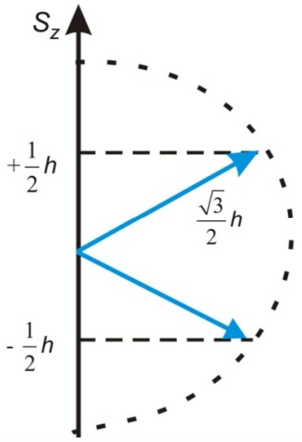


Fig. 4.16: The components of the spin angular momentum in *z*-direction.

The spin angular momentum can have its components, s_z in the z-direction which are given as $s_z = m_s\hbar$.

In the hydrogen atom spectrum, fine structure is observed as a doublet corresponding to two possibilities. For the given z-direction, the solution of the above equation for an electron gives two values for the *z*-component.

$$s_z = \pm\frac{1}{2}\hbar$$

whose solution has only two possible z-components for the electron. For the electron, the two different spin orientations are sometimes called “spin-up” or “spin-down”.

When the direction of the spin of the electron is *anticlockwise*, then the direction of the magnetic moment is *parallel* to the applied to the magnetic field. And, this represents the *lower* energy state called the β state having $m_s = -\frac{1}{2}$.

On the other hand, when the direction of the spin of the electron is *clockwise*, then the direction of the magnetic moment is *antiparallel* to the applied to the magnetic field. And, this represents the *higher* energy state called the α state having $m_s = +\frac{1}{2}$.

4.6.2 Magnetic Spin Quantum Number (m_s)

As mentioned above, the discovery of the spin of the electron led to the spin quantum number which was fourth quantum number. The magnetic spin quantum number, m_s, can have values $+\frac{1}{2}$ and $-\frac{1}{2}$. The magnetic spin quantum number shows two spin states of the electron which could be represented by arrows or the Greek letters α and β, respectively. The anticlockwise spin is represented by an upward arrow, ↑, and the clockwise spin is represented by the downward arrow, ↓.

The spin property of an electron would give rise to magnetic moment, which was a requisite for the fourth quantum number. In β state, the magnetic moment is *parallel* to the applied field. The *lower en*ergy state represented by β has $m_s = -\frac{1}{2}$ while in the higher energy state given by α having $m_s = +\frac{1}{2}$, the magnetic moment is *anti-parallel* to the applied field.

4.7 SUMMARY

In this Unit, you studied about the Schrödinger equation for hydrogen and hydrogen-like atoms. You learnt that when Schrödinger equation written in polar co-ordinates, then solution obtained, i.e., the wave function, Ψ, can be separated into radial and angular components. The solution of Schrödinger equation yielded three quantum numbers – *principal quantum number, n, azimuthal quantum number, l* and magnetic *quantum number,* m_l. We, then, considered the radial and angular parts separately. The radial distribution functions were drawn for various orbitals which showed the variation of the electron density as a function of the distance from the nucleus. Under the discussion on angular dependence of wave functions, the shapes of various orbitals were described. The presence of radial and angular nodes in various orbitals was explained. Finally, a brief account on the discovery of spin and the origin of the spin quantum number was presented.

4.8 TERMINAL QUESTIONS

1. Which of the following combinations of quantum numbers are allowed?

	n	l	m_l	m_s
a)	3	2	1	0
b)	2	0	0	–1/2
c)	7	2	–2	½
d)	3	–3	–2	–1/2

2. What is the significance of the radial distribution function, $\boldsymbol{D}_{(r)}$?
3. What is the number of nodes present in 3*s* orbital?
4. Explain Stern-Gerlach experiment. What does it indicate?
5. What do the states α and β indicate?

4.9 ANSWERS

Self-Assessment Questions

1. The four quantum numbers are
    a) Principal quantum number, *n* which gives the major energy level.
    b) Azimuthal quantum number, *l* which gives the angular momentum and shape of the orbital.
    c) Magnetic quantum number, m_l **,** which gives the orientation of the angular momentum.
    d) Spin quantum number, *s* which gives the spin of the electron.
2. 9.10510×10^{-31}kg.
3. The + and – signs shown on the lobes of various orbitals refer to the symmetry of the wave function.
4. Nodes are areas having zero electron density.

Terminal Questions

1. a) Not allowed because m_s cannot be 0.
    b) allowed
    c) allowed
    d) Not allowed because *l* cannot be negative.
2. The radial distribution functions represent the probability of finding an electron in a spherical shell between the distance *r* and *r* + *dr* where *r* is the distance of the electron from the nucleus.
3. 2.

4. See Sec. 4.6.

5. The α state is the higher energy state of the electron having $m_s = +1/2$ while β state is the lower energy state having $m_s = -1/2$. The magnetic moment is *anti-parallel* or opposite to the direction of the applied magnetic field in the α state but it is *parallel* to the direction of the applied magnetic field in the β state.

UNIT 5

ELECTRONIC CONFIGURATION OF MULTI-ELECTRONATOMS

Structure

5.1 Introduction
    Expected Learning Outcomes
5.2 Energy Levels for Multi-Electron Atoms
5.3 Rules for Filling of Electrons in Various Orbitals
    The aufbau Principle
    Hund's Rule
    Pauli Exclusion Principle
5.4 Electronic Configuration of Some Multi-Electron Atoms
    Stability of Half-Filled and Completely Filled Orbitals
    Concept of Exchange Energy
    Anomalous Electronic Configurations
5.5 Summary
5.6 Terminal Questions
5.7 Answers

5.1 INTRODUCTION

Till now, we were dealing with the hydrogen atom. In Unit 4, you studied in detail about the shapes of various orbitals. We will now focus our attention on multi-electron atoms. In this unit, we will first see how the energy levels of multi-electron systems are different from those of the hydrogen atom. Then, the arrangement of different energy levels in the increasing order of energy will be explained on the basis of Madelung rule. This will be followed by discussion of various rules for filling of the orbitals. Here, aufbau principle, Hund's rule and Pauliexclusion principle will be explained. The electronic configuration of some simple multi-electron atoms will then be described. This discussion will also highlight the stability of half-filled and completely filled orbitals and the concept of exchange energy. Finally, the anomalous electronic configurations of some elements will be described.

Expected Learning Outcomes

After studying this unit, you should be able to:

❖ compare the energy levels of multi-electron atoms with those of the hydrogen atom;

- arrange the energy levels of multi-electron atoms in the increasing order of their energy according to Madelung rule;
- state aufbau principle;
- explain Hund's rule;
- discuss Pauli exclusion principle;
- write electronic configuration of multi-electronic atoms;
- describe the stability of half-filled and completely filled orbitals;
- explain the stability of electronic configurations in the light of the exchange energy; and
- give reason for anomalous electronic configurations of some elements.

5.2 ENERGY LEVELS FOR MULTI-ELECTRON ATOMS

The multi-electron systems can be considered as the extension of the hydrogen atom. But, it is not easy to solve the Schrödinger equation for such systems. Hence, various approximations have to be made and the energy values obtained for such systems are also not exact.

The energy levels so obtained from these energy values can be arranged, as shown in Fig. 5.1 b).

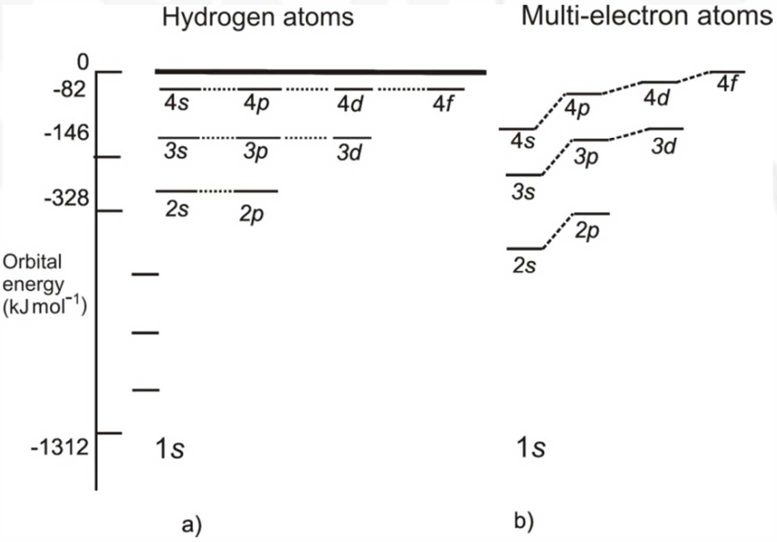


Fig. 5.1: a) Degenerate energy levels in case of hydrogen atom.
b) Splitting of orbital degeneracy in multi-electron atoms.

You can see in the Fig. 5.1 a) above that there is degeneracy among the sub-levels of a particular energy level in the case of hydrogen atom. But, such a degeneracy is lifted in the case of multi-electron atoms.

Thus, the above energy levels can be arranged according to increasing energy as given in the following sequence:

1*s*< 2*s*< 2*p*< 3*s*< 3*p*< 4*s*< 3*d*< 4*p*< 5*s*< 4*d*< 5*p*< 6*s*< 4*f*< 5*d*< 6*p*< 7*s*< 5*f*< 6*d*

This sequence is obtained on the basis of Bohr-Bury rule according to which the energy of the orbital is determined by (*n* + 1). The orbitals are arranged in the order of increasing *n* + *l* values and when *n* + *l* is same for the two orbitals, then the one with smaller *n* will have lower energy. You can easily understand this by taking the example of 3*p*and 4*s*orbitals. Both these orbitals have *n* + *l*= 4. The 3*p* orbitals has *n* = 3 and *l* = 1whereas 4*s*orbital has *n* = 4 and *l* = 0; hence, due to lower *n* value 3*p*orbital will be lower in energy than 4*s* orbital. After knowing the energies of various levels in multi-electron atoms, let us study various rules which will be helpful in arriving of their electronic configuration.

SAQ 1

Which orbital in following pairs will have higher energy?

i) 3*p* or 3*d*

ii) 4*s* or 3*d*

iii) 6*s* or 4*f*

5.3 RULES FOR FILLING OF ELECTRONS IN ORBITALS

When we try to fill up various orbitals according to the number of available electrons in the atom of an element, certain rules are to be followed. Let us first study these rules. Then we will discuss the filling of electrons in the orbitals in the light of the guidelines provided by these rules.

Friedrich Hermann Hund
(4 Feb. 1896 – 31 March 1997)

Wolfgang Ernst Pauli
(25 April 1900-15 Dec.1958)

He received Nobel Prize in Physics in 1945.

1) **The *aufbau* principle-** In German, the word ***aufbau*** stands for 'building up'. It states that the orbitals will be filled up according to the increasing order of energy, i.e., the electrons will be filled up first in lower energy orbital and then in the higher energy orbital.

2) **Hund's rule** says that in a given energy level, the number of unpaired electrons is maximum, i.e., the electrons will first fill the available orbitals singly and then the pairing of electrons will start.

   This is so since there will be repulsion between the two electrons occupying the same orbital. The energy associated with the mutual repulsion resulting from pairing of electrons when they are present in the same orbital is called *Coulombic energy of repulsion*,Π_C, per pair of electrons. Hence, if orbitals of equivalent energy are available, the electrons prefer occupying the orbitals singly with parallel spins.

   If two electrons share the same orbital, for example 1*s* level, then their spins remain antiparallel.

3) **Pauli exclusion principle-** You have studied earlier that each electron can be defined by a set of four quantum numbers: n, l, m_l and and m_s. Pauli exclusion principle states that no two electrons in an atom can have the same set of four quantum numbers.

Since n, l, and m_l are the same for a particular orbital, the two electrons occupying it must have different spin quantum numbers. In other words, the two electrons should have opposite spins, if they are to occupy the same orbital.

Thus, you can calculate the maximum number of electrons which occupy the various orbitals with the help of the Pauli exclusion principle. This is illustrated below in Table 5.1.

Table 5.1: Maximum number of electrons which could be present in different orbitals and their quantum numbers

n	l	m_l	m_s	No. of electrons	Orbital designation	Total electrons in a particular n level
$n = 1$	0	0	$\pm 1/2$	2	1s	2
$n = 2$	0	0	$\pm 1/2$	2	2s	
	1	+1	$\pm 1/2$	2		
		0	$\pm 1/2$	2 6	2p	8
		-1	$\pm 1/2$	2		
$n = 3$	0	0	$\pm 1/2$	2	3s	
	1	+1	$\pm 1/2$	2		
		0	$\pm 1/2$	2 6	3p	
		-1	$\pm 1/2$	2		
	2	+2	$\pm 1/2$	2		18
		+1	$\pm 1/2$	2		
		0	$\pm 1/2$	2 10	3d	
		-1	$\pm 1/2$	2		
		-2	$\pm 1/2$	2		
$n = 4$	0	0	$\pm 1/2$	2	4s	
	1	+1	$\pm 1/2$	2		
		0	$\pm 1/2$	2 6	4p	
		-1	$\pm 1/2$	2		
	2	+2	$\pm 1/2$	2		
		+1	$\pm 1/2$	2		
		0	$\pm 1/2$	2 10	4d	
		-1	$\pm 1/2$	2		
		-2	$\pm 1/2$	2		32
	3	+3	$\pm 1/2$	2		
		+2	$\pm 1/2$	2		
		+1	$\pm 1/2$	2		
		0	$\pm 1/2$	2 14	4f	
		-1	$\pm 1/2$	2		
		-2	$\pm 1/2$	2		
		-3	$\pm 1/2$	2		

Thus, an s orbital can accommodate a maximum of 2 electrons, p orbital 6 electrons, d orbital 10 electrons and f orbital 14 electrons.

Having understood the above ideas, try the following SAQ before studying the next section.

Bohr-Bury proposed the following rules simultaneously:

Rule 1: The maximum number of electrons in a shell is $2n^2$ where n is the principal quantum number of the shell. i.e., *K, L, M, N* shells can have a maximum of 2, 8, 18 and 32 electrons, respectively.

Rule 2: The electrons may enter a new outer shell although the inner shell are incompletely filled.

Rule 3: The outer-most shell cannot have more than 8 electrons while the penultimate shell cannot have more than 18 electrons.

Rule 4: Even if the capacity of the penultimate shell exceeds 8, it cannot have more than 8 electrons unless there are 2 electrons in the outermost shell. Also, it cannot have more than 9 electrons unless anti-penultimate shell is full.

SAQ 2

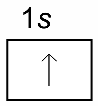
What is the maximum number of electrons which could be accommodated in 3*d* orbitals? Give reason for your answer.

5.4 ELECTRONIC CONFIGURATION OF SOME MULTI-ELECTRON ATOMS

Let us take some examples and study the electron configurations of some elements. We will start with hydrogen atom and write its electronic configuration. Here, the subscript indicates the number of electrons occupying that particular orbital.

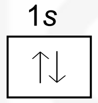
Since the lowest energy orbital is 1*s*, the electron in hydrogen atom occupies this obrtial and the electronic configuration of hydrogen atom is written as $1s^1$.

H – $1s^1$



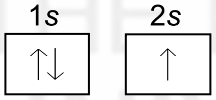
Helium having two electrons has the configuration $1s^2$ because the 1*s* orbital can hold two electrons, provided the two electrons have opposite spins.

He – $1s^2$

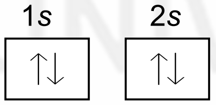


The third electron in case of lithium is in the next higher level, i.e., 2*s* orbital. Similarly, the fourth electron in case of beryllium is in 2*s* orbital.

Li – $1s^2 2s^1$

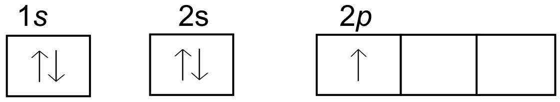


Be – $1s^2 2s^2$



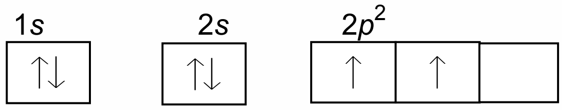
For boron which has five electrons has the following electron configuration because 2*p* orbital is the next higher energy level:

$1s^2 2s^2 2p^1$



The next element, carbon, has six electrons. In conformity with Hund's rule which says that there should be a maximum number of unpaired electrons, the carbon has the configuration,

$1s^2 2s^2 2p_x^1 2p_y^1$



i.e., both the electrons in the 2*p* orbitals occupy the *p* orbitals singly and remain unpaired.

Similarly, in case of nitrogen (7 electron system), the configuration is

	$1s$	$2s$	$2p^3$		
$1s^2 2s^2 2p^3$	↑↓	↑↓	↑	↑	↑

with all the three electrons in $2p$ level remaining unpaired.

Then, we have oxygen having eight electrons which can be represented as follows:

	$1s$	$2s$	$2p^4$		
$1s^2 2s^2 2p^4$	↑↓	↑↓	↑↓	↑	↑

Now since, $2p$orbitals contain four electrons, they can be filled as $2p_x^2\, 2p_y^1\, 2p_z^1$

Similarly, in case of fluorine having nine electrons, the electron configuration is,

	$1s$	$2s$	$2p^5$		
$1s^2 2s^2 2p^5$	↑↓	↑↓	↑↓	↑↓	↑

Then, we have neon (10 electrons) which has the configuration

	$1s$	$2s$	$2p^6$		
$1s^2 2s^2 2p^6$	↑↓	↑↓	↑↓	↑↓	↑↓

with all the orbitals completely filled.

You will learn a little later in this section that the elements having completely or exactly half-filled orbitals have more stable configuration as compared to those which have partially-filled orbitals. You can easily remember the sequence of filling of energy levels, using the diagram given in Fig. 5.2.Note that you have already learnt about the order of increasing energies of these orbitals in Sec. 5.2.

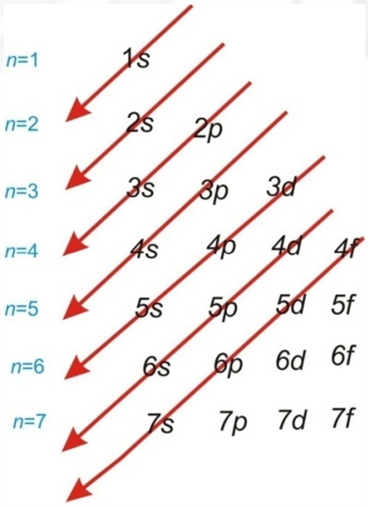


Fig. 5.2: Sequence of filing of various orbitals.

Based upon the above sequence of filling of various orbitals, it is possible to write the electronic configuration of any given element provided its atomic number is known.

Table 5.2 gives the electron configuration of all the elements. Certain anomalies are marked by asterisk (*) and (**) and these are explained in the discussion given after the Table. You will learn more about these elements, i.e., their electron configuration and its relationship to various periodic properties in Inorganic Chemistry courses later.

Table 5.2: Electron Configuration of Elements

	Shell		***K***	***L***	***M***	***N***	***O***	***P***	***Q***
	Orbital		**1*s***	**2*s* 2*p***	**3*s* 3*p* 3*d***	**4*s* 4*p* 4*d* 4*f***	**5*s* 5*p* 5*d* 5*f***	**6*s* 6*p* 6*d* 6*f***	**7*s* 7*p***
	Element	**At. No.**							
***n* =1**	H	1	1						
	He	2	2						
***n* = 2**	Li	3	2	1					
	Be	4	2	2					
	B	5	2	2 1					
	C	6	2	2 2					
	N	7	2	2 3					
	O	8	2	2 4					
	F	9	2	2 5					
	Ne	10	2	2 6					
***n* = 3**	Na	11	2	2 6	1				
	Mg	12	2	2 6	2				
	Al	13	2	2 6	2 1				
	Si	14	2	2 6	2 2				
	P	15	2	2 6	2 3				
	S	16	2	2 6	2 4				
	Cl	17	2	2 6	2 5				
	Ar	18	2	2 6	2 6				
***n* = 4**	K	19	2	2 6	2 6	1			
	Ca	20	2	2 6	2 6	2			
	Sc	21	2	2 6	2 6 1	2			
	Ti	22	2	2 6	2 6 2	2			
	V	23	2	2 6	2 6 3	2			
	*Cr	24	2	2 6	2 6 5	1			
	Mn	25	2	2 6	2 6 5	2			
	Fe	26	2	2 6	2 6 6	2			
	Co	27	2	2 6	2 6 7	2			
	Ni	28	2	2 6	2 6 8	2			
	*Cu	29	2	2 6	2 6 10	1			
	Zn	30	2	2 6	2 6 10	2			
	Ga	31	2	2 6	2 6 10	2 1			
	Ge	32	2	2 6	2 6 10	2 2			
	As	33	2	2 6	2 6 10	2 3			
	Se	34	2	2 6	2 6 10	2 4			
	Br	35	2	2 6	2 6 10	2 5			
	Kr	36	2	2 6	2 6 10	2 6			

	Shell		K	L		M			N				O				P				Q	
	Orbital		1*s*	2*s*	2*p*	3*s*	3*p*	3*d*	4*s*	4*p*	4*d*	4*f*	5*s*	5*p*	5*d*	5*f*	6*s*	6*p*	6*d*	6*f*	7*s*	7*p*
	Element	At. No.																				
n = 5	Rb	37	2	2	6	2	6	10	2	6			1									
	Sr	38	2	2	6	2	6	10	2	6			2									
	Y	39	2	2	6	2	6	10	2	6	1		2									
	Zr	40	2	2	6	2	6	10	2	6	2		2									
	**Nb	41	2	2	6	2	6	10	2	6	4		1									
	*Mo	42	2	2	6	2	6	10	2	6	5		1									
	Tc	43	2	2	6	2	6	10	2	6	5		2									
	**Ru	44	2	2	6	2	6	10	2	6	7		1									
	**Rh	45	2	2	6	2	6	10	2	6	8		1									
	*Pd	46	2	2	6	2	6	10	2	6	10											
	*Ag	47	2	2	6	2	6	10	2	6	10		1									
	Cd	48	2	2	6	2	6	10	2	6	10		2									
	In	49	2	2	6	2	6	10	2	6	10		2	1								
	Sn	50	2	2	6	2	6	10	2	6	10		2	2								
	Sb	51	2	2	6	2	6	10	2	6	10		2	3								
	Te	52	2	2	6	2	6	10	2	6	10		2	4								
	I	53	2	2	6	2	6	10	2	6	10		2	5								
	Xe	54	2	2	6	2	6	10	2	6	10		2	6								
n = 6	Cs	55	2	2	6	2	6	10	2	6	10		2	6			1					
	Ba	56	2	2	6	2	6	10	2	6	10		2	6			2					
	La	57	2	2	6	2	6	10	2	6	10		2	6	1		2					
	Ce	58	2	2	6	2	6	10	2	6	10	1	2	6	1		2					
	Pr	59	2	2	6	2	6	10	2	6	10	2	2	6	1		2					
	Nd	60	2	2	6	2	6	10	2	6	10	3	2	6	1		2					
	Pm	61	2	2	6	2	6	10	2	6	10	4	2	6	1		2					
	Sm	62	2	2	6	2	6	10	2	6	10	5	2	6	1		2					
	Eu	63	2	2	6	2	6	10	2	6	10	6	2	6	1		2					
	Gd	64	2	2	6	2	6	10	2	6	10	7	2	6	1		2					
	Tb	65	2	2	6	2	6	10	2	6	10	8	2	6	1		2					
	Dy	66	2	2	6	2	6	10	2	6	10	9	2	6	1		2					
	Ho	67	2	2	6	2	6	10	2	6	10	10	2	6	1		2					
	Er	68	2	2	6	2	6	10	2	6	10	11	2	6	1		2					
	Tm	69	2	2	6	2	6	10	2	6	10	12	2	6	1		2					
	Yb	70	2	2	6	2	6	10	2	6	10	13	2	6	1		2					
	Lu	71	2	2	6	2	6	10	2	6	10	14	2	6	1		2					
	Hf	72	2	2	6	2	6	10	2	6	10	14	2	6	2		2					
	Ta	73	2	2	6	2	6	10	2	6	10	14	2	6	3		2					
	W	74	2	2	6	2	6	10	2	6	10	14	2	6	4		2					

Shell		K	L	M	N	O	P	Q
Orbital		1*s*	2*s* 2*p*	3*s* 3*p* 3*d*	4*s* 4*p* 4*d* 4*f*	5*s* 5*p* 5*d* 5*f*	6*s* 6*p* 6*d* 6*f*	7*s* 7*p*
Element	**At. No.**							
Re	75	2	2 6	2 6 10	2 6 10 14	2 6 5	2	
Os	76	2	2 6	2 6 10	2 6 10 14	2 6 6	2	
Ir	77	2	2 6	2 6 10	2 6 10 14	2 6 7	2	
**Pt	78	2	2 6	2 6 10	2 6 10 14	2 6 9	1	
*Au	79	2	2 6	2 6 10	2 6 10 14	2 6 10	1	
Hg	80	2	2 6	2 6 10	2 6 10 14	2 6 10	2	
Tl	81	2	2 6 2	2 6 10	2 6 10 14	2 6 10	2 1	
Pb	82	2	6	2 6 10	2 6 10 14	2 6 10	2 2	
Bi	83	2	2 6	2 6 10	2 6 10 14	2 6 10	2 3	
Po	84	2	2 6	2 6 10	2 6 10 14	2 6 10	2 4	
At	85	2	2 6	2 6 10	2 6 10 14	2 6 10	2 5	
Rn	86	2	2 6	2 6 10	2 6 10 14	2 6 10	2 6	
Fr	87	2	2 6	2 6 10	2 6 10 14	2 6 10	2 6	1
Ra	88	2	2 6	2 6 10	2 6 10 14	2 6 10	2 6	2
Ac	89	2	2 6	2 6 10	2 6 10 14	2 6 10	2 6 1	2
Th	90	2	2 6	2 6 10	2 6 10 14	2 6 10 1	2 6 1	2
Pa	91	2	2 6	2 6 10	2 6 10 14	2 6 10 2	2 6 1	2
U	92	2	2 6	2 6 10	2 6 10 14	2 6 10 3	2 6 1	2
Np	93	2	2 6	2 6 10	2 6 10 14	2 6 10 4	2 6 1	2
Pu	94	2	2 6	2 6 10	2 6 10 14	2 6 10 5	2 6 1	2
Am	95	2	2 6	2 6 10	2 6 10 14	2 6 10 6	2 6 1	2
Cm	96	2	2 6	2 6 10	2 6 10 14	2 6 10 7	2 6 1	2
Dk	97	2	2 6	2 6 10	2 6 10 14	2 6 10 8	2 6 1	2
Cf	98	2	2 6	2 6 10	2 6 10 14	2 6 10 9	2 6 1	2
Es	99	2	2 6	2 6 10	2 6 10 14	2 6 10 10	2 6 1	2
Fm	100	2	2 6	2 6 10	2 6 10 14	2 6 10 11	2 6 1	2
Md	101	2	2 6	2 6 10	2 6 10 14	2 6 10 12	2 6 1	2
No	102	2	2 6	2 6 10	2 6 10 14	2 6 10 13	2 6 1	2
Lr	103	2	2 6	2 6 10	2 6 10 14	2 6 10 14	2 6 1	2

$n = 7$

* As a result of inter-electronic repulsions, the electrons differing slightly in their energies have a preference to enter into those orbitals which thereby get either completely filled or just half-filled. This explains the anomalous configurations of Cr, Cu, Mo, Ag, Pd, Au, etc., see sub-Sec 5.4.1.

** Anomalous configurations of Nb, Ru, Rh and Pt can be explained on the basis of nucleus- electron and electron-electron forces, see sub-Sec 5.4.2.

5.4.1 Stability of Half-filled and Completely Filled Orbitals

You can see in Table 5.2 above that upto calcium (atomic number 20), the electrons are filled in the orbitals according to the sequence given in Fig. 5.2. Thus for calcium, the electronic configuration can be written as follows:

$$\text{Ca} \quad - \quad 1s^2\, 2s^2\, 2p^6\, 3s^2\, 3p^6\, 4s^2$$

Then, in scandium (Sc) having atomic number, $Z = 21$, the electrons start filling up the 3*d* orbital. And, in titanium (Ti, $Z = 22$) and Vanadium (V, $Z = 23$), there are 2 and 3 electrons, respectively in the 3*d* orbital. However, the next element chromium (Cr, $Z = 24$) has the following configuration;

Cr – $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^1\ 3d^5$

in which 5 electrons are present in 3*d* orbitals while 1 electron is present in 4*s* orbital. This configuration is different from the expected one. We would have expected in continuity with the filling of *3d* orbitals in scandium, titanium and vanadium, the last electron in chromium to enter into 3*d* orbital to give the following configuration;

Cr – $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^4$

The actual configuration of chromium shown above $(4s^1\,3d^5)$ has half-filled 4*s* and 3*d* orbitals. There are other elements also, shown by asterisk (*) mark in Table 5.2 in which the electrons fill the orbitals in such a way that the orbitals are either completely filled or are half-filled. The electronic configuration of some such elements are given below:

Mo ($Z = 42$) – $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^{10}\ 4p^6\ 5s^1\ 4d^5$

Ag ($Z = 47$) – $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^{10}\ 4p^6\ 5s^1\ 4d^{10}$

The extra stability associated with elements such as chromium, copper, molybdenum, silver, palladium, gold etc., can be explained on the basis of their electronic configuration and half-filled or completely-filled orbitals. The extra stability associated with half-filled or completely-filled orbitals can be accounted for due to more symmetrical distribution of electrons in such arrangements and the stability gained by exchange of electrons with each other. Such an exchange stabilises that particular configuration and the energy associated with the exchange process is known as exchange energy. This is discussed below in detail.

5.4.2 Concept of Exchange Energy

The extra stability associated with electronic configurations having electrons with parallel spins can be explained on the basis of the exchange energy. ***Exchange energy* is the energy released when two or more electrons with the same spin *exchange* their positions when present in the degenerate orbitals of a sub-shell.**

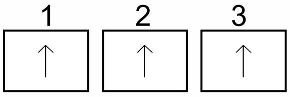
The exchange energy is a quantum-mechanical concept. It is given by the following equation:

$$E_{ex} = \sum \frac{N(N-1)}{2} K \qquad \dots (5.1)$$

where *N* is the number of electrons with parallel spins. From the above equation, you can see that the exchange energy increases rapidly as the number of electrons with parallel spins increases. Using Eq. 5.1, we can calculate the exchange energy for different values of *N* and can, thereby, compare the electronic configurations having different *N* values.

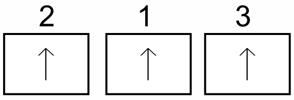
Let us see the exchange energy in case of nitrogen atom. The electronic configuration of nitrogen is $1s^2\,2s^2\,2p^3$.

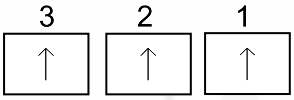
Here, the three *p* electrons can be arranged in the following ways in the three *p* orbitals.



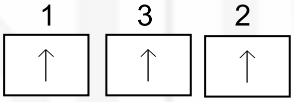
Here, all the three electrons are present in separate *p* orbitals and they have parallel spins. Let us see how various exchanges are possible between the above three electrons.

i) when electron 1 exchanges positions, it can do with electrons 2 and 3 as shown below:





ii) when electron 2 exchanges position with electron 3, we get the following:



Thus, in total three exchanges are possible giving rise to exchange energy, $E_{ex} = \prod_e = 3K$.

The number of exchanges possible determine the exchange energy. Thus, the higher the number of possible exchanges, the lower will be the exchange energy.

Having understood the concept of exchange energy one can analyse the situation for the expected as well as the actual electronic configuration of elements mentioned above which have half-filled or completely filled orbitals.

Why don't you try yourself to workout the number of exchanges possible for the expected and the actual configuration of chromium. We hope that you get the following correct answer for this. For the configuration $3d^4\,4s^2$, the number of exchanges is 6 while for the configuration $3d^5\,4s^1$, the number of exchanges in 10. Hence, the exchange energy associated with $3d^5\,4s^1$ configuration is more as compared to $3d^4\,4s^2$ configuration.

Thus, we can say that the number of possible exchanges is higher in half-filled and completely filled orbitals; hence, more exchange energy leading to their greater stability.

In addition to exchange energy, there are other factors such as electron-electron repulsion and nucleus-electron attraction which also influence the stability of a particular arrangement of electrons in the orbitals. Let us now study the configurations of some more elements which are unusual, when the electrons are filled in their various orbitals.

5.4.3 Anomalous Electronic Configurations

There are few more elements which have electronic configurations not predicted by the *aufbau* principle and they do not have half-filled or completely-filled orbitals. These elements are said to have *anomalous configurations.*

The example of such elements are niobium (Nb), ruthenium (Ru), rhodium (Rh) and platinum (Pt). These elements are shown in Table 5.2 above with double asterisks (**) mark.

The electronic configuration of some of these elements are given below.

Nb (Z= 41) − $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^1 4d^4$

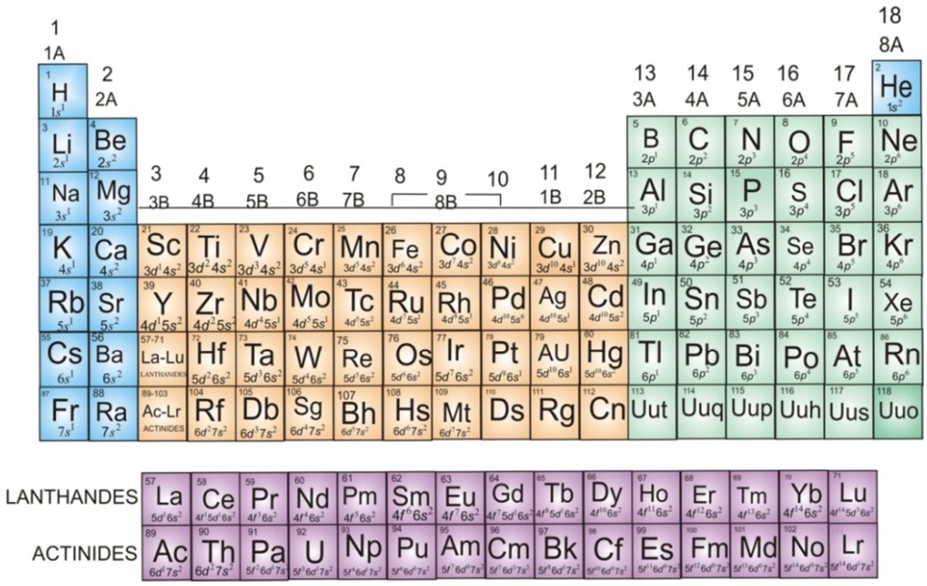
Ru (Z= 44) − $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^1 4d^7$

Rh (Z = 45) − $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^1 4d^8$

The anomalous configuration of these elements can be explained by taking into account electron-electron repulsion and nucleus-electron attractions in these elements.

Based on their electronic configurations, the various elements can be arranged into different blocks of the Periodic Table according to the filling of the electrons in various orbitals. For example, the elements in which the *s* orbitals are being filled constitute the *s* block. Similarly, *p, d* and *f* block elements can be interpreted. Such a periodic table is given in Fig. 5.3. The various groups are numbered according to both the old and new conventions of numbering. Numbering the groups from 1 to 18 has been recently adopted by IUPAC.

Table 5.3: Periodic Table showing Electronic Configurations of Elements



1 1A	2 2A	3 3B	4 4B	5 5B	6 6B	7 7B	8	9 8B	10	11 1B	12 2B	13 3A	14 4A	15 5A	16 6A	17 7A	18 8A
1 H $1s^1$																	2 He $1s^2$
3 Li $2s^1$	4 Be $2s^2$											5 B $2p^1$	6 C $2p^2$	7 N $2p^3$	8 O $2p^4$	9 F $2p^5$	10 Ne $2p^6$
11 Na $3s^1$	12 Mg $3s^2$											13 Al $3p^1$	14 Si $3p^2$	15 P $3p^3$	16 S $3p^4$	17 Cl $3p^5$	18 Ar $3p^6$
19 K $4s^1$	20 Ca $4s^2$	21 Sc $3d^1 4s^2$	22 Ti $3d^2 4s^2$	23 V $3d^3 4s^2$	24 Cr $3d^5 4s^1$	25 Mn $3d^5 4s^2$	26 Fe $3d^6 4s^2$	27 Co $3d^7 4s^2$	28 Ni $3d^8 4s^2$	29 Cu $3d^{10} 4s^1$	30 Zn $3d^{10} 4s^2$	31 Ga $4p^1$	32 Ge $4p^2$	33 As $4p^3$	34 Se $4p^4$	35 Br $4p^5$	36 Kr $4p^6$
37 Rb $5s^1$	38 Sr $5s^2$	39 Y $4d^1 5s^2$	40 Zr $4d^2 5s^2$	41 Nb $4d^4 5s^1$	42 Mo $4d^5 5s^1$	43 Tc $4d^5 5s^2$	44 Ru $4d^7 5s^1$	45 Rh $4d^8 5s^1$	46 Pd $4d^{10} 5s^0$	47 Ag $4d^{10} 5s^1$	48 Cd $4d^{10} 5s^2$	49 In $5p^1$	50 Sn $5p^2$	51 Sb $5p^3$	52 Te $5p^4$	53 I $5p^5$	54 Xe $5p^6$
55 Cs $6s^1$	56 Ba $6s^2$	57-71 La-Lu LANTHANIDES	72 Hf $5d^2 6s^2$	73 Ta $5d^3 6s^2$	74 W $5d^4 6s^2$	75 Re $5d^5 6s^2$	76 Os $5d^6 6s^2$	77 Ir $5d^7 6s^2$	78 Pt $5d^9 6s^1$	79 AU $5d^{10} 6s^1$	80 Hg $5d^{10} 6s^2$	81 Tl $6p^1$	82 Pb $6p^2$	83 Bi $6p^3$	84 Po $6p^4$	85 At $6p^5$	86 Rn $6p^6$
87 Fr $7s^1$	88 Ra $7s^2$	89-103 Ac-Lr ACTINIDES	104 Rf $6d^2 7s^2$	105 Db $6d^3 7s^2$	106 Sg $6d^4 7s^2$	107 Bh $6d^5 7s^2$	108 Hs $6d^6 7s^2$	109 Mt $6d^7 7s^2$	110 Ds	111 Rg	112 Cn	113 Uut	114 Uuq	115 Uup	116 Uuh	117 Uus	118 Uuo

LANTHANDES	57 La $5d^1 6s^2$	58 Ce $4f^1 5d^1 6s^2$	59 Pr $4f^3 6s^2$	60 Nd $4f^4 6s^2$	61 Pm $4f^5 6s^2$	62 Sm $4f^6 6s^2$	63 Eu $4f^7 6s^2$	64 Gd $4f^7 5d^1 6s^2$	65 Tb $4f^8 5d^1 6s^2$	66 Dy $4f^{10} 6s^2$	67 Ho $4f^{11} 6s^2$	68 Er $4f^{12} 6s^2$	69 Tm $4f^{13} 6s^2$	70 Yb $4f^{14} 6s^2$	71 Lu $4f^{14} 5d^1 6s^2$
ACTINIDES	89 Ac $6d^1 7s^2$	90 Th $6d^2 7s^2$	91 Pa $5f^2 6d^1 7s^2$	92 U $5f^3 6d^1 7s^2$	93 Np $5f^4 6d^1 7s^2$	94 Pu $5f^6 6d^0 7s^2$	95 Am $5f^7 6d^0 7s^2$	96 Cm $5f^7 6d^1 7s^2$	97 Bk $5f^8 6d^1 7s^2$	98 Cf $5f^{10} 6d^0 7s^2$	99 Es $5f^{11} 6d^0 7s^2$	100 Fm $5f^{12} 6d^0 7s^2$	101 Md $5f^{13} 6d^0 7s^2$	102 No $5f^{14} 6d^0 7s^2$	103 Lr $5f^{14} 6d^1 7s^2$

SAQ 3

Write electron configurations of P and Ca and indicate the block of the periodic table, in which they occur.

SAQ 4

Write and explain the electronic configuration of palladium having atomic number 46.

SAQ 5

Write the electronic configuration of platinum (Z = 78) and explain your answer.

5.5 SUMMARY

In this unit, we have learnt about the electronic configuration of multi-electron atoms. We studied that the degeneracy of orbitals is lifted in case of multi-electron atoms. Thus, these energy levels could be arranged in the increasing order of their energy. We also explained various rules for filling of electrons into the energy levels in case of multi-electron atoms. Under these rules, we discussed *aufbau* principle, Hund's rule and Pauli exclusion principle. Then, we learnt about the filling of electrons in the orbitals in the light of these rules. The electronic configurations of some simple atoms were discussed. The stability of half-filled and completely-filled orbitals was described in the light of the exchange energy. Finally, the anomalous electronic configurations of some elements were explained.

5.6 TERMINAL QUESTIONS

1. Arrange the following orbitals in the increasing order of their energies:

   $4s$, $4p$, $3d$, $5p$, $4f$, $6p$

2. State Pauli exclusion principle.

3. Why does Cr have electronic configuration $1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,4s^1\,3d^5$ and not $1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,4s^2\,3d^4$?

4. Explain the extra stability associated with copper and gold.

5. Write the electron configuration for the following elements:

   Si, S, Cl, Ar.

6. Write electron configuration for the following ions:

   H^-, Li^+, O^{2-}, Na^+ and Mg^{2+}

5.7 ANSWERS

Self-Assessment Questions

1. i) $3d$

   ii) $3d$

   iii) $4f$

2. 10 because each $3d$ orbital can accommodate a maximum of two electrons according to Pauli exclusion principle and there are five such $3d$orbtials.

3. Electron configurations of P (At. No. 15) and Ca (At. No. 20) are,

   P $= 1s^2 2s^2 2p^6 3s^2 3p^3$ *p* block

   Ca $= 1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$ *s* block

4. The electronic configuration of palladium is

   $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 4d^{10}$

   Since all orbitals in palladium are completely filled, it has the stable configuration shown above.

5. The electronic configuration of platinum is $[\text{Xe}]\, 6s^1 4f^{14} 5d^9$. The stability of this configuration can be explained by taking into a account the electron-electron repulsion and nucleus-electron attractions in the atom.

Terminal Questions

1. $3d < 4s < 4p < 5p < 4f < 6p$

2. Pauli exclusion principle states that no two electrons in an atom can have the same set of four quantum numbers.

3. Cr has electronic configuration $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1 3d^5$ because here, the $3d$ and $4s$ orbitals are half-filled; therefore, this configuration is more stable than $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^4$.

4. Copper having 29 electrons has electronic configuration [Ar] $4s^1 3d^{10}$. Here, $3d$ orbital is completely filled and $4s$ orbital is half-filled. Similarly, gold having 79 electrons has configuration [Xe] $6s^1 4f^{14} 5d^{10}$. Here, $4f$ and $3d$ orbitals are completely filled while $6s$ orbital half-filled. Since elements with partially filled and completely filled orbitals show extra stability, copper and gold are stable in nature.

5. Si $1s^2 2s^2 2p^6 3s^2 3p^2$

   S $1s^2 2s^2 2p^6 3s^2 3p^4$

   Cl $1s^2 2s^2 2p^6 3s^2 3p^5$

   Ar $1s^2 2s^2 2p^6 3s^2 3p^6$

6. H^- $1s^2$

   Li^+ $1s^2$

   O^{2-} $1s^2\,2s^2\,2p^6$

   Na^+ $1s^2\,2s^2\,2p^6$

   Mg^{2+} $1s^2\,2s^2\,2p^6$

Further Reading

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