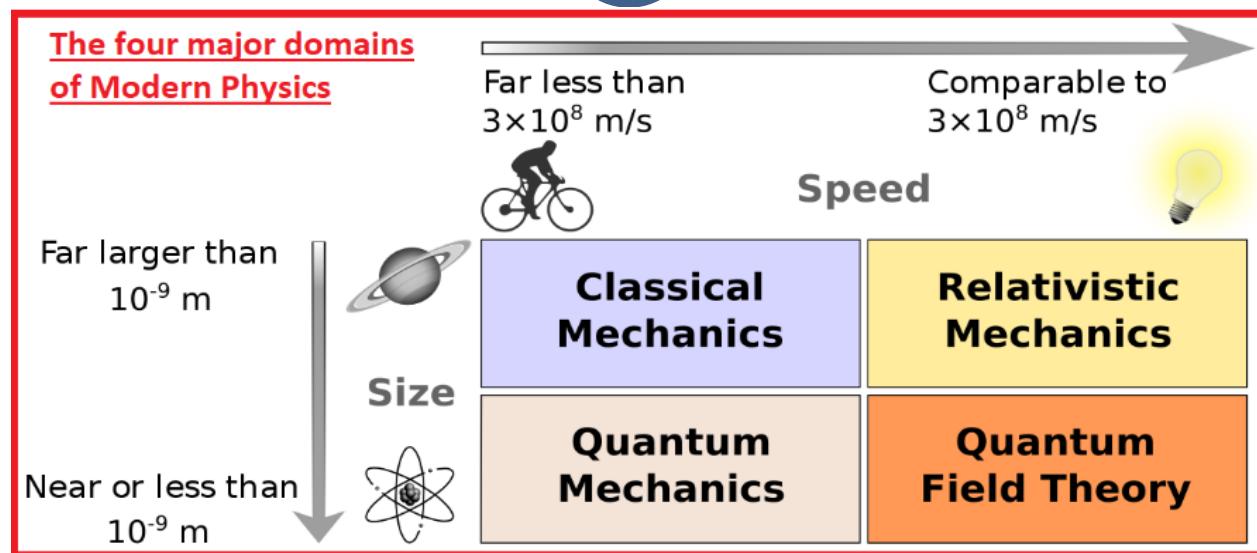


Chapter 12 : ATOMS

The following clipping is from NCERT book (Volume 2)

CHAPTER TWELVE ATOMS

- 12.1** Introduction
- 12.2** Alpha-particle Scattering and Rutherford's Nuclear Model of Atom
- 12.3** Atomic Spectra
- 12.4** Bohr Model of the Hydrogen Atom
- 12.5** The Line Spectra of the Hydrogen Atom
- 12.6** DE Broglie's Explanation of Bohr's Second Postulate of Quantisation



- The definition of a classical theory depends on context. Classical physical concepts are often used when modern theories are unnecessarily complex for a particular situation.
- In practice, physical objects ranging from those larger than atoms and molecules, to objects in the macroscopic and astronomical realm, can be well-described (understood) with classical mechanics. Beginning at the atomic level and lower, the laws of classical physics break down and generally do not provide a correct description of nature.
- Traditionally, light was reconciled with classical mechanics by assuming the existence of a stationary medium through which light propagated, the luminiferous aether, which was later shown not to exist.
- Mathematically, classical physics equations are those in which Planck's constant does not appear. According to the **correspondence principle** and **Ehrenfest's theorem**, as a system becomes larger or more massive the classical dynamics tends to emerge, with some exceptions, such as **superfluidity**. This is why we can usually ignore quantum mechanics when dealing with everyday objects and the classical description will suffice.
- See glossary of classical physics : https://en.wikipedia.org/wiki/Glossary_of_classical_physics#Y

Definition of Matter

- Matter is defined as anything that takes up space and has mass. Everything around you is made up of matter. Matter is a generic term for the "stuff" around you. (Matter is any substance that has mass and takes up space by having volume)
- Taking up space means that an object has a measurable size or volume.
- Mass is a property of matter that is a measure of its resistance to acceleration.
- Another property of matter is that it has a gravitational force, such that objects attract each other with a weak force.
- However, the matter does not include massless particles such as **photons**, or other energy phenomena or waves such as **light** or **sound**. Matter exists in various states (also known as phases). These include classical everyday phases such as solid, liquid, and gas – for example water exists as ice, liquid water, and gaseous steam – but other states are possible, including plasma, Bose–Einstein condensates, fermionic condensates, and quark–gluon plasma.
- See later “The Atomic Theory of Matter” (aka “Atomic Hypothesis of Matter”)

Atoms

An atom is the smallest constituent unit of ordinary **matter** that has the properties of a chemical element. Every solid, liquid, gas, and plasma is composed of neutral or ionized atoms. Atoms are extremely small; Typical sizes are around **100 picometers (pico = 10^{-12}) → $100\text{pm} = 10^{-10}\text{m} = 1 \text{ angstrom } (\text{\AA}) = 1 \text{ \AA}$**

Atoms are small enough that attempting to predict their behaviour using classical physics – as if they were billiard balls, for example – gives noticeably incorrect predictions due to quantum effects. Through the development of physics, atomic models have incorporated quantum principles to better explain and predict this behaviour.

Every atom is composed of a nucleus and one or more electrons bound to the nucleus. The nucleus is made of one or more protons and typically a similar number of neutrons. **Protons and neutrons are called nucleons.** More than 99.94% of an atom's mass is in the nucleus. The protons have a positive electric charge, the electrons have a negative electric charge, and the neutrons have no electric charge. If the number of protons and electrons are equal, that atom is electrically neutral.

If an atom has more or fewer electrons than protons, then it has an overall negative or positive charge, respectively, and **it is called an ion.**

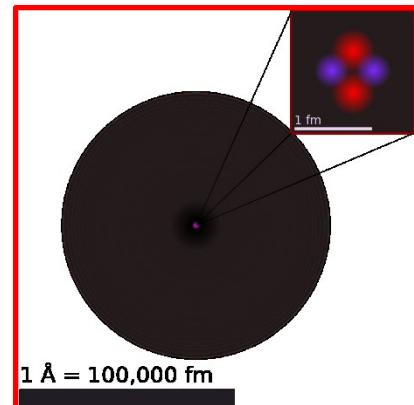
The electrons of an atom are attracted to the protons in an atomic nucleus by this **electromagnetic force**. The protons and neutrons in the nucleus are attracted to each other by a different force, the **nuclear force**, which is usually stronger than the electromagnetic force repelling the positively charged protons from one another. Under certain circumstances, the repelling electromagnetic force becomes stronger than the nuclear force, and nucleons can be ejected from the nucleus, leaving behind a different element: nuclear decay resulting in nuclear transmutation.

The number of protons in the nucleus defines to what chemical element the atom belongs: for example,

- All copper atoms contain 29 protons.
- The number of neutrons defines the isotope of the element.
- The number of electrons influences the magnetic properties of an atom.
- Atoms can attach to one or more other atoms by chemical bonds to form chemical compounds such as molecules. The ability of atoms to associate and dissociate is responsible for most of the physical changes observed in nature and is the subject of the discipline of chemistry.

Prefix		Base 10
Name	Symbol	
yotta	Y	10^{24}
zetta	Z	10^{21}
exa	E	10^{18}
peta	P	10^{15}
tera	T	10^{12}
giga	G	10^9
mega	M	10^6
kilo	k	10^3
hecto	h	10^2
deca	da	10^1
		10^0
deci	d	10^{-1}
centi	c	10^{-2}
milli	m	10^{-3}
micro	μ	10^{-6}
nano	n	10^{-9}
pico	p	10^{-12}
femto	f	10^{-15}
atto	a	10^{-18}
zepto	z	10^{-21}
yocto	y	10^{-24}

Atomic Radius or Diameter : Difficulty in describing size of an atom



➤ **Definitions**: Widely used definitions of atomic radius include:

- **Van der Waals radius:** in principle, half the minimum distance between the nuclei of two atoms of the element that are not bound to the same molecule.
 - **Ionic radius:** the nominal radius of the ions of an element in a specific ionization state, deduced from the spacing of atomic nuclei in crystalline salts that include that ion. In principle, the spacing between two adjacent oppositely charged ions (the length of the ionic bond between them) should equal the sum of their ionic radii.
 - **Covalent radius:** the nominal radius of the atoms of an element when covalently bound to other atoms, as deduced from the separation between the atomic nuclei in molecules. In principle, the distance between two atoms that are bound to each other in a molecule (the length of that covalent bond) should equal the sum of their covalent radii.
 - Metallic radius: the nominal radius of atoms of an element when joined to other atoms by metallic bonds.
 - **Bohr radius:** the radius of the lowest-energy electron orbit predicted by Bohr model of the atom (1913). It is only applicable to atoms and ions with a single electron, such as hydrogen, singly ionized helium, and positronium. Although the model itself is now obsolete, the Bohr radius for the hydrogen atom is still regarded as an important physical constant.

Calculated atomic radii [edit]

The following table shows atomic radii computed from theoretical models, as published by Enrico Clementi and others in 1967.^[10] The values are in picometres (pm).

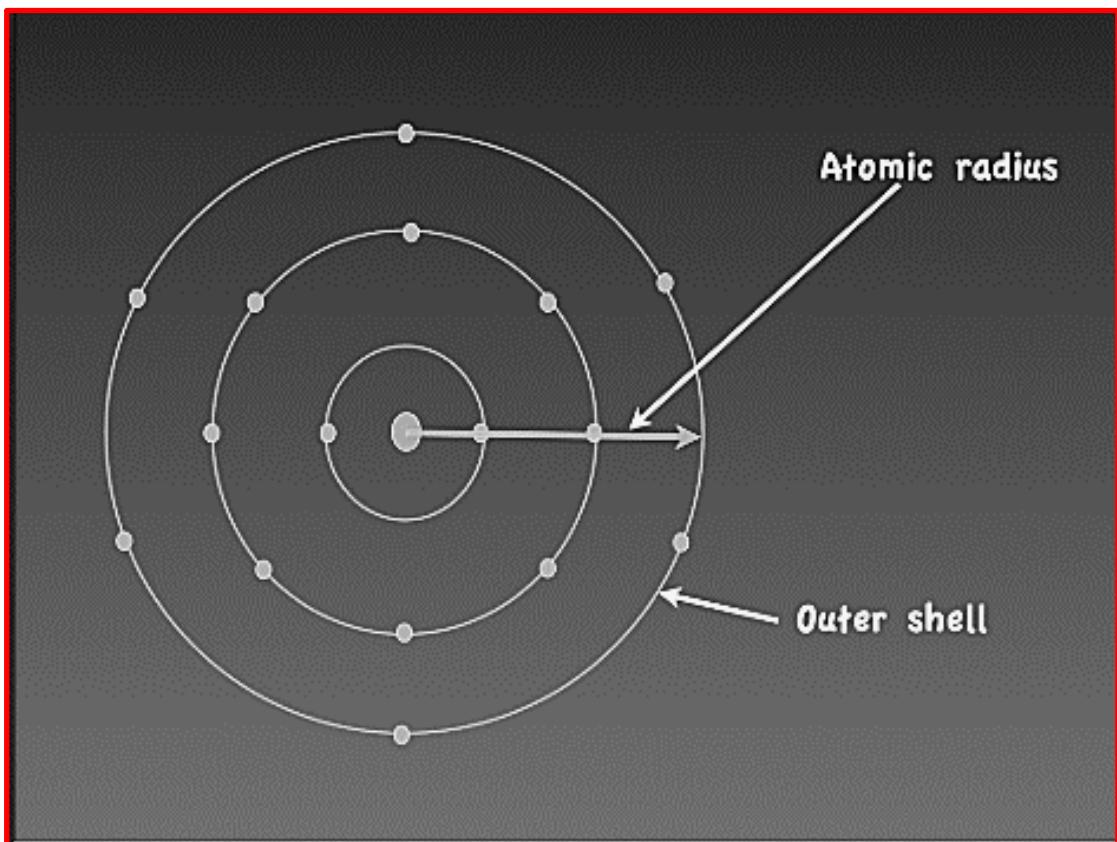
Group (column)	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
Period (row)	H 53	Li 167	Be 112										B 87	C 67	N 56	O 48	F 42	He 31
1																		Ne 38
2													Al 118	Si 111	P 98	S 88	Cl 79	Ar 71
3																		Kr 88
4	K 243	Ca 194	Sc 184	Ti 176	V 171	Cr 166	Mn 161	Fe 156	Co 152	Ni 149	Cu 145	Zn 142	Ga 136	Ge 125	As 114	Se 103	Br 94	Rn 86
5	Rb 265	Sr 219	Y 212	Zr 206	Nb 198	Mo 190	Tc 183	Ru 178	Rh 173	Pd 169	Ag 165	Cd 161	In 156	Sn 145	Sb 133	Te 123	I 115	Xe 108
6	Cs 298	Ba 253	*	Hf 208	Ta 200	W 193	Re 188	Os 185	Ir 180	Pt 177	Au 174	Hg 171	Tl 156	Pb 154	Bi 143	Po 135	At 127	Rn 120
7	Fr Ra		**	Rf 208	Db 200	Sg 193	Bh 188	Hs 185	Mt 180	Ds 177	Rg 174	Cn 171	Nh 156	Fl 154	Mc 143	Lv 135	Ts 127	Og 120
Lanthanides	*	La 226	Ce 210	Pr 247	Nd 206	Pm 205	Sm 238	Eu 231	Gd 233	Tb 225	Dy 228	Ho 226	Er 226	Tm 222	Yb 222	Lu 217		
Actinides	**	Ac 227	Th 229	Pa 231	U 234	Np 237	Pu 241	Am 243	Cm 247	Bk 249	Cf 251	Es 252	Fm 253	Md 254	No 255	Lr 256		

The following table shows empirically measured **covalent radii** for the elements, as published by J. C. Slater in 1964.^[8] The values are in picometers (pm or 1×10^{-12} m), with an accuracy of about 5 pm. The shade of the box ranges from red to yellow as the radius increases; gray indicates lack of data.

Group (column)	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	
Period (row)																			
1	H 25															He			
2	Li 145	Be 105													B 85	C 70	N 65	O 60	F 50
3	Na 180	Mg 150													Al 125	Si 110	P 100	S 100	Cl 100
4	K 220	Ca 180	Sc 160	Ti 140	V 135	Cr 140	Mn 140	Fe 140	Co 135	Ni 135	Cu 135	Zn 135	Ga 130	Ge 125	As 115	Se 115	Br 115	Kr	
5	Rb 235	Sr 200	Y 180	Zr 155	Nb 145	Mo 145	Tc 135	Ru 130	Rh 135	Pd 140	Ag 160	Cd 155	In 155	Sn 145	Sb 145	Te 140	I 140	Xe	
6	Cs 260	Ba 215	*	Hf 155	Ta 145	W 135	Re 135	Os 130	Ir 135	Pt 135	Au 135	Hg 150	Tl 190	Pb 180	Bi 160	Po 190	At	Rn	
7	Fr 215	Ra 215	**	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn	Nh	Fl	Mc	Lv	Ts	Og	
Lanthanides	*	La 195	Ce 185	Pr 185	Nd 185	Pm 185	Sm 185	Eu 185	Gd 180	Tb 175	Dy 175	Ho 175	Er 175	Tm 175	Yb 175	Lu 175			
Actinides	**	Ac 195	Th 180	Pa 180	U 175	Np 175	Pu 175	Am 175	Cm 175	Bk	Cf	Es	Fm	No	Lr				

- An atom is one of the basic units of matter.
- Everything around us is made up of atoms.
- An atom is a million times smaller than the thickest human hair.
- The **diameter** of an atom ranges from about 0.1 to 0.5 nm (nanometers) → (1×10^{-10} m to 5×10^{-10} m).
 - $0.1\text{nm} = 0.1 \times 10^{-9}\text{ m} = 1 \times 10^{-10}\text{ m} = 1\text{ \AA}$
 - $0.5\text{nm} = 0.5 \times 10^{-9}\text{ m} = 5 \times 10^{-10}\text{ m} = 5\text{ \AA}$
- The **Radius** of an atom ranges from about 0.05 to 0.25 nm (nanometers) → (0.5×10^{-10} m to 2.5×10^{-10} m).
 - $0.05\text{nm} = 0.05 \times 10^{-9}\text{ m} = 0.05 \times 10^{-10}\text{ m} = 0.05\text{ \AA}$
 - $0.25\text{nm} = 0.25 \times 10^{-9}\text{ m} = 0.25 \times 10^{-10}\text{ m} = 0.25\text{ \AA}$
- An atom is one of the basic units of matter. Atoms form the building blocks of the simplest substances, the chemical elements. Nearly everything on earth is made up of atoms. Each element consists of one basic kind of atom.
 - An atom is incredibly small -- more than a million times smaller than the thickness of a human hair. Tiny as atoms are, they consist of even more minute particles.
 - The three basic types are protons, neutrons, and electrons.
 - Protons have a positive electrical charge, and electrons have a negative charge. Neutrons are electrically neutral.
 - The protons and neutrons are crowded into the nucleus, a tiny region at the center of the atom. The nucleus makes up nearly all the mass of an atom. The rest of the atom outside the nucleus is mostly empty space.
 - The electrons whirl through this space.
 - All atoms of the same element have the same number of protons. The atomic number tells how many protons an atom has.
- **The size of an atom is difficult to describe because atoms have no definite outer boundary.**
 - To overcome this problem, the size of an atom is estimated by describing its radius.
 - In metals, this is done by measuring the distance between two nuclei in the solid state and dividing this distance by 2.
 - For non-metallic elements that exist in pure form as molecules measurements can be made of the distance between nuclei for two atoms covalently bonded together.
 - The **diameter** of an atom ranges from 1×10^{-10} m to 5×10^{-10} m. There is no one definite diameter of an atom because since the number of electrons in the outer principal energy level increases as you go from left to right in each period, the corresponding increase in the nuclear charge due to the additional protons pulls the electrons more tightly around the nucleus. This attraction results in the radius to be generally reduced. For a group of elements in the periodic table, the atoms of each successive member have another outer principal energy level in the electron configuration that electrons can move to. The increased distance from the nucleus results in the atomic radius to increase in a group.
 - **The Bohr radius of the Hydrogen atom is 0.529×10^{-10} m (= 52.9pm) or (= 0.529\AA)**
 - The other atoms are bigger.

Bibliographic Entry	Result (w/surrounding text)	Standardized Result
Brown, LeMay, Bursten. <i>Chemistry-The Central Science</i> . New Jersey: Prentice Hall, 1997: 44.	"Atoms are extremely small; most have diameters between 1×10^{-10} m and 5×10^{-10} m."	0.1–0.5 nm
<i>The World book Encyclopedia</i> . vol. 1 Chicago: World Book, 1996: 870.	"The diameter of an atom ranges from about 0.1 to 0.5 nanometer."	0.1–0.5 nm
<i>The World of Science: Chemistry in Everyday Life</i> . vol. 14. Oxford: Equinox, 1989: 31.	"Atom ... name given to a relatively stable package of matter, typically about 0.1 nm across."	0.1 nm
Bixby, William. <i>Great Experimenters</i> . New York: David McKay, 1964: 150.	"According to Rutherford, the radius of the entire atom was 0.00000001 cm."	0.1 nm
Baylis, William E. <i>Macmillan Encyclopedia of Physics</i> . New York: Prentice Hall, 1996: 71.	"the Bohr radius $a_0 = 5.2917725 \times 10^{-11}$ m is the unit of length."	0.106 nm



"The Atomic Theory of Matter" (aka "Atomic Hypothesis of Matter")

Chemists make their observations in the macroscopic world and seek to understand the fundamental properties of matter at the level of the microscopic world (i.e. molecules and atoms). The reason why certain chemicals react the way they do is a direct consequence of their atomic structure.

➤ **The Atomic Theory of Matter:**

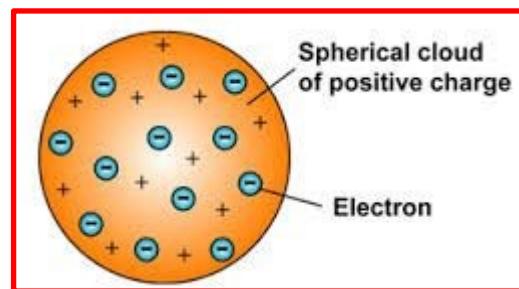
- The word "atom" is derived from the Greek word "atomos", meaning indivisible. The philosopher Democritus (460-370 B.C.) believed that matter was composed of fundamentally indivisible particles, called "atomos".

➤ **Dalton's atomic theory (1803 – 1808):**

- Each element (or matter) is composed of extremely small particles called atoms
- **Atoms are the basic building blocks of matter; they are the smallest units of an element.**
- He said atoms could not be subdivided further.
- All atoms of a given element are identical; the atoms of different elements are different and have different properties (including different masses)
 - An element is composed of only one kind of atom
 - In compounds the atoms of two or more elements combine in definite arrangements
- Atoms of an element are not changed into different types of atoms by chemical reactions; atoms are neither created nor destroyed in chemical reactions
- Compounds are formed when atoms of more than one element combine; a given compound always has the same relative number and kind of atoms.
- Atoms are the smallest particle of an element which retains the chemical properties of that element
- Simple "laws" (i.e. theories) of chemical combination which were known at the time of Dalton:
 - The law of constant composition (in a given compound the relative number and kind of atoms are constant)
 - The law of conservation of mass (the total mass of materials present after a chemical reaction is the same as the total mass before the reaction)
 - Dalton used the above "laws" to derive another "law" - the law of multiple proportions (if two elements, A and B, can combine to form more than one compound, then the ratios of the relative masses of each element which can combine can be represented by characteristically small whole numbers).
- However, Dalton could not come out with **the structure of an atom** (since during his time 1766 - 1844, the three basic particles of an atom → electron, proton and neutron were not yet discovered.)
 - Electron was discovered by Sir J.J. Thomson in 1897
 - Proton was discovered by Ernest Rutherford in 1909
 - Eugen Goldstein discovered positively charged particles, but with no clear idea of why they existed or whether they had a wider role. Rutherford correctly identified them as being individually the nucleus of a hydrogen atom. And existing in all atomic nuclei. So, it is a matter of definitions who discovered the Proton. So, Rutherford is usually given credit for discovering the proton, and he is often referred to as the "Father of Nuclear Physics".
 - Neutron was discovered by James Chadwick in 1932

➤ **Thomson's model of Atom**

- In 1897, the first model of the atom was proposed by Sir J.J. Thomson. The discovery of electron, a negatively charged particle, by Thomson led him to propose the structure of atoms.
- In 1897, when he was carrying out experiment on electric discharge through gases he discovered that atoms of different elements contain negatively charged particles (called by him as **electrons**) that are identical for all atoms.
- But since, atom as a whole is electrically neutral, an equal amount of **positive** charge must also be present somewhere in the atom. (At that time, proton was not yet discovered).
- So, what is arrangement of positive charges and electrons inside the atom? In other words, what is the structure of an atom?
- After predicting equal amount of positive charge (and his discovery of electrons) to support electrical neutral nature of the atom, Thomson proposed the FIRST model (structure) of atom in 1898.
- As per his model, the positive charge of the atom is uniformly distributed throughout the volume of the atom and the negatively charged electrons are embedded in it like seeds in a watermelon (or like plums in the pudding). This model is hence called "plum pudding model" of the atom.
 - However, in subsequent studies of atoms, the distribution proposed by Thomson is very different. We will see later the other models proposed by Rutherford and Niels Bohr.
- Thomson assumed that the harmonic oscillations of the electrons about their mean positions cause the emission of light.
- Thomson predicted if a beam of α -particles passed through an atom, it suffered only a small deflection due to weak electric forces exerted on it by positive charges.



➤ Limitations of Thomson's model :

- Thomson model could not explain the presence of discrete spectral lines (line spectra) emitted by hydrogen and other atoms, observed experimentally.
- **Line spectra and Continuous spectra:** We know that condensed matter (solids and liquids) and dense gases at all temperatures emit electromagnetic radiation in which a continuous distribution of several wavelengths is present, though with different intensities. This radiation is considered to be due to oscillations of atoms and molecules, governed by the interaction of each atom or molecule with its neighbours. In contrast, light emitted from rarefied gases heated in a flame, or excited electrically in a glow tube such as the familiar neon sign or mercury vapour light has only certain discrete wavelengths. The spectrum appears as a series of bright lines. In such gases, the average spacing between atoms is large. Hence, the radiation emitted can be considered due to individual atoms rather than because of interactions between atoms or molecules.
- In the early nineteenth century it was also established that each element is associated with a characteristic spectrum of radiation, for example, hydrogen always gives a set of lines with fixed relative position between the lines. This fact suggested an intimate relationship between the internal structure of an atom and the spectrum of radiation emitted by it. In 1885, Johann Jakob Balmer (1825 – 1898) obtained a simple empirical formula which gave the wavelengths of a group of lines emitted by atomic hydrogen. Since hydrogen is simplest of the elements known, we shall consider its spectrum in detail in this chapter.
- It cannot explain the large angle scattering of α -particles when incident on a thin metallic foil (say Gold)
- The almost free passage of cathode rays through an atom is not consistent with Thomson's model. For the atom should have a lot of empty space as suggested by Lenard, so, the positive charge should be in the form of tiny particles occupying a very small volume and not distributed uniformly.
- Hence efforts were made to look for a better model of atom. It was Ernest Rutherford who solved this problem by conducting a series of experiments from 1906 to 1911 on α -particle scattering.

➤ Rutherford's Planetary model of atom (aka Nuclear Model of the Atom)

- Rutherford and his collaborators, based on their results from α -ray scattering from a thin gold foil and arrived at radical changes in the structure of the atom (as compared to Thomson's model)
- According to their model, the entire positive charge and most of the mass of the atom is concentrated in a small volume called the nucleus with electrons revolving around the nucleus just as planets revolve around the sun. This has been proved by α -ray scattering experiment by Geiger-Marsden.
- Let us first see what is this α -ray scattering experiment by Geiger-Marsden as suggested by Rutherford (in 1911)

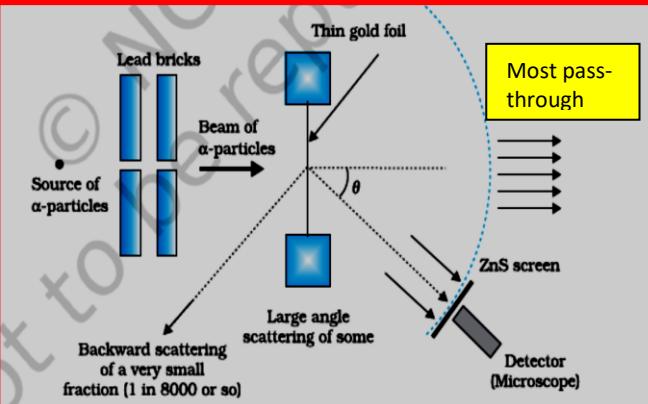
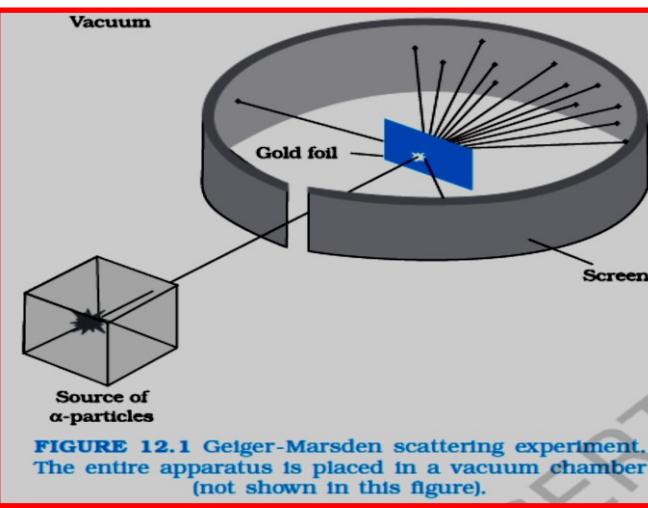


Fig. 12.1, they directed a beam of 5.5 MeV α -particles emitted from a $^{214}_{83}\text{Bi}$ radioactive source at a thin metal foil made of gold. Figure 12.2 shows a schematic diagram of this experiment. Alpha-particles emitted by a $^{214}_{83}\text{Bi}$ radioactive source were collimated into a narrow beam by their passage through lead bricks. The beam was allowed to fall on a thin foil of gold of thickness 2.1×10^{-7} m. The scattered alpha-particles were observed through a rotatable detector consisting of zinc sulphide screen and a microscope. The scattered alpha-particles on striking the screen produced brief light flashes or scintillations. These flashes may be viewed through a microscope and the distribution of the number of scattered particles may be studied as a function of angle of scattering.

- A typical graph of the total number of α -particles scattered at different angles, in a given interval of time, is shown in Fig. 12.3.
- The dots in this figure represent the data points and the solid curve is the theoretical prediction based on the assumption that the target atom has a small, dense, positively charged nucleus. Many of the α -particles pass through the foil. It means that they do not suffer any collisions.
- Only about 0.14% of the incident α -particles scatter by more than 1° ; and about 1 in 8000 deflect by more than 90° . Rutherford argued that, to deflect the α -particle backwards, it must experience a large repulsive force. This force could be provided if the greater part of the mass of the atom and its positive charge were concentrated tightly at its centre. Then the incoming α -particle could get very close to the positive charge without penetrating it, and such a close encounter would result in a large deflection. This agreement supported the hypothesis of the nuclear atom. **This is why Rutherford is credited with the discovery of the nucleus.**
- In Rutherford's nuclear model of the atom, the entire positive charge and most of the mass of the atom are concentrated in the nucleus with the electrons some distance away. The electrons would be moving in orbits about the nucleus just as the planets do around the sun.
- Rutherford's experiments suggested the size of the nucleus (**radius**) to be about 10^{-15} m to 10^{-14} m.
- From kinetic theory, the size (**diameter**) of an atom was known to be 10^{-10} m, about 10,000 to 100,000 times larger than the size of the nucleus.
- Thus, the electrons would seem to be at a distance from the nucleus of about 10,000 to 100,000 times the size of the nucleus itself.
- **Thus, most of an atom is empty space.** With the atom being largely empty space, it is easy to see why most α -particles go right through a thin metal foil. However, when α -particle happens to come near a nucleus, the intense electric field there scatters it through a large angle. The atomic electrons, being so light, do not appreciably affect the α -particles.
- The scattering data shown in Fig. 12.3 can be analysed by employing Rutherford's nuclear model of the atom. As the gold foil is very thin, it can be assumed that α -particles will suffer not more than one scattering during their passage through it. Therefore, computation of the trajectory of an alpha-particle scattered by a single nucleus is enough.
- α -particle is a helium atom from which two electrons have been removed. Thus charge on α -particle is $+2e$ and mass of α -particle is nearly 4 times the mass of a proton. α -particle is denoted by He^{2+} .
- The charge of the gold nucleus is Ze , where Z is the atomic number of the atom; for gold $Z = 79$. Since the nucleus of gold is about 50 times heavier than an α -particle, it is reasonable to assume that it remains stationary throughout the scattering process. Under these assumptions, the trajectory of an alpha-particle can be computed employing Newton's second law of motion and the Coulomb's law for electrostatic force of repulsion between the alpha-particle and the positively charged nucleus. The magnitude of this force is....

$$F = \frac{1}{4\pi\epsilon_0} \frac{(2e)(Ze)}{r^2}$$

Where r is the distance between the α -particle and the nucleus. The force is directed along the line joining the α -particle and the nucleus. The magnitude and direction of the force on an α -particle continuously changes as it approaches the nucleus and recedes away from it.

➤ Why Gold foil:

*For example, let us calculate the radius of gold atom. According to Avogadro, there are 6×10^{23} atoms in 1 gram-atom of any substance. Therefore, the volume of 6×10^{23} atoms of gold is

$$V = \frac{\text{atomic mass of gold}}{\text{density of gold}} = \frac{197 \text{ g}}{19.8 \text{ g/cm}^3} = 10 \text{ cm}^3.$$

$$\therefore \text{volume of one gold atom} = \frac{10 \text{ cm}^3}{6 \times 10^{23}} \approx 17 \times 10^{-24} \text{ cm}^3.$$

If r be the radius of the gold atom, then its volume is

$$\frac{4}{3} \pi r^3 = 17 \times 10^{-24} \text{ cm}^3.$$

$$\therefore r = \left[\frac{3 \times 17 \times 10^{-24} \text{ cm}^3}{4\pi} \right]^{1/3} \approx (4 \times 10^{-24} \text{ cm}^3)^{1/3} \approx 1.5 \times 10^{-8} \text{ cm} \approx 1.5 \times 10^{-10} \text{ m.}$$

** A "thin" gold-foil was taken to ensure that α -particle was deflected by a 'single' collision. 'Gold' foil was taken because gold can be beaten into a very thin foil and, secondly, gold-nucleus being heavy produces a large deflection in α -particle.

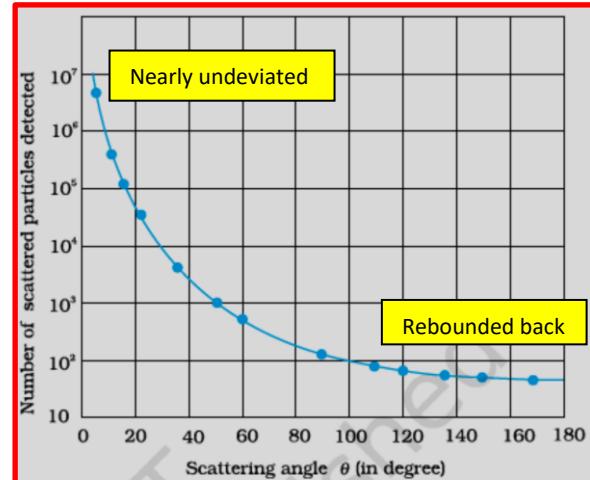


FIGURE 12.3 Experimental data points (shown by dots) on scattering of α -particles by a thin foil at different angles obtained by Geiger and Marsden using the setup shown in Figs. 12.1 and 12.2. Rutherford's nuclear model predicts the solid curve which is seen to be in good agreement with experiment.

Alpha particle trajectory and Impact parameter

- The trajectory traced by an α -particle depends on the impact parameter, b of collision.
- The impact parameter is the perpendicular distance of the initial velocity vector of the α -particle from the centre of the nucleus, when the particle is far away from the nucleus of the atom. It is denoted by 'b' in the figure → → → → → → →

 - In fact, impact parameter determines the trajectory traced by the α -particle in passing through the gold foil.

- A given beam of α -particles has a distribution of impact parameters b , so that the beam is scattered in various directions with different probabilities (Fig. 12.4). (In a beam, all particles have nearly same kinetic energy.)
- It is seen that an α -particle close to the nucleus (small impact parameter) suffers large scattering.
- In case of head-on collision, the impact parameter is minimum and the α -particle rebounds back ($\theta \approx \pi$).
- For a large impact parameter, the α -particle goes nearly undeviated and has a small deflection ($\theta \approx 0$).
- The fact that only a small fraction of the number of incident particles rebound back indicates that the number of α -particles undergoing head on collision is small. This, in turn, implies that the mass of the atom is concentrated in a small volume. Rutherford scattering therefore, is a powerful way to determine an upper limit to the size of the nucleus.
- The expression for the impact parameter (b) is derived by Rutherford in terms of θ and initial velocity U .

$$b = \frac{Ze^2 \cot\left(\frac{\theta}{2}\right)}{4\pi\epsilon_0 E}$$

; where $E = \frac{1}{2} mU^2$ is the KE of α -particle, when it is far away from the target nucleus

- For example, for gold $Z = 79$ (The atomic number or proton number (symbol Z) of a chemical element is the number of protons found in the nucleus of an atom. It is identical to the charge number of the nucleus. The atomic number uniquely identifies a chemical element. In an uncharged atom, the atomic number is also equal to the number of electrons.)
- For large values of 'b', $\cot(\theta/2)$ is large and hence scattering angle θ is small. This implies α -particles travelling far away from the target nucleus suffer small deflections. If 'b' is very very large, the α -particles suffer no deflection at all.
- For small values of 'b', $\cot(\theta/2)$ is small and hence scattering angle θ is large. This implies α -particles travelling close to the target nucleus suffer large deflections.
- So, from above equation $\cot(\theta/2)$ is proportional to 'b'; It is clear that θ decreases, when b increases.
- When $b = 0$ (α -particle is directed towards the centre of target nucleus), the $\cot(\theta/2) = 0$; $\rightarrow (\theta/2) = 90^\circ$ or $\theta = 180^\circ$.
 - Thus, α -particle travelling directly towards the centre of target nucleus retraces its path.

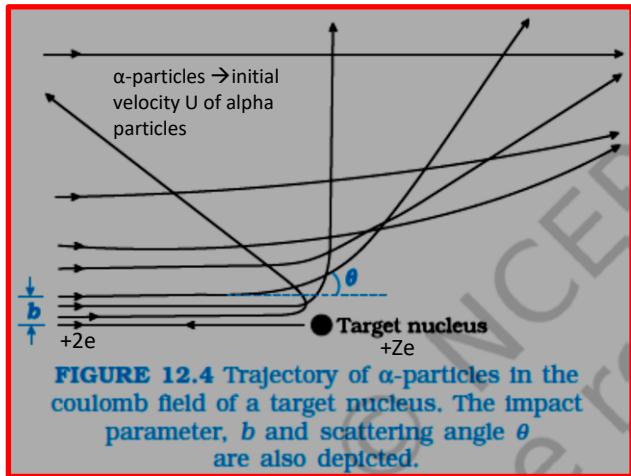


FIGURE 12.4 Trajectory of α -particles in the coulomb field of a target nucleus. The impact parameter, b and scattering angle θ are also depicted.

Example 12.1 In the Rutherford's nuclear model of the atom, the nucleus (radius about 10^{-15} m) is analogous to the sun about which the electron move in orbit (radius $\approx 10^{-10}$ m) like the earth orbits around the sun. If the dimensions of the solar system had the same proportions as those of the atom, would the earth be closer to or farther away from the sun than actually it is? The radius of earth's orbit is about 1.5×10^{11} m. The radius of sun is taken as 7×10^8 m.

Solution The ratio of the radius of electron's orbit to the radius of nucleus is $(10^{-10} \text{ m})/(10^{-15} \text{ m}) = 10^5$, that is, the radius of the electron's orbit is 10^5 times larger than the radius of nucleus. If the radius of the earth's orbit around the sun were 10^5 times larger than the radius of the sun, the radius of the earth's orbit would be $10^5 \times 7 \times 10^8 \text{ m} = 7 \times 10^{13} \text{ m}$. This is more than 100 times greater than the actual orbital radius of earth. Thus, the earth would be much farther away from the sun.

It implies that an atom contains a much greater fraction of empty space than our solar system does.

Example 12.2 In a Geiger-Marsden experiment, what is the distance of closest approach to the nucleus of a 7.7 MeV α -particle before it comes momentarily to rest and reverses its direction?

Solution The key idea here is that throughout the scattering process, the total mechanical energy of the system consisting of an α -particle and a gold nucleus is conserved. The system's initial mechanical energy is E_i , before the particle and nucleus interact, and it is equal to its mechanical energy E_f when the α -particle momentarily stops. The initial energy E_i is just the kinetic energy K of the incoming α -particle. The final energy E_f is just the electric potential energy U of the system. The potential energy U can be calculated from Eq. (12.1).

Let d be the centre-to-centre distance between the α -particle and the gold nucleus when the α -particle is at its stopping point. Then we can write the conservation of energy $E_i = E_f$ as

$$K = \frac{1}{4\pi\epsilon_0} \frac{(2e)(Ze)}{d} = \frac{2Ze^2}{4\pi\epsilon_0 d}$$

Thus the distance of closest approach d is given by

$$d = \frac{2Ze^2}{4\pi\epsilon_0 K}$$

The maximum kinetic energy found in α -particles of natural origin is 7.7 MeV or 1.2×10^{-12} J. Since $1/4\pi\epsilon_0 = 9.0 \times 10^9 \text{ N m}^2/\text{C}^2$. Therefore with $e = 1.6 \times 10^{-19} \text{ C}$, we have,

$$\begin{aligned} d &= \frac{(2)(9.0 \times 10^9 \text{ N m}^2/\text{C}^2)(1.6 \times 10^{-19} \text{ C})^2 Z}{1.2 \times 10^{-12} \text{ J}} \\ &= 3.84 \times 10^{-16} Z \text{ m} \end{aligned}$$

The atomic number of foil material gold is $Z = 79$, so that $d(\text{Au}) = 3.0 \times 10^{-14} \text{ m} = 30 \text{ fm}$. (1 fm (i.e. fermi) = 10^{-15} m .)

The radius of gold nucleus is, therefore, less than $3.0 \times 10^{-14} \text{ m}$. This is not in very good agreement with the observed result as the actual radius of gold nucleus is 6 fm. The cause of discrepancy is that the distance of closest approach is considerably larger than the sum of the radii of the gold nucleus and the α -particle. Thus, the α -particle reverses its motion without ever actually touching the gold nucleus.

Distance of Closet approach: Estimation of the size (radius) of the nucleus

Definition: The minimum distance up to which an energetic α -particle travelling directly towards a nucleus can move before coming to rest and then retracing its path is known as distance of closest approach. It is denoted by r_0 . This distance gives estimation of the size (radius) of the nucleus

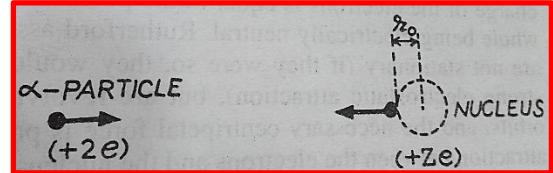
➤ Assumptions made by Rutherford:

- Motion of the nucleus is not taken into account since nucleus under consideration (gold) is very heavy as compared to α -particle
- α -particle as well as nucleus are taken as point charges

➤ Expression for distance of Closest approach:

- The α -particles are emitted with KE from a radioactive source. The particles which goes straight (head-on) towards the nucleus, reaches closest to the nucleus.
- As the α -particles approaches the nucleus, the electrostatic repulsive force due to the nucleus increases and the KE of the α -particle goes on converting into the electrostatic PE.
- When the whole of KE is converted into electrostatic PE, the α -particle can go no more towards the nucleus and returns back on its own path (see fig). Thus, the α -particle is scattered through an angle of 180° .
- Let the positive charge of target nucleus = Ze (where Z = Number of protons in the nucleus of an target atom) ; for gold $Z = 79$
- The positive charge of α -particle = $+2e$
- As the α -particle moves towards the nucleus, the force of repulsion between α -particle and the nucleus increases. This force is given by

$$F = \frac{(Ze)(2e)}{4\pi\epsilon_0 r^2} = \frac{1}{4\pi\epsilon_0} \frac{2Ze^2}{r^2} ; \text{ therefore } F \propto 1/r^2$$



- Due to this force of repulsion, the velocity of α -particle goes on decreasing, when the distance between α -particle and the nucleus = the distance of closest approach (r_0), the α -particle comes to rest. At this point or distance, the KE of α -particle is completely converted into electric PE of the system.
 - **Note: The KE of α -particle is completely converted into the PE only if impact parameter 'b' = 0**
- If u is the initial velocity of α -particle, then $KE = \frac{1}{2}mu^2$
- Electric PE of the system at the distance of closest approach = electric potential at distance r_0 due to nucleus \times charge on α -particle

$$= \frac{1}{4\pi\epsilon_0} \frac{Ze}{r_0} \times 2e = \frac{1}{4\pi\epsilon_0} \frac{2Ze^2}{r_0}$$

- At the distance of closest approach, KE of α -particle = PE of the system; i.e.

$$\frac{1}{2}mu^2 = \frac{1}{4\pi\epsilon_0} \frac{2Ze^2}{r_0}$$

$$r_0 = \frac{1}{4\pi\epsilon_0} \frac{2Ze^2}{\frac{1}{2}mu^2} = \frac{1}{4\pi\epsilon_0} \frac{2Ze^2}{K}$$

$$r_0 = \frac{1}{4\pi\epsilon_0} \frac{2Ze^2}{K} \quad ----- \quad (1)$$

- Where K is the initial kinetic energy of the α -particle
- Equation (1) is the expression for the distance of closest approach r_0 of the α -particle to the nucleus. Clearly, for a given nucleus, the value of r_0 depends upon the initial KE of the α -particle. This equation also determines the radius of the nucleus.

Example #1 : if the velocity of an α -particle (mass = 6.7×10^{-27} kg) moving towards the gold nucleus ($Z = 79$) was 2.1×10^7 ms $^{-1}$. the KE is the particle is

➤ $K = \frac{1}{2} m_\alpha v_\alpha^2 = \frac{1}{2} (6.7 \times 10^{-27}) \times (2.1 \times 10^7)^2 = 1.48 \times 10^{-12}$ J

Substituting $Z = 79$, $e = 1.6 \times 10^{-19}$ C , $K = 1.48 \times 10^{-12}$ J & $1/4\pi\epsilon_0 = 9 \times 10^9$ Nm 2 C $^{-2}$ in equation (1)

$$r_0 = (9 \times 10^9) \times 2 \times 79 \times (1.6 \times 10^{-19})^2 / 1.48 \times 10^{-12} = 2.5 \times 10^{-14}$$
 m

- So, α -particles having the above energy can approach the nucleus upto a closest distance of 2.5×10^{-14} m. Clearly, the radius of the gold nucleus will be < this because an α -particle cannot touch the periphery of the nucleus because of strong repulsion. Therefore, equation (1) gives the upper limit of the radius of the scattering nucleus.
 - If the KE of the α -particle is very large, then the particle will reach extremely close to the nucleus. In this condition, the nucleus will no more be a “point-charge” for the α -particle and the Coulomb’s law will no more be applicable.
 - In addition to it, nuclear forces (which are attractive in nature) will become active. Hence, the α -particle, instead of returning back, will penetrate into the nucleus.
 - Clearly, particles with KE > a certain limit, cannot be scattered back by the nucleus.
 - The distance of the closest approach of the α -particles with this maximum limit of KE decides the radius of the nucleus.
 - On the basis of this, the radius of the gold-nucleus has been estimated to be 6.9×10^{-15} m
-

Example #2 : An α -particle having KE = 5.5 MeV is found to retrace the path when deflected by the gold nucleus. Calculate the distance of closest approach ($Z = 79$)

➤ KE = 5.5 MeV = $5.5 \times 1.6 \times 10^{-19}$ J = 8.8×10^{-13} J

➤ $Z = 79$ and $1/4\pi\epsilon_0 = 9 \times 10^9$ Nm 2 C $^{-2}$

➤ $r_0 = \frac{1}{4\pi\epsilon_0} \frac{2Ze^2}{K} = 9 \times 10^9 \times 2 \times 79 \times (1.6 \times 10^{-19})^2 / 8.8 \times 10^{-13} = 4.13 \times 10^{-14}$ m

➤ Thus, the distance of closest approach = 4.13×10^{-14} m

➤ Radius of nucleus is taken of the order of 10^{-14} m to 10^{-15} m

Note : Hydrogen, the smallest atom has a diameter of about 1 Å. A small dot (.) as shown has a diameter of about say 1mm = 10^{-7} Å. Therefore, number of hydrogen atoms that would form a line across this dot = $1/10^{-7} = 10^7 = 10$ million or one crore. Imagine how small an atom is.

Rutherford's Nuclear Model of Atom (Postulates) (based on the results of α -scattering experiment)

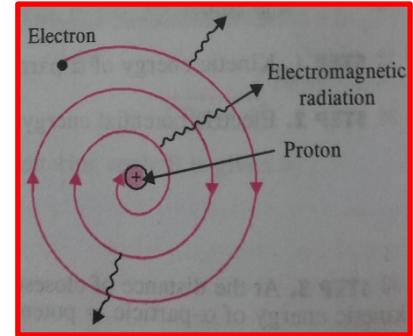
- **Postulate 1:**
 - Almost all of the mass and all the positive charges of an atom are concentrated in a very small region named as nucleus of the atom
- **Postulate 2:**
 - The size of the nucleus is extremely small (radius 10^{-14} to 10^{-15} m) as compared to the size of the atom (diameter $\approx 10^{-10}$ m)
- **Postulate 3:**
 - The negatively charged electrons revolve around the nucleus. So, most of the space in an atom is empty. The centripetal force required for revolving the electrons around the nucleus is provided by the Coulomb’s force of attraction between the nucleus and the electrons OR
 - In other words, Rutherford assumed that the electrons in the atom are not stationary (if they were so, they would be pulled into the nucleus due to the strong electrostatic attraction), but are revolving around the nucleus in different orbits, and the necessary centripetal force is provided by the electrostatic force of attraction between the electrons and nucleus.
- **Postulate 4:**
 - The number of revolving electrons = number of positive charges in the nucleus. Hence, the atom is electrically neutral.
- **Postulate 5:**
 - Rutherford’s model justified the periodic table on the basis of atomic number instead of atomic weight. In other words, Rutherford’s atomic model was supported by the periodic table of elements.

Drawbacks of Rutherford's Nuclear Model of Atom

Although Rutherford's model justified the periodic table on the basis of atomic number instead of atomic weight and the scattering of α -particles due to atoms of thin foil, yet Rutherford's model of atom suffered from the following drawbacks:

➤ **It failed to explain the stability of the atom**

- According to Rutherford, electrons revolve around the nucleus in circular paths.
- We know that anything that revolves in a circular path is accelerated towards the centre of the circular path and has centripetal acceleration, $a = v^2/r$; where v is the velocity and r is the radius. Thus, the electrons revolving around the nucleus are accelerated towards the nucleus of the atom.
- According to classical electrodynamics, accelerated charged particle radiate energy (electromagnetic waves). Hence, electromagnetic waves would be continuously radiated by the revolving electrons. Due to this, electrons must lose energy continuously.
- Due to this continuous loss of energy of electrons, the radii of their orbits should be continuously decreasing and ultimately the electrons should fall into the nucleus following a spiral path (see fig).
- So, the atom should collapse. But, in fact, it never happens. The electrons keep on revolving round the nucleus without falling into it. Rutherford could not explain this fact. Hence, Rutherford's model failed to explain the stability of the atom.



➤ **It failed to explain complex line spectrum emitted by an atom**

- According to Rutherford, electron can revolve around a nucleus in circular orbits of all possible radii. Due to this continuously changing radii of the circular orbits of electrons, the frequency of revolution of the electrons must also be changing. As a result, electrons should radiate electromagnetic waves of all frequencies, meaning → the spectrum of these waves should be 'continuous' in nature. In other words, the atom should emit continuous energy spectrum of all wavelengths.
- But, experimentally the atomic spectra are not continuous; they have many sharp lines and each spectral line corresponds to a particular frequency. So, an atom should radiate waves of some definite frequencies only, not of all frequencies. Thus, Rutherford model was unable to explain the line spectrum.
- Even the simplest atom i.e. **hydrogen atom** has line spectrum of definite wavelengths instead of a continuous spectrum. Hence, Rutherford model was unable to explain this line spectrum of hydrogen atom.
 - These difficulties were solved by Niels Bohr with the help of quantum theory.

Comparison between Rutherford's Nuclear Model of Atom and the Solar System

Rutherford's Nuclear Model of an atom can be compared to the solar system. The nucleus of an atom is comparable to the Sun of the solar system. The electrons in an atom move in orbits around the nucleus and planets move in orbits around the sun. In the solar system, the centripetal force needed by a planet (say earth) is provided by the gravitational force of attraction between the planet and the sun. In an atom, centripetal force needed by an electron to move in an orbit around the nucleus is provided by the Coulomb's force of attraction between the electron and the nucleus. Thus, Rutherford's Nuclear Model of atom is analogous to the solar system.

Electron orbits

The Rutherford nuclear model of the atom which involves classical concepts, pictures the atom as an electrically neutral sphere consisting of a very small, massive and positively charged nucleus at the centre surrounded by the revolving electrons in their respective dynamically stable orbits. The electrostatic force of attraction, F_e between the revolving electrons and the nucleus provides the requisite centripetal force (F_c) to keep them in their orbits. Thus, for a dynamically stable orbit in a hydrogen atom

$$\frac{F_e}{r} = \frac{mv^2}{r} = \frac{1}{4\pi\epsilon_0} \frac{e^2}{r^2} \quad (12.2)$$

Thus the relation between the orbit radius and the electron velocity is

$$r = \frac{e^2}{4\pi\epsilon_0 mv^2} \quad (12.3)$$

The kinetic energy (K) and electrostatic potential energy (U) of the electron in hydrogen atom are

$$K = \frac{1}{2}mv^2 = \frac{e^2}{8\pi\epsilon_0 r} \text{ and } U = -\frac{e^2}{4\pi\epsilon_0 r}$$

(The negative sign in U signifies that the electrostatic force is in the $-r$ direction.) Thus the total energy E of the electron in a hydrogen atom is

$$\begin{aligned} E &= K + U = \frac{e^2}{8\pi\epsilon_0 r} - \frac{e^2}{4\pi\epsilon_0 r} \\ &= -\frac{e^2}{8\pi\epsilon_0 r} \end{aligned} \quad (12.4)$$

The total energy of the electron is negative. This implies the fact that the electron is bound to the nucleus. If E were positive, an electron will not follow a closed orbit around the nucleus.

Example 12.3 It is found experimentally that 13.6 eV energy is required to separate a hydrogen atom into a proton and an electron. Compute the orbital radius and the velocity of the electron in a hydrogen atom.

Solution Total energy of the electron in hydrogen atom is $-13.6 \text{ eV} = -13.6 \times 1.6 \times 10^{-19} \text{ J} = -2.2 \times 10^{-18} \text{ J}$. Thus from Eq. (12.4), we have

$$-\frac{e^2}{8\pi\epsilon_0 r} = -2.2 \times 10^{-18} \text{ J}$$

This gives the orbital radius

$$\begin{aligned} r &= -\frac{e^2}{8\pi\epsilon_0 E} = -\frac{(9 \times 10^9 \text{ N m}^2/\text{C}^2)(1.6 \times 10^{-19} \text{ C})^2}{(2)(-2.2 \times 10^{-18} \text{ J})} \\ &= 5.3 \times 10^{-11} \text{ m} \end{aligned}$$

The velocity of the revolving electron can be computed from Eq. (12.3) with $m = 9.1 \times 10^{-31} \text{ kg}$,

$$v = \frac{e}{\sqrt{4\pi\epsilon_0 mr}} = 2.2 \times 10^6 \text{ m/s.}$$

Atomic Spectra

- Each element has a characteristic spectrum of radiation, which it emits.

Line Emission spectrum:

- When an atomic gas or vapour is excited at low pressure, usually by passing an electric current through it, the emitted radiation has a spectrum which contains certain specific wavelengths only. A spectrum of this kind is termed as emission line spectrum and it consists of bright lines on a dark background. The spectrum emitted by atomic hydrogen is shown in figure. →
 - Figure does not show dark background, but assume back background and lines are bright lines and some are coloured lines
 - Study of emission line spectra of a mat

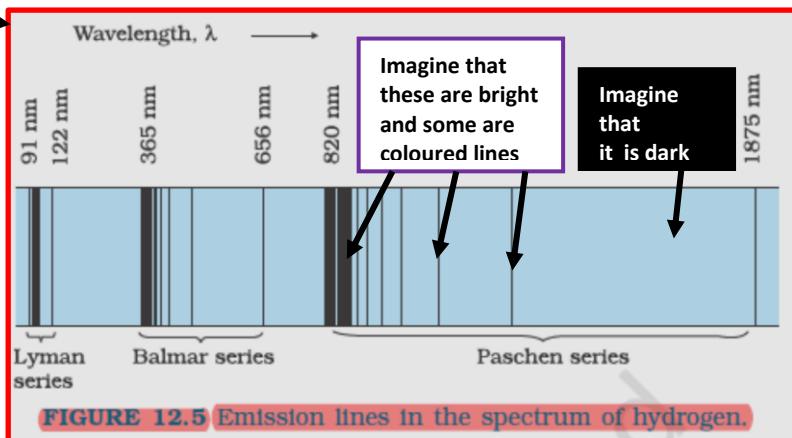
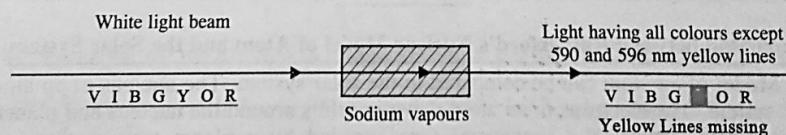


FIGURE 12.5 Emission lines in the spectrum of hydrogen.

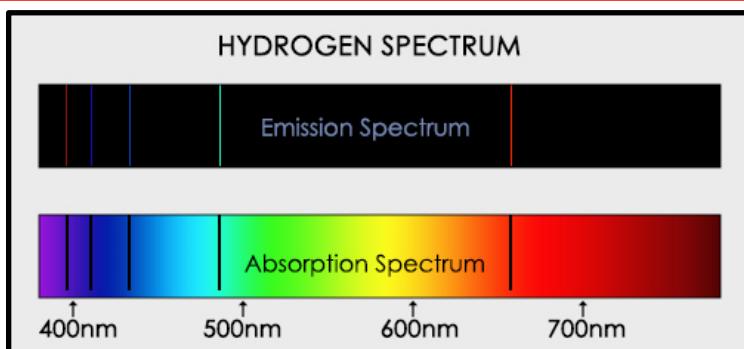
Line Absorption Spectrum

- When white light passes through the same gas/vapour, we observe a bright background crossed by a few dark lines in the spectrum signifying the missing wavelengths or the wavelengths that are absorbed by the gas. They form the Line Absorption spectrum of the material of the gas.

White light consists of colours or wavelengths ranging from 400 nm to 760 nm. When white light passes through the rarefied element say sodium vapours, the characteristic wavelengths of sodium or yellow light (*i.e.*, 590 nm and 596 nm seen bright in the emission spectrum) are absorbed by the sodium vapours. Hence, the transmitted light will have all wavelengths ranging from 400 nm to 760 nm except the characteristic wavelengths (in the case of sodium 590 nm and 596 nm yellow lines) as shown in figure 8. The spectrum of such transmitted light is known as absorption spectrum.



- The fact that every gas/vapour has its own characteristic line emission/absorption spectrum shows that the line spectra serve as fingerprints for identification of the gas.
 - An attempt is made to show in the right side figure a part of hydrogen spectrum (Balmer series) for both line emission and line absorption spectrum



Group →	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	
Period ↓	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	
1	1 H															2 He			
2	3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne	
3	11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar	
4	19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr	
5	37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe	
6	55 Cs	56 Ba	57 La	*	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
7	87 Fr	88 Ra	89 Ac	*	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Nh	114 Fl	115 Mc	116 Lv	117 Ts	118 Og
	*	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu				
	*	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr				

Spectral Series of Hydrogen → (Hydrogen is the simplest atom)

- At first sight, it looks like there is no resemblance of order or regularity in spectral lines of hydrogen emission spectrum. However, a close look at the figure → → → shows that the spectral lines are in groups.
- Further, the spacing between lines within certain sets of the hydrogen spectrum decreases in a regular way. Each of these sets is called a “spectral series” (namely Lyman series, Balmer series, Paschen series, Brackett series and Pfund series)

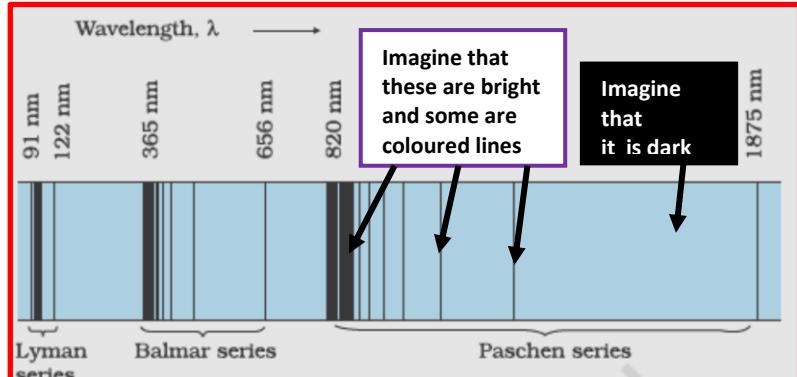


FIGURE 12.5 Emission lines in the spectrum of hydrogen.

- Balmer series:** Balmer was the first to observe such spectral series in the visible region of the hydrogen spectrum. It is called “Balmer Series”. See figure below.



The “visible” hydrogen emission spectrum lines in the Balmer series. H-alpha is the red line at the right. Four lines (counting from the right) are formally in the visible range. Lines five and six can be seen with the naked eye, but are considered to be ultraviolet as they have wavelengths less than 400 nm

- The spectral line with largest $\lambda = 656.3\text{nm}$ is in the red region and called as H α line.
- Next $\lambda = 486.1\text{nm}$ is in blue-green region and called as H β line.
- Next $\lambda = 434.1\text{nm}$ is in violet region and called as H γ line.
- Next $\lambda = 410.2\text{nm}$ is in violet region and called as H δ line.
- Next $\lambda = 364.6\text{nm}$ is in ultraviolet region and called as H ∞ line.

- *****
- The spacing of successive lines and their intensity goes on decreasing. As the wavelength decreases, the lines appear closer together and are weaker in intensity. Balmer found a simple empirical formula for the observed wavelengths.

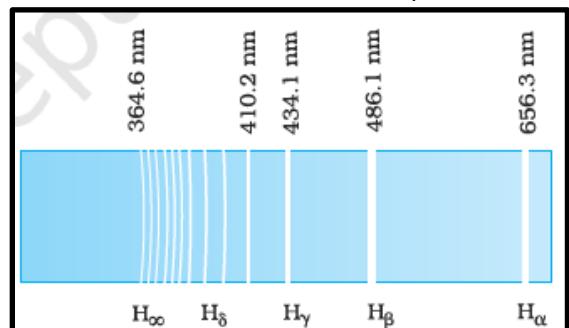


FIGURE 12.6 Balmer series in the emission spectrum of hydrogen.

- **Balmer series empirical formula:** The following equation is also called Balmer formula.

$$\frac{1}{\lambda} = R \left[\frac{1}{2^2} - \frac{1}{n^2} \right] \quad \text{--- (1)}$$

where R is a constant called the Rydberg constant = $1.097 \times 10^7 \text{ m}^{-1}$; 'n' may have integer values 3, 4, 5, etc. and λ = wavelength.

- For H_α line : n = 3 and $\lambda = 656.3 \text{ nm}$ (using Balmer formula)
- For H_β line : n = 4 and $\lambda = 486.13 \text{ nm}$ (using Balmer formula)
- For H_γ line : n = 5 and $\lambda = 434.1 \text{ nm}$ (using Balmer formula)
- For H_∞ line: n = ∞ and $\lambda = 364.6 \text{ nm}$ (using Balmer formula) → which is the limit of the Balmer series. Beyond this limit, there are no further distinct lines. Instead, the spectrum becomes continuous, though faint.
- Balmer formula can be written in terms of frequency: We know that $c = f\lambda$; therefore $1/\lambda = f/c$

$$f = Rc \left[\frac{1}{2^2} - \frac{1}{n^2} \right]$$

- Other series of spectra for hydrogen were subsequently discovered. These are known, after their discoverers, as Lyman, Paschen, Brackett, and Pfund series. These are represented by the formulae:

Color	Wavelength	Frequency	Photon energy
Violet	380–450 nm	680–790 THz	2.95–3.10 eV
Blue	450–485 nm	620–680 THz	2.64–2.75 eV
Cyan	485–500 nm	600–620 THz	2.48–2.52 eV
Green	500–565 nm	530–600 THz	2.25–2.34 eV
Yellow	565–590 nm	510–530 THz	2.10–2.17 eV
Orange	590–625 nm	480–510 THz	2.00–2.10 eV
Red	625–740 nm	405–480 THz	1.65–2.00 eV

<i>Lyman series:</i>	$\frac{1}{\lambda} = R \left(\frac{1}{1^2} - \frac{1}{n^2} \right)$	n = 2,3,4...
<i>Paschen series:</i>	$\frac{1}{\lambda} = R \left(\frac{1}{3^2} - \frac{1}{n^2} \right)$	n = 4,5,6...
<i>Brackett series:</i>	$\frac{1}{\lambda} = R \left(\frac{1}{4^2} - \frac{1}{n^2} \right)$	n = 5,6,7...
<i>Pfund series:</i>	$\frac{1}{\lambda} = R \left(\frac{1}{5^2} - \frac{1}{n^2} \right)$	n = 6,7,8...

The Lyman series is in the ultraviolet region ----- (2)

The Paschen series is in the Infrared region ----- (3)

The Brackett series is in the Infrared region ----- (4)

The Pfund series is in the far Infrared region ----- (5)

$$\frac{1}{\lambda} = R \left[\frac{1}{2^2} - \frac{1}{n^2} \right]$$

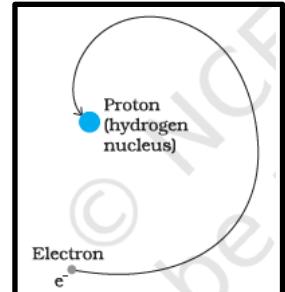
The Balmer series is in the Visible region ----- (1)

- There are only a few elements (hydrogen, singly ionised helium, and doubly ionised lithium) whose spectra can be represented by simple formula like Equations (1) to (5).
- Equations (1) to (5) are useful as they give the wavelengths that hydrogen atoms radiate or absorb.
- **However, these results are empirical and do not give any reasoning why only certain frequencies are observed in the hydrogen spectrum.**
- Though Rutherford model is superior to Thomson's model in some regards, it could not interpret the origin of hydrogen spectrum i.e., the origin of line spectra.
- Neils Bohr in the year 1913 realised that the origin of line spectra is based on two central ideas
 - **(1) photon concept and**
 - **(2) Energy levels of the atom.**
 - He made some epoch-making and bold assumptions which provided a major breakaway from the 19th century ideas.

BOHR MODEL OF THE HYDROGEN ATOM

Background:

- The model of the atom proposed by Rutherford assumes that the atom, consisting of a central nucleus and revolving electron is stable much like sun-planet system which the model imitates. However, there are some fundamental differences between the two situations.
- While the planetary system is held by gravitational force, the nucleus-electron system being charged objects, interact by Coulomb's Law of force.
- We know that an object which moves in a circle is being constantly accelerated – the acceleration being centripetal in nature. According to classical electromagnetic theory, an accelerating charged particle emits radiation in the form of electromagnetic waves. The energy of an accelerating electron should therefore, continuously decrease. **The accelerated electron must spiral inward and eventually fall into the nucleus (See fig → → →)**
- Thus, such an atom cannot be stable.
- Further, according to the classical electromagnetic theory, the frequency of the electromagnetic waves emitted by the revolving electrons is equal to the frequency of revolution. As the electrons spiral inwards, their angular velocities and hence their frequencies would change continuously, and so will the frequency of the light emitted.
- Thus, they would emit a continuous spectrum, in contradiction to the line spectrum actually observed. Clearly Rutherford model tells only a part of the story implying that the classical ideas are not sufficient to explain the atomic structure.



Example 12.4 According to the classical electromagnetic theory, calculate the initial frequency of the light emitted by the electron revolving around a proton in hydrogen atom.

Solution From Example 12.3 we know that velocity of electron moving around a proton in hydrogen atom in an orbit of radius 5.3×10^{-11} m is 2.2×10^6 m/s. Thus, the frequency of the electron moving around the proton is

$$v = \frac{v}{2\pi r} = \frac{2.2 \times 10^6 \text{ m s}^{-1}}{2\pi (5.3 \times 10^{-11} \text{ m})}$$

$$\approx 6.6 \times 10^{15} \text{ Hz.}$$

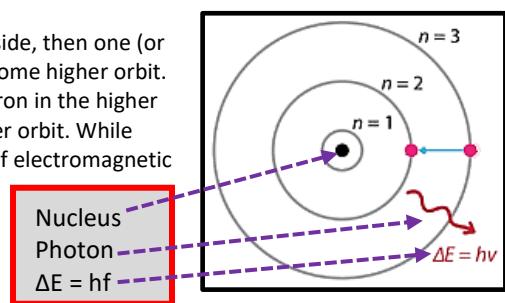
According to the classical electromagnetic theory we know that the frequency of the electromagnetic waves emitted by the revolving electrons is equal to the frequency of its revolution around the nucleus. Thus the initial frequency of the light emitted is 6.6×10^{15} Hz.

In uniform circular motion of radius r , we know that $S = r\theta$. Differentiating this, we get $v = r\omega$, where v is linear velocity and ω is angular velocity. Since $\omega = 2\pi f$; So, $v = 2\pi r f$. Therefore $f = v/2\pi r$

- It was Niels Bohr (1885 – 1962) who made certain modifications in this model by adding the ideas of the newly developing quantum hypothesis. Niels Bohr studied in Rutherford's laboratory for several months in 1912 and he was convinced about the validity of Rutherford nuclear model.
- Faced with the dilemma as discussed above, Bohr, in 1913, concluded that in spite of the success of electromagnetic theory in explaining large-scale phenomena, it could not be applied to the processes at the atomic scale.
- It became clear that a fairly radical departure from the established principles of classical mechanics and electromagnetism would be needed to understand the structure of atoms and the relation of atomic structure to atomic spectra.
- Bohr combined classical and early quantum concepts and gave his theory in the form of three postulates. These are :
 - **Bohr's first postulate** was that an electron in an atom could revolve only in certain stable orbits without the emission of radiant energy, contrary to the predictions of electromagnetic theory. According to this postulate, each atom has certain definite stable states in which it can exist, and each possible state has definite total energy. These are called the stationary states of the atom.
 - In other words, while revolving in certain stable orbits, the electrons do not radiate energy inspite of their acceleration towards the centre of the orbit. Hence the atom remains stable and is said to exist in a stationary state.
 - **Bohr's second postulate defines these stable orbits.** This postulate states that the electron revolves around the nucleus only in those orbits for which the angular momentum is some integral multiple of $h/2\pi$ where h is the Planck's constant ($= 6.6 \times 10^{-34}$ J s). **Thus the angular momentum (L) of the orbiting electron is quantised.**
 - If the mass of the electron be m and it is revolving with velocity v in an orbit of radius r , then its angular momentum (L) = mvr . According to this postulate, $mvr = nh/2\pi$. Where n is an integer ($n = 1, 2, 3, \dots$) and is called the "**principal quantum number**" of the orbit. This equation is called "**Bohr quantization condition**".

- Bohr's third postulate incorporated into atomic theory the early quantum concepts that had been developed by Planck and Einstein. It states that an electron might make a transition from one of its specified non-radiating orbits to another of lower energy. When it does so, a photon is emitted having energy equal to the energy difference between the initial and final states. The frequency of the emitted photon is then given by $hf = E_i - E_f$ where E_i and E_f are the energies of the initial and final states and $E_i > E_f$. Therefore, $f = (E_i - E_f)/h$. This equation is called "Bohr's frequency condition"

- In other words, when an atom receives energy from outside, then one (or more) of its outer electrons leaves its orbit and goes to some higher orbit. This state of the atom is called "excited state". The electron in the higher orbit stay only for 10^{-8} second and returns back to a lower orbit. While retuning back, the electron radiates energy in the form of electromagnetic waves.

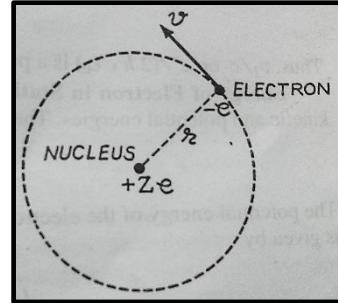


Bohr's theory of hydrogen atom (or Hydrogen-like atoms)

- Any hydrogen-like atom consists of a tiny positively-charged nucleus and an electron revolving in a stable circular orbit around the nucleus (see figure →)
- Let e , m , v be respectively the charge, mass and velocity of the electron and r be the radius of the orbit.
- The positive charge on the nucleus is Ze , where Z is the atomic number (for hydrogen $Z = 1$)
- As the centripetal force is provided by the electrostatic force of attraction, we have

$$\frac{mv^2}{r} = \frac{1}{4\pi\epsilon_0} \frac{(Ze)e}{r^2}$$

$$mv^2 = \frac{Ze^2}{4\pi\epsilon_0 r} \quad \dots \dots \dots (1)$$



From the angular momentum postulate of Bohr, we have

$$mvr = n \frac{h}{2\pi} \quad \text{where } n = 1, 2, 3, \dots \text{is quantum number} \quad \dots \dots \dots (2)$$

$$\text{Squaring equation (2), we get } m^2v^2r^2 = n^2h^2/4\pi^2 \quad \dots \dots \dots (3)$$

$$(3) / (1), \text{ we get } \frac{m^2v^2r^2}{mv^2} = \frac{n^2h^2}{4\pi^2} \times \frac{4\pi\epsilon_0 r}{Ze^2} \dots \text{ Simplifying } r = \frac{n^2h^2}{\pi m} \times \frac{\epsilon_0}{Ze^2}$$

$$r = n^2 \frac{h^2\epsilon_0}{\pi m Z e^2} \quad \dots \dots \dots (4)$$

This is the equation for the radii of the permitted orbits. As per this equation $r \propto n^2$, since $n = 1, 2, 3, \dots$ it follows that the radii of the permitted orbits increase in the ratio $1 : 4 : 9 : 16 \dots$ from the first orbit.

Bohr's Radius: The radius of the first orbit r_1 ($n=1$) of hydrogen atom ($Z = 1$) will be

$$r = n^2 \frac{h^2\epsilon_0}{\pi m Z e^2} \rightarrow r_1 = \frac{h^2\epsilon_0}{\pi m e^2} \quad \text{Substituting values of } h, m, \epsilon_0 \text{ and } e \text{ gives } r_1 = 0.529 \times 10^{-10} \text{ m} = 0.529 \text{ \AA}$$

Since $r \propto n^2$, the radius of the 2nd orbit of hydrogen atom will be $(4 \times 0.529) \text{ \AA}$
the radius of the 3rd orbit of hydrogen atom will be $(9 \times 0.529) \text{ \AA}$

Velocity of Electron in Stationary Orbits :

We know from equation (2) $mvr = n \frac{h}{2\pi}$ where $n = 1, 2, 3, \dots$ is quantum number $\dots \dots \dots (2)$

$$v = n \frac{h}{2\pi mr} \quad \text{where } n = 1, 2, 3, \dots \quad \dots \dots \dots (5)$$

We know that equation for radius $r = n^2 \frac{h^2\epsilon_0}{\pi m Z e^2} \quad \dots \dots \dots (4)$

Plugging r in equation (5), we get

$$v = \frac{nh}{2\pi m} \left[\frac{1}{r} \right] = \frac{nh}{2\pi m} \times \frac{\pi m Z e^2}{n^2 h^2 \epsilon_0} = \left[\frac{1}{n} \right] \frac{Z e^2}{2h\epsilon_0} \text{ where } n = 1, 2, 3, \dots \text{ So, } v \propto \frac{1}{n}$$

$$v = \left[\frac{1}{n} \right] \frac{Z e^2}{2h\epsilon_0} \text{ where } n = 1, 2, 3, \dots \quad (6)$$

The velocity of electron in the FIRST orbit ($n=1$) of hydrogen atom ($Z = 1$), then

$$v_1 = \frac{e^2}{2h\epsilon_0} \text{ Plugging values of } e, h \text{ and } \epsilon_0; v_1 = 2.19 \times 10^6 \text{ ms}^{-1}$$

$$\text{Let us note that } \frac{v_1}{c} = \frac{2.19 \times 10^6}{3 \times 10^8} = \frac{1}{137}$$

Thus, $\frac{v_1}{c}$ or $\frac{e^2}{2hce_0}$ is a pure number. It is known as "**fine-structure constant**" and is denoted by α

Energy of Electron in Stationary Orbit:

- The energy E of an electron in an orbit is the sum of Kinetic Energy (K) and Potential Energy (U).
 - The KE of the electron is given by ...we know from equation (1)
 - $mv^2 = \frac{Ze^2}{4\pi\epsilon_0 r}$ ----- (1), therefore

$$K = \frac{1}{2} mv^2 = \frac{Ze^2}{8\pi\epsilon_0 r}$$
- The PE of the electron in an orbit of radius r due to the electrostatic attraction by the nucleus is

$$U = \frac{1}{4\pi\epsilon_0} \frac{(Ze)(-e)}{r} = - \frac{1}{4\pi\epsilon_0} \frac{Ze^2}{r}$$
- The total energy of the electron is therefore $E = K + U$

$$E = \frac{Ze^2}{8\pi\epsilon_0 r} - \frac{1}{4\pi\epsilon_0} \frac{Ze^2}{r} = - \frac{Ze^2}{8\pi\epsilon_0 r}$$
- We know that from equation $r = n^2 \frac{h^2 \epsilon_0}{\pi m Z e^2}$ (4); substituting r in above equation of E , we get

$$E = - \left[\frac{1}{n^2} \right] \frac{m Z^2 e^4}{8\epsilon_0^2 h^2} \quad \text{--- (7); where } n = 1, 2, 3, \dots \text{ This is the expression for the energy of the electron in the } n^{\text{th}} \text{ orbit}$$

- Suppose in the 'excited' atom, an electron jumps from some higher-energy state n_2 to a lower-energy state n_1 . The energy-difference between these states is

$$E_2 - E_1 = \frac{m Z^2 e^4}{8\epsilon_0^2 h^2} \left[\frac{1}{n_1^2} - \frac{1}{n_2^2} \right]$$
- According to Bohr's third postulate, the frequency f of the emitted e-m wave (photon) is given by

$$f = \frac{E_2 - E_1}{h} = \frac{m Z^2 e^4}{8\epsilon_0^2 h^3} \left[\frac{1}{n_1^2} - \frac{1}{n_2^2} \right] \text{ we know that } c = f\lambda; 1/\lambda = f/c$$
- The corresponding wavelength λ of the emitted e-m wave (photon) is given by

$$\frac{1}{\lambda} = \frac{f}{c} = \frac{m Z^2 e^4}{8\epsilon_0^2 c h^3} \left[\frac{1}{n_1^2} - \frac{1}{n_2^2} \right]$$
- $\frac{1}{\lambda}$ is called the 'wave number' (number of waves per unit length).
- In the last equation, the quantity $\frac{me^4}{8\epsilon_0^2 ch^3}$ is a constant, known as "Rydberg constant" (R). That is

$$R = \frac{me^4}{8\epsilon_0^2 ch^3} \text{ Thus, } \frac{1}{\lambda} = Z^2 R \left[\frac{1}{n_1^2} - \frac{1}{n_2^2} \right] \quad \dots \dots \dots \quad (8)$$

Equation (8) is Bohr's formula for hydrogen and hydrogen-like atoms (He^+ , Li^{++} , ...). For hydrogen $Z = 1$, therefore

$$\text{For hydrogen atom: } \frac{1}{\lambda} = R \left[\frac{1}{n_1^2} - \frac{1}{n_2^2} \right] \quad \dots \dots \dots \quad (9)$$

The value of Rydberg constant is

$$R = \frac{me^4}{8\epsilon_0^2 ch^3} = \frac{(9.11 \times 10^{-31} \text{ kg}) \times (1.6 \times 10^{-19} \text{ C})^4}{8 \times (8.85 \times 10^{-12} \text{ C}^2 \text{ N}^{-1} \text{ m}^{-2})^2 \times (3 \times 10^8 \text{ ms}^{-1}) \times (6.63 \times 10^{-34} \text{ Js})^3} = 1.090 \times 10^7 \text{ m}^{-1}$$

This value of R fairly agrees with empirical value $1.097 \times 10^7 \text{ m}^{-1}$ obtained experimentally by Balmer.

Thus, energy is radiated only when electron returns from some higher energy orbit to some lower orbit. hence, waves of some definite frequencies only are radiated from, the atom, because of which line spectrum having only certain discrete wavelengths is obtained.

The energy expression (7) $E = - \left[\frac{1}{n^2} \right] \frac{mZ^2 e^4}{8\epsilon_0^2 h^2}$ can be written in terms of Rydberg's constant R in a simplified form:

$$\text{Recall } R = \frac{me^4}{8\epsilon_0^2 ch^3} \text{ and } E = - \frac{me^4}{8\epsilon_0^2 ch^3} \left[\frac{1}{n^2} \right] Z^2 hc = - Z^2 \frac{Rhc}{n^2}; \text{ therefore } E = - Z^2 \frac{Rhc}{n^2}$$

Plugging values of R, h and c and taking $1\text{eV} = 1.6 \times 10^{-19} \text{ J}$

$$E = - Z^2 \frac{13.6}{n^2} \text{ eV} ; \text{ for hydrogen, } Z = 1, \text{ then } E_n = - \frac{13.6}{n^2} \text{ eV}$$

- The negative sign of the total energy of an electron moving in an orbit means that the electron is bound with the nucleus. Energy will thus be required to remove the electron from the hydrogen atom to a distance infinitely far away from its nucleus (or proton in hydrogen atom).
- The derivation of energy in the above equations involves the assumption that the electronic orbits are circular, though orbits under inverse square force are, in general elliptical. (Planets move in elliptical orbits under the inverse square gravitational force of the sun.) However, it was shown by the German physicist Arnold Sommerfeld (1868 – 1951) that, when the restriction of circular orbit is relaxed, these equations continue to hold even for elliptic orbits.

Frequency f_n of an electron in n^{th} orbit of radius r_n of Hydrogen atom : ($Z = 1$)

We know that for circular motion, $S = r\theta$; so $v_n = r_n \omega = r_n 2\pi f_n$; So $f_n = v_n / 2\pi r_n$

We know the expression for v_n and r_n (note the in the following equation, we have put $Z = 1$ for hydrogen atom)

$$v_n = \frac{e^2}{2nh\epsilon_0} \text{ and } r_n = \frac{n^2 h^2 \epsilon_0}{\pi me^2}; \text{ So } f_n = \frac{v_n}{2\pi r_n} = \frac{e^2}{2nh\epsilon_0} \times \frac{1}{2\pi} \times \frac{\pi me^2}{n^2 h^2 \epsilon_0} = \frac{me^4}{4h^3 \epsilon_0^2 n^3}; \quad f_n = \frac{me^4}{4h^3 \epsilon_0^2 n^3}$$

Since $\frac{me^4}{4h^3 \epsilon_0^2}$ is constant, therefore, $f_n \propto \frac{1}{n^3}$

For $n = 1$ (first orbit) of hydrogen atom, the number of revolutions made per second by the electron, i.e., the frequency of electron = 6.57×10^5 rps (Hz)

$$\text{K.E. of electron in ground state of hydrogen atom} = \frac{1}{2} \frac{ke^2}{r}, \text{ where } k = \frac{1}{4\pi \epsilon_0}$$

$$\text{P.E. of electron in ground state of hydrogen atom} = - \frac{ke^2}{r} = -2 \times \text{K.E.}$$

Total energy in ground state of hydrogen atom, $E = \text{K.E.} + \text{P.E.}$

$$= \frac{1}{2} \frac{ke^2}{r} - \frac{ke^2}{r} = - \frac{1}{2} \frac{ke^2}{r} = -\text{K.E}$$

NUMERICAL EXAMPLE. The ground state energy of hydrogen atom is -13.6 eV. Find the kinetic energy and potential energy of the electron in the ground state.

SOLUTION.

$$E = (\text{K.E.} + \text{P.E.}) = -13.6 \text{ eV}$$

$$\text{K.E.} = -E = -(-13.6 \text{ eV})$$

$$= 13.6 \text{ eV}$$

$$\text{P.E.} = -2 \times \text{K.E.}$$

$$= -2 \times 13.6 \text{ eV} = -27.2 \text{ eV}$$

Hydrogen-like atom of atomic number Z

It consists of a nucleus having charge $+Ze$ and (one electron of charge $-e$ revolving around the nucleus in a circular orbit).

For example, singly ionized helium atom He^+ and doubly ionized lithium atom Li^{2+} are hydrogen like atoms. They are called so because these ions have only one electron revolving around the nucleus as in the case of hydrogen atom.

Radius (r_n) of nth orbit of hydrogen-like atom

$$(r_n)_{\text{HL}} = \frac{(r_n)}{Z}, \text{ where } r_n \text{ is the radius of } n\text{th orbit of hydrogen atom and } Z = \text{atomic number of the element of hydrogen like atom.}$$

Example : For helium $Z = 2$. Therefore, radius of first orbit of singly ionised helium atom He^+ is given by

$$(r_0)_{\text{He}} = \frac{(r_0)}{Z} = \frac{0.53}{2} \text{ Å} = 0.265 \text{ Å}$$

Speed (v_n) of electron in the nth orbit of hydrogen-like atom

$$(v_n)_{\text{He}} = Z(v_n)_{\text{H}}$$

Example : For Lithium, $Z = 3$. Therefore, speed of electron in the first orbit of doubly ionised Lithium atom is given by

$$(v_1)_{\text{Li}^{2+}} = 3(v_1)_{\text{H}} \text{ Since, } (v_1)_{\text{H}} = 2 \times 10^6 \text{ m s}^{-1}$$

$$\therefore (v_1)_{\text{Li}^{2+}} = 3 \times 2 \times 10^6 \text{ m s}^{-1} = 6 \times 10^6 \text{ m s}^{-1}$$

Energy of electron in the nth orbit of hydrogen-like atom

$$(E_n)_{\text{HL}} = \frac{-13.6Z^2}{n^2} \text{ eV.}$$

Example : The energy of an electron in the first orbit of hydrogen atom is -13.6 eV.

For Helium, $Z = 2$. Therefore, energy of electron in the first orbit of He^+ atom is given by

$$\therefore (E_1)_{\text{He}} = -\frac{13.6 \times 4}{1} = -54.4 \text{ eV.}$$

Info: Electrons revolving around the nucleus are bound to the nucleus because total energy of electron revolving in any orbit is negative.

- The energy of the atom is least (= largest negative value) when $n = 1$, that is when electron is revolving in an orbit closest to the nucleus. This state of lowest energy of the atom is called "ground state". The energy of this state is $E_1 = -13.6/1^2$ eV.
- Therefore, the minimum energy required to remove the electron from the ground state of hydrogen atom is 13.6 eV. This is called the "ionisation energy" of hydrogen atom.
- As n increases, value of negative energy decreases, i.e., energy is progressively larger in the outer orbits. These are called "excited states"
- Note that stationary orbits of electrons are not equally spaced. Their radii are in the ratio $1^2 : 2^2 : 3^2 : 4^2 \dots (1 : 4 : 9 : 16) \dots$ In outer stationary orbits, velocity of electrons and their frequency of revolution decrease. Total energy of electron in outer orbits is more than that in inner orbits.

ORBIT VS STATE (ORBITAL PICTURE) OF ELECTRON IN ATOM

We are introduced to the Bohr Model of atom one time or the other in the course of physics. This model has its place in the history of quantum mechanics and particularly in explaining the structure of an atom. It has become a milestone since Bohr introduced the revolutionary idea of definite energy orbits for the electrons, contrary to the classical picture requiring an accelerating particle to radiate. Bohr also introduced the idea of quantisation of angular momentum of electrons moving in definite orbits. Thus it was a semi-classical picture of the structure of atom.

Now with the development of quantum mechanics, we have a better understanding of the structure of atom. Solutions of the Schrödinger wave equation assign a wave-like description to the electrons bound in an atom due to attractive forces of the protons.

An orbit of the electron in the Bohr model is the circular path of motion of an electron around the nucleus. But according to quantum mechanics, we cannot associate a definite path with the motion of the electrons in an atom. We can only talk about the probability of finding an electron in a certain region of space around the nucleus. This probability can be inferred from the one-electron wave function called the *orbital*. This function depends only on the coordinates of the electron.

It is therefore essential that we understand the subtle differences that exist in the two models:

- Bohr model is valid for only one-electron atoms/ions; an energy value, assigned to each orbit, depends on the principal quantum number n in this model. We know that energy associated with a stationary state of an electron depends on n only, for one-electron atoms/ions. For a multi-electron atom/ion, this is not true.
- The solution of the Schrödinger wave equation, obtained for hydrogen-like atoms/ions, called the wave function, gives information about the probability of finding an electron in various regions around the nucleus. This *orbital* has no resemblance whatsoever with the *orbit* defined for an electron in the Bohr model.

Example 12.5 A 10 kg satellite circles earth once every 2 h in an orbit having a radius of 8000 km. Assuming that Bohr's angular momentum postulate applies to satellites just as it does to an electron in the hydrogen atom, find the quantum number of the orbit of the satellite.

Solution

From Eq. (12.13), we have

$$m v_n r_n = nh/2\pi$$

Here $m = 10 \text{ kg}$ and $r_n = 8 \times 10^6 \text{ m}$. We have the time period T of the circling satellite as 2 h. That is $T = 7200 \text{ s}$.

Thus the velocity $v_n = 2\pi r_n/T$.

The quantum number of the orbit of satellite

$$n = (2\pi r_n)^2 \times m / (T \times h)$$

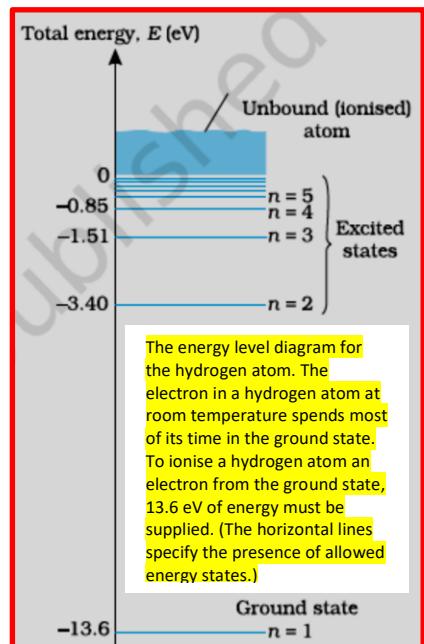
Substituting the values,

$$\begin{aligned} n &= (2\pi \times 8 \times 10^6 \text{ m})^2 \times 10 / (7200 \text{ s} \times 6.64 \times 10^{-34} \text{ J s}) \\ &= 5.3 \times 10^{45} \end{aligned}$$

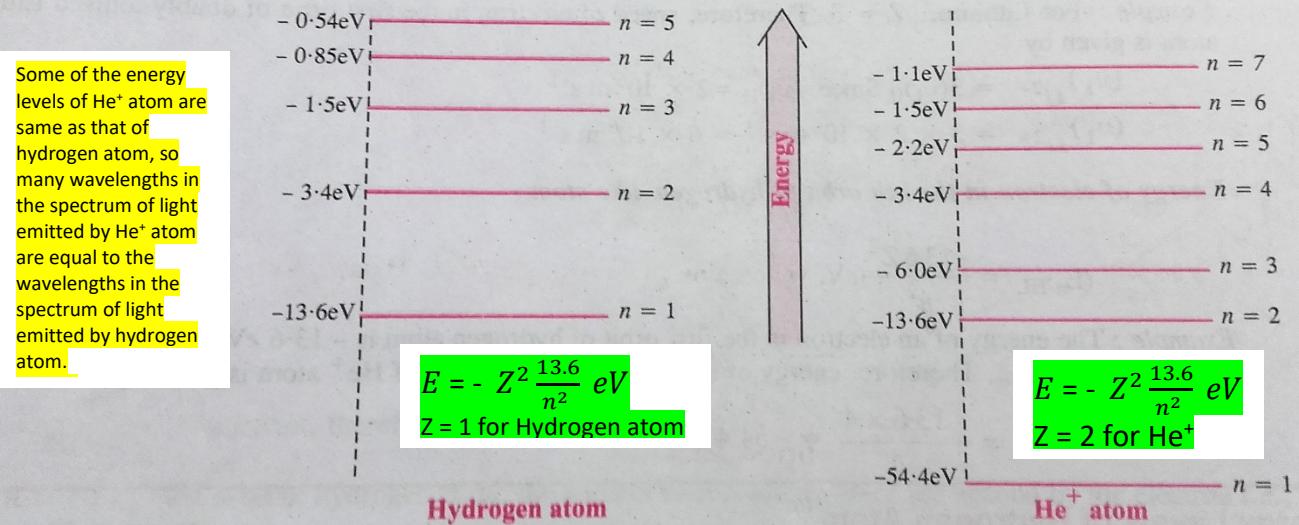
Note that the quantum number for the satellite motion is extremely large! In fact for such large quantum numbers the results of quantisation conditions tend to those of classical physics.

Draw Discrete Energy Levels of Atom (eg : Hydrogen atom)

- The energy of an atom is the least (largest negative value) when its electron is revolving in an orbit closest to the nucleus i.e., the one for which $n = 1$. For $n = 2, 3, \dots$ the absolute value of the energy E is smaller, hence the energy is progressively larger in the outer orbits. The lowest state of the atom, called the **ground state**, is that of the lowest energy, with the electron revolving in the orbit of smallest radius, the Bohr radius, r_0 . The energy of this state ($n = 1$), E_1 is -13.6 eV . Therefore, the minimum energy required to free the electron from the ground state of the hydrogen atom is 13.6 eV . It is called the ionisation energy of the hydrogen atom. This prediction of the Bohr's model is in excellent agreement with the experimental value of ionisation energy.
- At room temperature, most of the hydrogen atoms are in ground state.
- When a hydrogen atom receives energy by processes such as electron collisions, the atom may acquire sufficient energy to raise the electron to higher energy states. The atom is then said to be in an excited state.
- From Equation $E_n = -\frac{13.6}{n^2} \text{ eV}$, for $n = 2$; the energy E_2 is -3.40 eV . It means that the energy required to excite an electron in hydrogen atom to its first excited state, is an energy equal to $E_2 - E_1 = -3.40 \text{ eV} - (-13.6) \text{ eV} = 10.2 \text{ eV}$.
- Similarly, for $n = 3$, $E_3 = -1.51 \text{ eV}$ and $E_3 - E_1 = 12.09 \text{ eV}$. So, to excite the hydrogen atom from its ground state ($n = 1$) to second excited state ($n = 3$), 12.09 eV energy is required, and so on.
- When $n = \infty$, $E_\infty = -13.6/\infty = 0$. This is the energy of the highest energy state of the hydrogen atom. When $n = \infty$, the electron is completely free from the attractive force of the nucleus of the atom. In other words, the electron is no longer bound to the nucleus and becomes a free electron.
- From these excited states the electron can then fall back to a state of lower energy, emitting a photon in the process. Thus, as the excitation of hydrogen atom increases (that is as n increases) the value of minimum energy required to free the electron from the excited atom decreases.
- The energy level diagram for the stationary states of a hydrogen atom, computed from $E_n = -\frac{13.6}{n^2} \text{ eV}$, is given in the figure →
- The principal quantum number n labels the stationary states in the ascending order of energy. In this diagram, the highest energy state corresponds to $n = \infty$ in the figure and has an energy of 0 eV . This is the energy of the atom when the electron is completely removed ($r = \infty$) from the nucleus and is at rest.
- It is clear from the energy level diagram that when principal quantum number (n) increases, the energy levels or energy states come closer and closer to each other because the energy difference between successive energy levels decreases with the increase in principal quantum number.



The comparison of energy levels of hydrogen and hydrogen like atom He^+ is shown in figure 15.

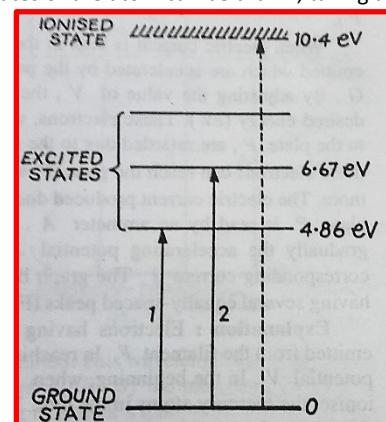
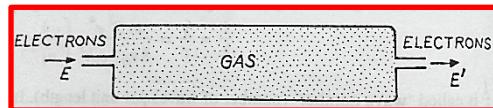


How do we know the existence of discrete stationary states as postulated by Bohr in his model of atom?

This is demonstrated by Frank and Hertz

Principle of Frank and Hertz

- The photoelectric effect and Compton scattering is explained using Planck's quantum theory. As per his theory, the exchange (emission and absorption) of radiant energy (or light) is not continuous; it takes place by photons of definite energy hf , where f is the frequency of radiation and h is the Planck's constant.
- This shows that the quantity of energy emitted or absorbed by a body can be hf , $2hf$, $3hf$,....not in between these quantities. Since light is emitted or absorbed by the atoms, it means that an atom can have only certain definite amounts of energy or there can only be some definite energy state of the atom.
This fact has been experimentally verified by Frank and Hertz.
- The principle of Frank and Hertz's experiment is explained in this figure →
- Suppose a gas is filled in a chamber. Electrons of energy E enter the chamber from one side. These electrons pass through the gas filled in the chamber and exit from the other side. Since the mass of an electron is negligible as compared to that of a gas atom; the electrons cannot lose energy by elastic collision with gas atoms. Thus, energy of an electron can only be lost when an atom of the gas acquires energy from the electron by internal 'excitation' (such collision is called the 'second kind of collision'). Clearly, if the energy of an exiting electron be E' , then the energy absorbed by an atom through internal excitation will be $(E-E')$.
- Frank and Hertz filled **mercury vapours** in the chamber and sent electrons of different energies E into it and measured the energy E' of the exiting electrons. They got the following observations from the experiment:
 - When $E = 0$ to 4.86 eV, then $E' = E$, thus $(E-E') = 0$. This implies when the energy E of the electrons entering the chamber was increased from 0 to 4.86 eV, the energy E' of the electrons exiting from the chamber was found always equal to the energy of the entering electrons. This meant that mercury atoms did not absorb energy between 0 and 4.86 eV.
 - When $E = 4.86$ eV, then $E' = 4.86$ eV or zero ; Thus $(E-E') = 0$ or 4.86 eV. When the energy of the entering electrons was exactly 4.86 eV, then the energy of some of the exiting electrons remained 4.86 eV, but the energy of most of them became zero. This meant that some of the electrons come out from the chamber without losing energy, but the energy of most of them was 'completely' absorbed by mercury atoms. From this it was concluded that mercury atom absorbs energy of 4.86 eV exactly, not less than this.
 - When $E > 4.86$ eV, then $E' = E$ or $(E-4.86)$ eV ; Thus $(E-E') = 0$ or 4.86 eV. When the energy of the entering electrons was increased beyond 4.86 eV, even then some of the electrons came out without losing their energy, but the energy of others was reduced by 4.86 eV. It was therefore concluded that when the electron has higher energy, the mercury atom absorbs only 4.86 eV, the rest remains with the electron.
 - When $E = 6.67$ eV, then $E' = 6.67$ or $(6.67-4.86)$ eV or 0 ; Thus $(E-E') = 0$ or 4.86 eV or 6.67 eV. When the energy of the entering electrons become 6.67 eV, then the energy of some of the exiting electrons remained 6.67 eV, energy of some was reduced by 4.86 eV and that of the rest became zero. It was concluded, that a mercury atom absorbs either an energy of 4.86 eV exactly, or of 6.67 eV exactly, but not in between these values.
 - When $E > 6.67$ eV, then $E' = E$ or $(E - 6.67)$ eV or $(E - 6.67)$ eV; Thus $(E-E') = 0$ or 4.86 eV or 6.67 eV. When the energy of the entering electrons was increased beyond 6.67 eV, then some of the electrons came out without losing energy, energy of some was reduced by 4.86 eV and that of the rest was reduced by 6.67 eV. From this it was concluded that when energy of electron is higher, the mercury atom absorbs exactly 4.86 eV or 6.67 eV of energy form the electron and rest of the energy remains with the electron.
 - When the energy of the entering electrons was increased to 10.4 eV, the number of exiting electron increased suddenly. It was concluded that when mercury atom absorbs energy 10.4 eV, it starts ejecting its own electrons.
- From the above observations, it is quite clear that except for some specific energy values, energy is not absorbed by the atoms. For example, if the energy of electron be 7.50 eV, then the mercury atom will not take energy as such. It will either not take any energy from the electron, or take exactly 4.86 eV or 6.67 eV out of it. It means that the energy states of an atom are definite and discrete. If the ground state of the mercury atom be taken to be the zero-energy state, then the excited state of the atom will be the 'ionised state' of the atom. All these energy-states of the atom can be drawn, taking a suitable scale. The energy states of mercury atom have been drawn (see fig →). This type of diagram is call the "energy-level diagram".
- The normal state of the atom is one in which the electrostatic energy of attraction between its nucleus and the electrons is minimum. This state is called the 'lowest' or the 'ground state' of the atom. When the atom gets appropriate energy from outside, it leaves its ground state and rises to some higher-energy state. Then the atom is said to be 'excited'. The shifting of the atom from one energy state to the other is called 'transition' and it can be shown by drawing an arrow between these two energy states in the energy-level diagram. In figure→, the shifting of mercury atom from the ground state to the first and the second excited states has been represented by transitions 1 and 2 respectively. In these transitions the atom absorbs 4.86 eV and 6.67 eV of energy respectively.
- If the atom gets so much of energy from outside that one if its electrons leaves the atom and goes out, then the atom is said to be 'ionised'. In figure, the ionisation of mercury atom has been shown the dotted transition. In this transition, the atom absorbs 10.4 eV of energy.

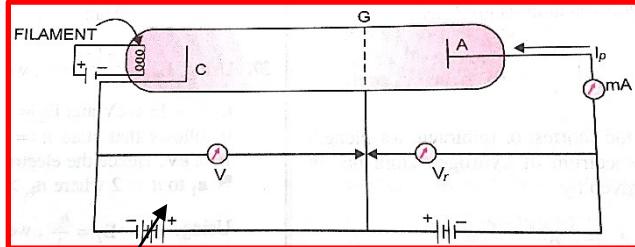


➤ Excitation and Ionisation Potentials:

- Generally, the atoms are excited or ionised by colliding them with electrons accelerated by high potentials. But the excitation, or ionisation, of the atom is possible only when the energy of the colliding electron is at least equal to that required for excitation or ionisation of the atom.
 - The minimum accelerating potential required to energise an electron which, on collision, can excite an atom is called the “excitation potential” of that atom. Similarly, the minimum accelerating potential required to energise an electron which can ionise an atom is called the “ionisation potential” of that atom.
 - The first excitation potential of mercury atom is 4.86 V and its ionisation potential is 10.4 V

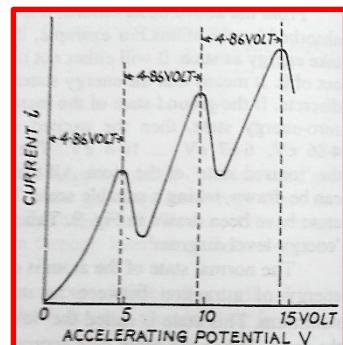
Frank and Hertz Experiment :

- The existence of discrete energy levels in atoms can be directly demonstrated by Frank and Hertz Experiment.



- Their experimental setup is shown in the figure → → →
 - It consists of a glass tube having a filament, cathode C, grid G and plate A.
 - **The grid is very near the plate A.**
 - The tube is filled at low pressure (nearly 1 mm of Hg) with the vapour of that element (as mercury) whose atomic energy levels are to be measured. An accelerating potential V is applied between cathode and the grid G by a variable battery. (Note that positive terminal of battery is connected to grid G).
 - A small 0.5 V retarding potential V_r is applied between grid G and plate A by another battery (note that the negative terminal of battery is connected to plate A).

terminal of battery is connected to plate A)



Explanation:

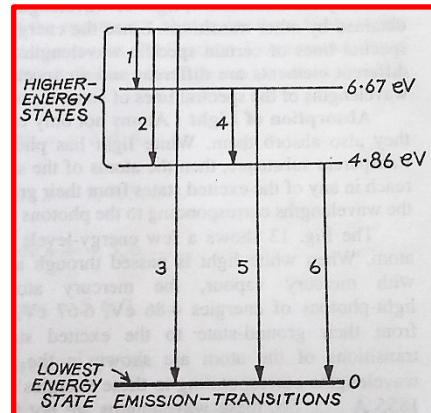
- Explanation:**

 - Electrons having different (low) energies are emitted from the filament. In reaching the grid, they acquire additional energy eV due to the accelerating potential V. In the beginning, when V is small, the electrons do not acquire energy enough to excite or ionise the mercury atoms in the tube. Hence the electrons reach the grid G without losing their energy. Of these, the electrons having energy $> eV_r$ reach the plate A and produce a current. As the voltage V is increased, the number of electrons reaching the plate goes on increasing. Hence the current i goes on increasing.
 - When $V = 4.86V$, the current suddenly falls. It means some electrons on their way towards the grid acquire energy enough to excite the mercury atoms by inelastic collisions. The electrons which do so lose their energy and are unable to reach plate A against the retarding potential V_r . hence, the current falls sharply. Clearly, $4.86V$ is the first excitation potential of mercury.
 - On further increasing V, more and more electrons are stopped by inelastic collision and they do not reach the plate A so that the current continues to fall. But a stage is reached when the electrons excite the atoms lone before reaching the grid, and when they reach the grid, once again they acquire energy enough to overcome the retarding potential V_r and reach the plate A. Hence the current begins to rise again. When $V = 9.72$, then after one inelastic collision between the filament and the grid G, the electrons acquire so much energy that they suffer a second inelastic collision and again lose their energy and fail to reach the plate A. hence the current falls again suddenly. This process is repeated. The distance between two successive peaks gives the first excitation potential of the mercury atom.
 - Actually atoms have more than one excitation potential and also an ionisation potential. For example, the second excitation potential of mercury is 6.67 V its ionisation potential is 10.4 V . Hence the second and third peaks of the curve become complicated.
 - From the above experiment, it is clear that electrons give energy to atoms only in “discrete” amounts. Mercury atoms are not excited so long the energy of the colliding electron is $< 4.86\text{ V}$. Frank and Hertz demonstrated this directly by experiment. They arranged for obtaining the spectrum of mercury vapour filled in the tube and found that so long the accelerating potential remained $< 4.86\text{ V}$, no spectral line was observed. As soon as the accelerating potential became 4.86 V , the spectral line of $\lambda = 2536\text{ \AA}$ was obtained. The energy corresponding to this wavelength is just $4.86\text{ eV} \approx 4.9\text{ eV}$
 - **We know that $E = 1.24/\lambda (\mu\text{m}) \text{ eV}$, where λ in μm ; here $\lambda = 2536\text{ \AA} = 253.6\text{ nm} = 0.2536\text{ }\mu\text{m}$**
 - **So $E = 1.24/0.2536 = 4.86\text{ eV} \approx 4.9\text{ eV}$**

Explanation of the Line (Emission & Absorption) Spectrum & Estimation of λ of Energy Transitions:

Emission of Light:

- Energy level diagram of Mercury atom AND transition from higher energy states to lower energy states is shown in fig → → → → → → → → → → → → → → →
 - We have seen that atoms can absorb some definite energy amounts only, which are different for the atoms of different elements. Thus, the atom of a particular element has some characteristic energy levels (or energy states).
 - At room temperature, generally, atoms remain in ground state (lowest-energy state).
 - When they receive appropriate energy from outside, they leave ground state and go to some excited states of higher energy.
 - But atom cannot remain in excited state for long and it returns to ground state or any other lower-energy state within a short time (nearly 10^{-8} second). When it returns, the atom radiates energy in the form of light (photons are emitted).
 - With each transition of the atom, light of definite λ is emitted. λ is calculated using simple formula



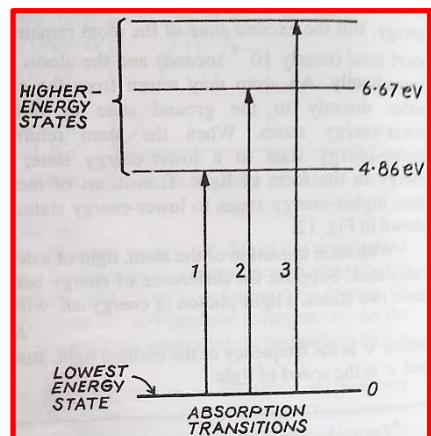
$E = 1.2375 / \lambda \text{ (\mu m)} \text{ eV}$, So $\lambda \text{ (\mu m)} = 1.2375 / \Delta E$; where ΔE is difference between two energy states

So the formula is $\lambda = 1.2375 / \Delta E$ nm; where ΔE is in eV. For example,

- Transition 4 : $\lambda = \frac{1.2375}{(6.67 \text{ eV} - 4.86 \text{ eV})} \mu\text{m} = \frac{1.2375}{1.81 \text{ eV}} \mu\text{m} = 0.6837 \mu\text{m} = 6837 \text{ \AA}$ (light of this λ is emitted)
 - Transition 5 : $\lambda = \frac{1.2375}{(6.67 \text{ eV} - 0 \text{ eV})} \mu\text{m} = \frac{1.2375}{6.67 \text{ eV}} \mu\text{m} = 0.1855 \mu\text{m} = 1855 \text{ \AA}$ (light of this λ is emitted)
 - Transition 6 : $\lambda = \frac{1.2375}{(4.86 \text{ eV} - 0 \text{ eV})} \mu\text{m} = \frac{1.2375}{4.86 \text{ eV}} \mu\text{m} = 0.2546 \mu\text{m} = 2546 \text{ \AA}$ (light of this λ is emitted) etc...
 - Hence by measuring wavelengths of the spectral lines pf some element, the element can be identified.

Absorption of Light:

- Energy level diagram of Mercury atom AND transition from **lower energy state** to higher energy states is shown in fig → → → → → → → → → → → → → → →
 - Atoms not only emit light, but if they light-photons of appropriate energy, they also absorb them. White light has photons of all energies. If we pass white light through some transparent substance, then the atoms of the substance absorb the photons of those energies by which they reach in any of the excited states from their ground state. Hence the light emerging from the substance lacks the wavelengths corresponding to the photons absorbed by the substance.
 - When white light is passed through a tube filled with mercury vapour, the mercury atoms absorb light-photons of energies 4.86 eV, 6.67 eV,... and rise from their ground-state to the excited states. The corresponding wavelengths are 2546 Å, 1855 Å, ...So, these wavelengths are not found the light emerging from the tube.
 - In general, number of the emission transitions > number of absorption transitions.
 - This is because the absorption transitions start from the lowest energy state only (i.e. ground state) and may end at any higher energy-level.
 - But emission transitions may start from any higher energy-level and end at
 - So, 6 emission transitions are possible and only 3 absorption transitions are
 - This is also due to the fact that atom cannot exist in excited state for long



FRANCK – HERTZ EXPERIMENT

The existence of discrete energy levels in an atom was directly verified in 1914 by James Franck and Gustav Hertz. They studied the spectrum of mercury vapour when electrons having different kinetic energies passed through the vapour. The electron energy was varied by subjecting the electrons to electric fields of varying strength. The electrons collide with the mercury atoms and can transfer energy to the mercury atoms. This can only happen when the energy of the electron is higher than the energy difference between an energy level of Hg occupied by an electron and a higher unoccupied level (see Figure). For instance, the difference between an occupied energy level of Hg and a higher unoccupied level is 4.9 eV. If an electron of having an energy of 4.9 eV or more passes through mercury, an electron in mercury atom can absorb energy from the bombarding electron and get excited to the higher level [Fig (a)]. The colliding electron's kinetic energy would reduce by this amount.



The excited electron would subsequently fall back to the ground state by emission of radiation [Fig. (b)]. The wavelength of emitted radiation is:

$$\lambda = \frac{hc}{E} = \frac{6.625 \times 10^{-34} \times 3 \times 10^8}{4.9 \times 1.6 \times 10^{-19}} = 253 \text{ nm}$$

By direct measurement, Franck and Hertz found that the emission spectrum of mercury has a line corresponding to this wavelength. For this experimental verification of Bohr's basic ideas of discrete energy levels in atoms and the process of photon emission, Frank and Hertz were awarded the Nobel prize in 1925.

Derive Rydberg formula for hydrogen atom spectrum and hence define wave number

According to the third postulate of Bohr's model, when an atom makes a transition from the higher energy state with quantum number n_i to the lower energy state with quantum number n_f ($n_f < n_i$), the difference of energy is carried away by a photon of frequency f_{if} such that $hf_{if} = E_{ni} - E_{nf}$

We know the energy expression from equation (7) $E = -\left[\frac{1}{n^2}\right]\frac{mZ^2e^4}{8\epsilon_0^2h^2}$, (putting Z=1 for hydrogen)

$$hf_{if} = \frac{me^4}{8\epsilon_0^2h^2} \left[\frac{1}{n_f^2} - \frac{1}{n_i^2} \right] \rightarrow f_{if} = \frac{me^4}{8\epsilon_0^2h^3} \left[\frac{1}{n_f^2} - \frac{1}{n_i^2} \right] \quad \text{---(10)}$$

In this relation, if we take $n_f = 2$ and $n_i = 3, 4, 5, \dots$, it reduces to the Balmer series.

We know that $c = f\lambda$ and $E = hf$, so, $f = c/\lambda$; substituting for f in equation (10), we get

$$\frac{c}{\lambda} = \frac{me^4}{8\epsilon_0^2h^3} \left[\frac{1}{n_f^2} - \frac{1}{n_i^2} \right]; \text{ simplifying } \frac{1}{\lambda} = \frac{me^4}{8\epsilon_0^2ch^3} \left[\frac{1}{n_f^2} - \frac{1}{n_i^2} \right]$$

The Rydberg constant R is readily identified to be $R = \frac{me^4}{8\epsilon_0^2h^3}$, SO

$$\frac{1}{\lambda} = R \left[\frac{1}{n_f^2} - \frac{1}{n_i^2} \right] \frac{1}{\lambda} \text{ is called the wave number (number of waves in unit distance is called wave number)} \quad \text{---(11)}$$

Equation (11) is Rydberg formula for the spectrum of the hydrogen atom. λ is the wavelength of the spectral line emitted and $R = \frac{me^4}{8\epsilon_0^2h^3}$ is the Rydberg constant;

Rydberg formula $\frac{1}{\lambda} = R \left[\frac{1}{n_f^2} - \frac{1}{n_i^2} \right]$ can be used in a simple way as $\lambda = \frac{970 \text{ \AA}}{\left[\frac{1}{n_f^2} - \frac{1}{n_i^2} \right]}$

Substituting all known values, $R = 1.03 \times 10^7 \text{ m}^{-1}$. This is a value very close to the value ($1.097 \times 10^7 \text{ m}^{-1}$) obtained from the empirical Balmer formula. This agreement between the theoretical and experimental values of the Rydberg constant provided a direct and striking confirmation of the Bohr's model.

- If the ionised state of hydrogen atom be taken as zero energy-level, then the energies of the different energy-levels of the hydrogen atom can be expressed by the following formula:

$$E_n = -\frac{Rhc}{n^2}; n = 1, 2, 3, \dots \text{ is the quantum number}$$

R = Rydberg constant = $1.097 \times 10^7 \text{ m}^{-1}$

C = Speed of light in vacuum = $3 \times 10^8 \text{ ms}^{-1}$

h = Planck's constant = $6.626 \times 10^{-34} \text{ Js}$

$$\begin{aligned} Rhc &= (1.097 \times 10^7 \text{ m}^{-1})(6.626 \times 10^{-34} \text{ Js})(3 \times 10^8 \text{ ms}^{-1}) \\ &= 21.81 \times 10^{-19} \text{ J} \quad (\text{since } 1 \text{ eV} = 1.602 \times 10^{-19} \text{ J}) \text{ or } (1 \text{ J} = 0.6244 \times 10^{19} \text{ eV}) \\ &= 21.81 \times 10^{-19} \times 0.6244 \times 10^{19} \text{ eV} \end{aligned}$$

Rhc = 13.6 eV

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

$$\text{In general } E_n = -\frac{Z^2 Rhc}{n^2} = -\frac{Z^2 \times 13.6}{n^2} \text{ eV}$$

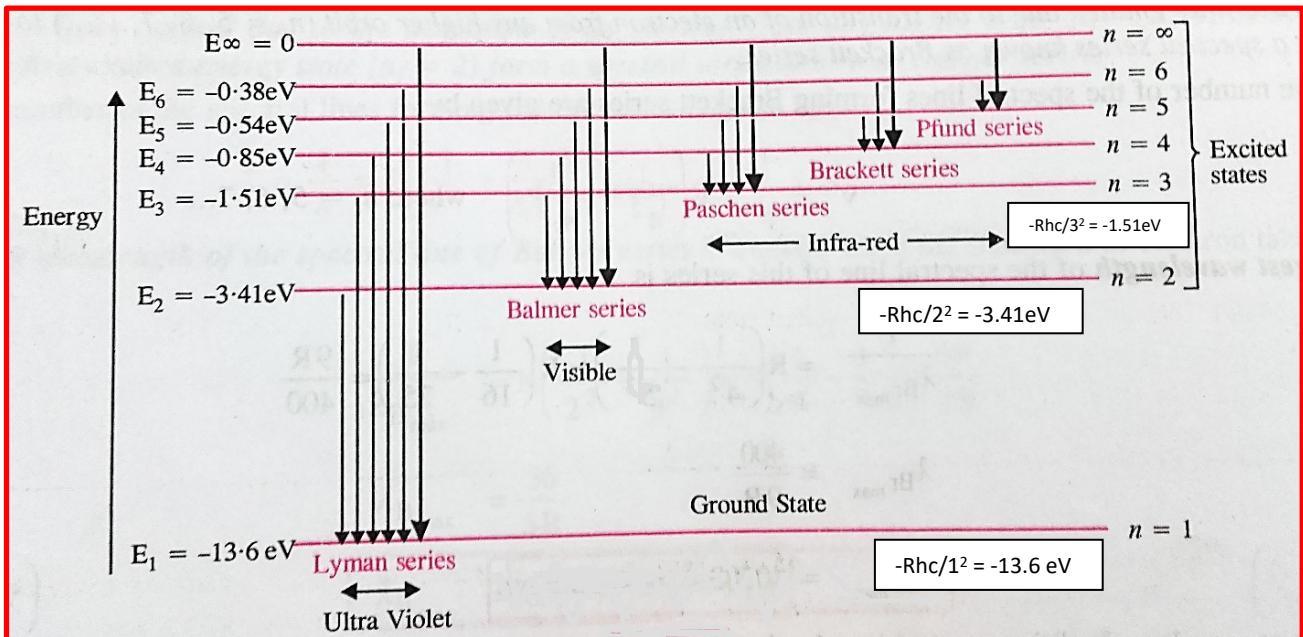
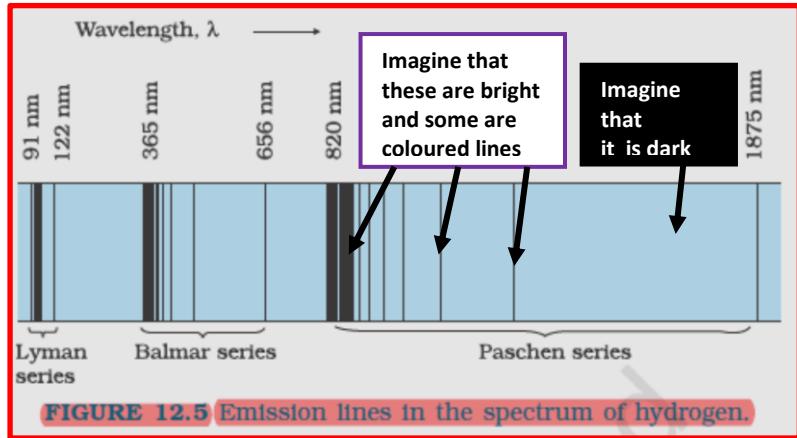
$$\text{For He}^+ \text{ atom, } Z = 2; \text{ therefore } E_n = -\frac{2^2 \times 13.6}{n^2} \text{ eV} = -\frac{4 \times 13.6}{n^2} \text{ eV} = -\frac{54.4}{n^2} \text{ eV}$$

$$\text{For He}^+ \text{ atom, } Z = 2; \text{ therefore } E_n = -\frac{54.4}{n^2} \text{ eV}$$

$$\text{For Hydrogen atom } Z = 1, E_n = -\frac{Z^2 Rhc}{n^2} = -\frac{13.6}{n^2} \text{ eV}$$

The Line Spectra of Hydrogen Atom (Sec 12.5 NCERT book)

- Since both n_f and n_i are integers, this immediately shows that in transitions between different atomic levels, light is radiated in various discrete frequencies. For hydrogen spectrum, the Balmer formula corresponds to $n_f = 2$ and $n_i = 3, 4, 5, \dots$, etc. The lines are $H_\alpha, H_\beta, H_\gamma, H_\delta, \dots, H_\infty$. One speciality of these lines is that in going from H_α to H_∞ , the brightness and separation between them decrease regularly. Thus, these lines are members of a series (Balmer series)
- The results of the Bohr's model suggested the presence of other series spectra for hydrogen atom → those corresponding to transitions resulting from $n_f = 1$ and $n_i = 2, 3, \dots$; $n_f = 3$ and $n_i = 4, 5, \dots$, and so on. Such series were identified in the course of spectroscopic investigations and are known as the Lyman, Balmer, Paschen, Brackett, and Pfund series.
- There are more series also, e.g. Humphrey's series. The spectral lines emitted due to transition of an electron from any outer orbit ($n_i = 7, 8, 9, \dots$) to the sixth orbit ($n_f = 6$) form a spectral series called Humphrey's series. It is in the IR region.
- The electronic transitions corresponding to these series are shown in the following figure.



- The various lines in the atomic spectra are produced when electrons jump from higher energy state to a lower energy state and photons are emitted. These spectral lines are called emission lines.
- But when an atom absorbs a photon that has precisely the same energy needed by the electron in a lower energy state to make transitions to a higher energy state, the process is called absorption. Thus if photons with a continuous range of frequencies pass through a rarefied gas and then are analysed with a spectrometer, a series of dark spectral absorption lines appear in the continuous spectrum. The dark lines indicate the frequencies that have been absorbed by the atoms of the gas.
- The explanation of the hydrogen atom spectrum provided by Bohr's model was a brilliant achievement, which greatly stimulated progress towards the modern quantum theory. In 1922, Bohr was awarded Nobel Prize in Physics.

For Hydrogen atom, the lines of Balmer series are found in the visible part of the spectrum. Other series were found in the invisible parts of the spectrum, i.e., Lyman series in the UV region and Paschen, Brackett and Pfund series in the IR region. The wavelengths of lines in these series can be expressed by the following formulae:

$$\frac{1}{\lambda} = Z^2 R \left[\frac{1}{n_1^2} - \frac{1}{n_2^2} \right] \quad \text{----- (8)}$$

like atoms (He^+ , Li^{++} ,). For hydrogen $Z = 1$, therefore for hydrogen atom

$$\frac{1}{\lambda} = R \left[\frac{1}{n_1^2} - \frac{1}{n_2^2} \right]$$
 Equation (8) is Bohr's formula for hydrogen and hydrogen-

Example 12.6 Using the Rydberg formula, calculate the wavelengths of the first four spectral lines in the Lyman series of the hydrogen spectrum.

Solution The Rydberg formula is

$$hc/\lambda_g = \frac{me^4}{8\varepsilon_0^2 h^2} \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right)$$

The wavelengths of the first four lines in the Lyman series correspond to transitions from $n_i = 2, 3, 4, 5$ to $n_f = 1$. We know that

$$\frac{me^4}{8\varepsilon_0^2 h^2} = 13.6 \text{ eV} = 21.76 \times 10^{-19} \text{ J}$$

Therefore,

$$\begin{aligned} \lambda_u &= \frac{hc}{21.76 \times 10^{-19} \left(\frac{1}{1} - \frac{1}{n_i^2} \right)} \text{ m} \\ &= \frac{6.625 \times 10^{-34} \times 3 \times 10^8 \times n_i^2}{21.76 \times 10^{-19} \times (n_i^2 - 1)} \text{ m} = \frac{0.9134 n_i^2}{(n_i^2 - 1)} \times 10^{-7} \text{ m} \\ &= 913.4 n_i^2 / (n_i^2 - 1) \text{ Å} \end{aligned}$$

Substituting $n_i = 2, 3, 4, 5$, we get $\lambda_{21} = 1218 \text{ Å}$, $\lambda_{31} = 1028 \text{ Å}$, $\lambda_{41} = 974.3 \text{ Å}$, and $\lambda_{51} = 951.4 \text{ Å}$.

- For Lyman series:

$$\frac{1}{\lambda} = R \left[\frac{1}{1^2} - \frac{1}{n^2} \right], \text{ where } n = 2, 3, 4, \dots \text{ in the UV region}$$

- For Balmer series:

$$\frac{1}{\lambda} = R \left[\frac{1}{2^2} - \frac{1}{n^2} \right], \text{ where } n = 3, 4, 5, \dots \text{ in the visible region}$$

- For Paschen series:

$$\frac{1}{\lambda} = R \left[\frac{1}{3^2} - \frac{1}{n^2} \right], \text{ where } n = 4, 5, 6, \dots \text{ in the IR region}$$

- For Brackett series:

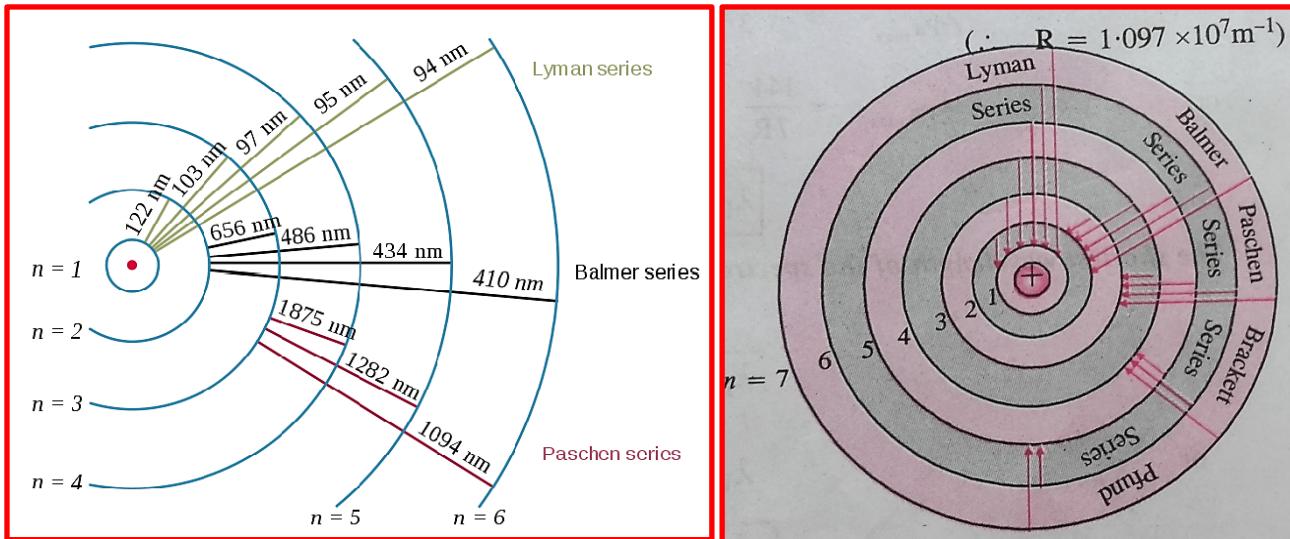
$$\frac{1}{\lambda} = R \left[\frac{1}{4^2} - \frac{1}{n^2} \right], \text{ where } n = 5, 6, 7, \dots \text{ in the IR region}$$

- For Pfund series:

$$\frac{1}{\lambda} = R \left[\frac{1}{5^2} - \frac{1}{n^2} \right], \text{ where } n = 6, 7, 8, \dots \text{ in the IR region}$$

- For Humphrey's series:

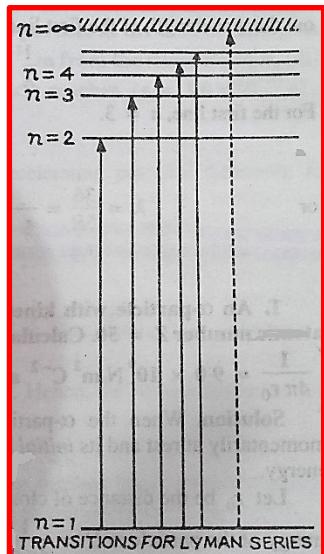
$$\frac{1}{\lambda} = R \left[\frac{1}{6^2} - \frac{1}{n^2} \right], \text{ where } n = 7, 8, 9, \dots \text{ in the IR region}$$



- For Lyman series: $\frac{1}{\lambda} = R \left[\frac{1}{1^2} - \frac{1}{n^2} \right]$, where $n = 2, 3, 4, \dots$ → When $n = 2$, longest $\lambda = 1216 \text{ \AA}$; when $n = \infty$, shortest $\lambda = 912 \text{ \AA}$
- For Balmer series: $\frac{1}{\lambda} = R \left[\frac{1}{2^2} - \frac{1}{n^2} \right]$, where $n = 3, 4, 5, \dots$ → When $n = 3$, longest $\lambda = 6559 \text{ \AA}$; when $n = \infty$, shortest $\lambda = 3644 \text{ \AA}$
- For Paschen series: $\frac{1}{\lambda} = R \left[\frac{1}{3^2} - \frac{1}{n^2} \right]$, where $n = 4, 5, 6, \dots$ → When $n = 4$, longest $\lambda = 1874 \text{ \AA}$; when $n = \infty$, shortest $\lambda = 8199 \text{ \AA}$
- For Brackett series: $\frac{1}{\lambda} = R \left[\frac{1}{4^2} - \frac{1}{n^2} \right]$, where $n = 5, 6, 7, \dots$ → When $n = 5$, longest $\lambda = 4059 \text{ \AA}$; when $n = \infty$, shortest $\lambda = 1458 \text{ \AA}$
- For Pfund series: $\frac{1}{\lambda} = R \left[\frac{1}{5^2} - \frac{1}{n^2} \right]$, where $n = 6, 7, 8, \dots$ → When $n = 6$, longest $\lambda = 7454 \text{ \AA}$; when $n = \infty$, shortest $\lambda = 2278 \text{ \AA}$
- For Humphrey's series: $\frac{1}{\lambda} = R \left[\frac{1}{6^2} - \frac{1}{n^2} \right]$, where $n = 7, 8, 9, \dots$ → When $n = 7$, longest $\lambda = 123694 \text{ \AA}$; when $n = \infty$, shortest $\lambda = 32817 \text{ \AA}$

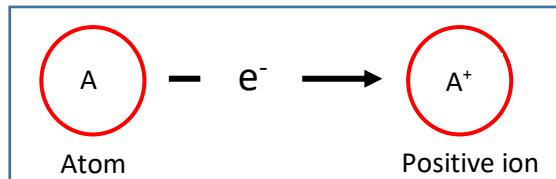
Absorption Transitions of Hydrogen atom: (very important)

- Normally all atoms remain in their lowest energy level. When we pass white light through a tube filled with hydrogen, then the hydrogen atoms absorb photons of appropriate energies and rise to various higher energy levels. These transitions are shown in the figure → → → →
- All these transitions are of Lyman series, because all of them are starting from the lowest energy level ($n = 1$).
- Absorption transitions of Balmer series are those which will start from the 2nd energy level ($n = 2$). But at ordinary temperatures, almost all the atoms remain in their lowest energy level ($n = 1 \rightarrow$ ground state) and so absorption transitions can start only from $n = 1$ level (not from $n = 2, 3, 4, \dots$ levels).
- Hence, only Lyman series is found the absorption spectrum of hydrogen atom (whereas in the emission spectrum, all the series are found).
- Hydrogen atoms are present in the sun. Hence hydrogen spectral series are found the solar spectrum. However, the “absorption” spectrum of sun has Balmer series also, besides the Lyman series. The reason is that the hydrogen atoms present in the sun are at very high temperature, so that many atoms are in higher energy-levels ($n=2$) also. Hence, absorption transitions start from $n = 2$ level also and the Balmer series is obtained.



Use of Rydberg Constant: (finding ionisation energy and λ)

- Determination of Ionisation Energy:
 - There is only one electron in the hydrogen atom. If this electron leaves the atom, the atom is ionised. The external energy required to ionise the atom is called its “ionisation energy”.
 - Hydrogen atom normally stays in lowest energy state ($n = 1$), where its energy is $-Rhc/1^2 = - Rhc$. On being ionised, its energy becomes zero (we have supposed the ionised state as zero-energy state, for which $n = \infty$). Thus, the ionisation energy of hydrogen atom is
 - Energy after ionisation – energy before ionisation = $0 - (-Rhc) = Rhc$
 - $Rhc = (1.097 \times 10^7 \text{ m}^{-1})(6.626 \times 10^{-34} \text{ Js})(3 \times 10^8 \text{ ms}^{-1})$
 - $= 21.81 \times 10^{-19} \text{ J}$ (since $1 \text{ eV} = 1.602 \times 10^{-19} \text{ J}$) or $(1 \text{ J} = 0.6244 \times 10^{19} \text{ eV})$
 - $= 21.81 \times 10^{-19} \times 0.6244 \times 10^{19} \text{ eV} = 13.6 \text{ eV}$
 - **Rhc = 13.6 eV**
 - The ionisation potential of hydrogen atom is 13.6 V.
- Ionisation and associated terms (for information only)
 - **Ionisation:** The process of detaching or knocking out an electron from an atom is called “ionisation”.
 - When the electron is completely detached from an atom, there is a deficit of one electron in the atom and it becomes positive ion. This process is called “ionisation”.



- Ionisation Energy :
 - The energy required to knock out an electron from an atom is called **Ionisation Energy of the atom**.
 - When electron is taken to the energy state corresponding to $n = \infty$, then electron is no longer bound to the nucleus of the atom and is detached from the atom.
 - The **Ionisation Energy of hydrogen atom** : The energy required to raise the electron from the ground state ($n = 1$) to the energy state corresponding to $n = \infty$ is called **Ionisation Energy of the hydrogen atom. It is given by**
 - $E = E_{\infty} - E_1 = 0 - (-13.6 \text{ eV}) = 13.6 \text{ eV}$
- Ionisation Potential :
 - The potential difference through which an electron of the atom is accelerated so that it is knocked out of the atom. The **Ionisation Potential of hydrogen atom = 13.6 V**
- Ionisation Energy of hydrogen atom is maximum (i.e., 13.6 eV) if the hydrogen atom is ionised when it is originally in the ground state
- If the atom is in the excited states, the **Ionisation Energy of hydrogen atom decreases. For example**
 - When the hydrogen atom is in the 1st excited state ($E_2 = 3.4 \text{ eV}$), then the Ionisation Energy of this excited hydrogen atom = $E_{\infty} - E_2 = 0 - (-3.4 \text{ eV}) = 3.4 \text{ eV}$
 - When the hydrogen atom is in the 2nd excited state ($E_3 = 1.51 \text{ eV}$), then the Ionisation Energy of this excited hydrogen atom = $E_{\infty} - E_3 = 0 - (-1.51 \text{ eV}) = 1.51 \text{ eV}$ and so on.

➤ **Determination of Wavelengths:**

Using the value of R, the λ of any line in any series of hydrogen spectrum can be determined by the corresponding formula. For example, suppose we have to find out the wavelength of the FIRST line of Balmer series. For Balmer series we have

$$\frac{1}{\lambda} = R \left[\frac{1}{2^2} - \frac{1}{n^2} \right], \text{ where } n = 3, 4, 5, \dots$$

$$\text{For the FIRST line, } n = 3, \frac{1}{\lambda} = R \left[\frac{1}{2^2} - \frac{1}{3^2} \right] = \frac{5}{36} R ; \text{ So, } \lambda = \frac{36}{5R} = \lambda = \frac{36}{5 \times (1.097 \times 10^7) m^{-1}} = 6.563 \times 10^{-7} \text{ m} = 6563 \text{ Å}$$

Excitation and associated terms

- **Excitation:** It is a process of absorption of energy by an electron of the atom as a result of which electron of the atom goes from the lower energy state to the higher state.
 - At room temperature, hydrogen atoms are usually ion the ground state. When an electron absorbs energy equal; to the difference between the energies of a lower energy state and the higher energy state, the electron goes from the lower energy state to the higher energy state and the atoms is said to be in the “excited state”.
- **Excitation Energy:** The amount of energy absorbed by an electron to go from the ground state or lower energy state to the higher energy state is called the **Excitation Energy**.
 - A hydrogen atom from the ground state can be excited to higher energy states by supplying external energy to the atom. The energy needed to excite the hydrogen atom from the ground state to the different excited states increases as the value of n increases. This fact is illustrated in the following table:

S.No.	Excited State	Excitation Energy
1	From ground state ($n = 1$) to 1 st excited state ($n = 2$)	$E = E_2 - E_1 = -3.4 - (-13.6) = 10.2 \text{ eV}$
2	From ground state ($n = 1$) to 2 nd excited state ($n = 3$)	$E = E_3 - E_1 = -1.51 - (-13.6) = 12.09 \text{ eV}$
3	From ground state ($n = 1$) to 3 rd excited state ($n = 4$)	$E = E_4 - E_1 = -0.85 - (-13.6) = 12.75 \text{ eV}$
4	From ground state ($n = 1$) to 4 th excited state ($n = 5$)	$E = E_5 - E_1 = -0.54 - (-13.6) = 13.06 \text{ eV}$
5	From ground state ($n = 1$) to infinite excited state ($n = \infty$)	$E = E_{\infty} - E_1 = 0 - (-13.6) = 13.6 \text{ eV}$

- **Excitation Potential:** Potential difference through which an electron of an atom must be accelerated so that it may go from the ground state to the excited state is called **Excitation Potential** of the atom. Whenever an electron passes through a potential difference of V volts, it acquires an energy = eV
 - When an electron in the hydrogen atom goes from the ground state to the first excited state, it needs an energy = 10.2 eV. Thus, the potential difference through which an electron must be accelerated to acquire energy to go to the first excited state is 10.2 V. this potential difference is known as “first excitation potential”. Similarly, the electron can be raised to the 2nd excited state if it is accelerated through a potential difference of 12.09 V, which is “second excitation potential” of the atom.
-

Question: A hydrogen atom can be excited to higher state by supplying external energy. A photon of energy 9.2 eV is allowed to fall on the hydrogen atom. Will hydrogen atom be excited? Explain?

- Minimum energy required to excite the hydrogen atom to the 1st excited state is given by
 - $E = E_2 - E_1 = -3.4 - (-13.6) = 10.2 \text{ eV}$
 - Since energy of incident photon (=9.2eV) is < the minimum energy required to excite, the hydrogen atom will not be excited.
-

What is the significance of experimentally determining different wavelengths in spectral series?

- ➔ Bohr's atomic theory predicted the wavelength in a series which are exactly same as found experimentally. This signifies the authenticity and validity of Bohr's atomic theory.

De Broglie's explanation of Bohr's Second Postulate of Quantisation:

- Of all the postulates, Bohr made in his model of the atom, perhaps the most puzzling is his second postulate.
- It states that the **angular momentum of the electron orbiting around the nucleus is quantised**. That is $mvr = \frac{nh}{2\pi}$; $n = 1, 2, 3 \dots$ Why should the angular momentum have only those values that are integral multiples of $\frac{h}{2\pi}$? The French physicist Louis de Broglie explained this puzzle in 1923, ten years after Bohr proposed his model.
- We know from chapter "Dual Nature of Radiation and Matter" (wave-particle duality) that the matter (or particle) (eg. Electron) can also behave like a wave (*The wave nature of electrons was first experimentally verified by Davisson and Germer in 1927 and independently by G.P. Thomson, in 1928, who observed diffraction effects with beams of electrons scattered by crystals.*).
- Therefore, as per de Broglie, the electron in its circular orbit, as proposed by Bohr, must be seen as a **particle wave**.
- De Broglie hypothesis is analogous to the standing waves formed on a vibrating string of certain length. He assumed the circumference of the orbit of an electron as the length of the string.
- We know that when a string fixed at two ends is plucked, a large number of wavelengths are produced. But only those waves which have nodes at the two ends form the standing waves and survive. It means that in a string, standing waves form when total distance travelled by a wave down the string and back is any integral number of wavelengths. Waves with other wavelengths interfere with themselves upon reflection and hence their amplitudes vanish quickly.
- Hence, according to de Broglie, a stationary orbit is that which contains an integral number of de Broglie waves associated with the revolving electron.
- Thus, the circumference of the orbit of an electron is equal to the integral multiple of the de Broglie wavelength of the electron moving in the orbit.

For an electron revolving in n^{th} circular orbit if radius r_n

Total distance covered = the circumference of the orbit = $2\pi r_n$

Therefore, for the permissible orbit, $2\pi r_n = n\lambda$; where $n = 1, 2, 3, \dots$

We know that the de Broglie wavelength is given by $\lambda = h/p = h/mv_n$ (where p is momentum and v_n is velocity of electron in the n^{th} orbit, m is mass of electron); Substituting $\lambda = h/m v_n$ in $2\pi r_n = n\lambda$, we get

$$2\pi r_n = nh/mv_n$$

$$mv_n r_n = \frac{nh}{2\pi}; \text{ where } mv_n r_n \text{ is the angular momentum } L.$$

i.e., **angular momentum of electron revolving in n^{th} orbit must be an integral multiple of $\frac{h}{2\pi}$, which is the quantum condition proposed by Bohr in second postulate.**

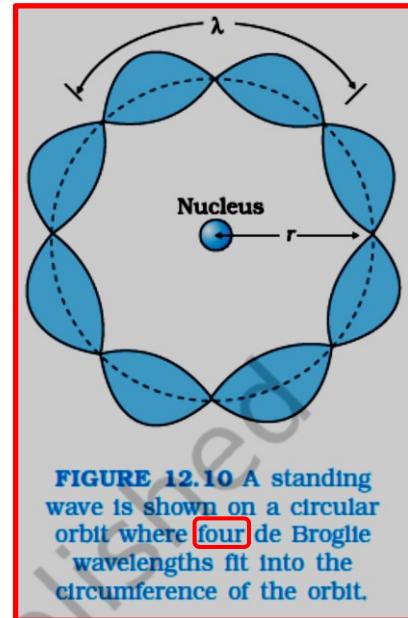


FIGURE 12.10 A standing wave is shown on a circular orbit where **four** de Broglie wavelengths fit into the circumference of the orbit.

Thus, the wave particle duality plays the central role in the structure of the atom. **The figure shows a standing particle wave on a circular orbit for $n = 4$ i.e., $2\pi r_n = 4\lambda$**

Thus de Broglie hypothesis provided an explanation for Bohr's second postulate for the quantisation of angular momentum of the orbiting electron. The quantised electron orbits and energy states are due to the wave nature of the electron and only resonant standing waves can persist.

Drawbacks or Limitations of Bohr's theory:

Background: Bohr's model, involving classical trajectory picture (planet-like electron orbiting the nucleus), correctly predicts the gross features of the Hydrogenic atoms*, in particular, the frequencies of the radiation emitted or selectively absorbed. This model however has many limitations.

- * Hydrogenic atoms are the atoms consisting of a nucleus with positive charge $+Ze$ and a single electron, where Z is the proton number. Examples are hydrogen atom, singly ionised helium, doubly ionised lithium, and so forth. In these atoms more complex electron-electron interactions are non-existent.

Limitations of Bohr's theory (Important): (long answer)

- The Bohr model is applicable to Hydrogenic atoms. It cannot be extended even to mere two electron atoms such as helium. The analysis of atoms with more than one electron was attempted on the lines of Bohr's model for Hydrogenic atoms but did not meet with any success. Difficulty lies in the fact that each electron interacts not only with the positively charged nucleus but also with all other electrons. The formulation of Bohr model involves electrical force between positively charged nucleus and electron. **It does not include the electrical forces between electrons which necessarily appear in multi-electron atoms. It fails to explain the spectra of multi-electron atoms.**
- While the Bohr's model correctly predicts the frequencies of the light emitted by Hydrogenic atoms, the model is unable to explain the relative intensities of the frequencies in the spectrum. In emission spectrum of hydrogen, some of the visible frequencies have weak intensity, others strong. Why? Experimental observations depict that some transitions are more favoured than others. Bohr's model is unable to account for the intensity variations.
- When a spectral line is observed under a high resolving-power microscope, it is found to be made up of a number of closely-spaced lines. Bohr's theory does not explain this "fine structure" of spectral lines even in hydrogen atom.
- The theory cannot fully explain the splitting of a spectral line into a number of component-lines (or spectral lines) under the effect of a magnetic field (Zeeman Effect).
- The theory cannot fully explain the splitting of a spectral line into a number of component-lines (or spectral lines) under the effect of an electric field (Stark effect).
- The theory does not explain the distribution of electrons in different orbits.
- It goes no information about the wave-nature of electron.
- The theory does not explain why orbits of electrons are taken as circular, while elliptical orbits are also possible.

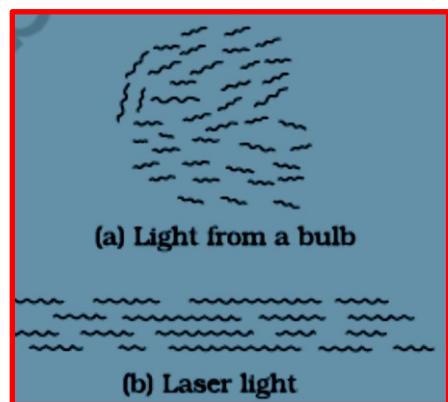
Bohr's model presents an elegant picture of an atom & cannot be generalised to complex atoms. For complex atoms we have to use a new & radical theory based on Quantum Mechanics, which provides a more complete picture of the atomic structure.

Limitations of Bohr's theory (Important): (short answer)

- The theory is applicable to only to simplest atom like hydrogen, with $Z = 1$. The theory fails in case of atoms of other elements for which $Z > 1$.
- Bohr's theory does not say anything about the relative intensities of spectral lines.
- Bohr's theory does not explain the fine structure of spectral lines even in hydrogen atom.
- The theory cannot fully explain the splitting of a spectral line into a number of component-lines (or spectral lines) under the effect of a magnetic field (Zeeman Effect) or an electric field (Stark effect).
- The theory does not explain the distribution of electrons in different orbits.
- Bohr's theory does not take into account the wave properties of electrons.
- The theory does not explain why orbits of electrons are taken as circular, while elliptical orbits are also possible.

Laser Light:

- Imagine a crowded market place or a railway platform with people entering a gate and going towards all directions. Their footsteps are random and there is no phase correlation between them. On the other hand, think of a large number of soldiers in a regulated march. Their footsteps are very well correlated. See figure.
- This is similar to the difference between light emitted by an ordinary source like a candle or a bulb and that emitted by a laser. The acronym LASER stands for Light Amplification by Stimulated Emission of Radiation. Since its development in 1960, it has entered into all areas of science and technology. It has found applications in physics, chemistry, biology, medicine, surgery, engineering, etc. There are low power lasers, with a power of 0.5 mW, called pencil lasers, which serve as pointers. There are also lasers of different power, suitable for delicate surgery of eye or glands in the stomach. Finally, there are lasers which can cut or weld steel.
- Light is emitted from a source in the form of packets of waves. Light coming out from an ordinary source contains a mixture of many wavelengths. There is also no phase relation between the various waves.



Therefore, such light, even if it is passed through an aperture, spreads very fast and the beam size increases rapidly with distance. In the case of laser light, the wavelength of each packet is almost the same. Also the average length of the packet of waves is much larger. This means that there is better phase correlation over a longer duration of time. This results in reducing the divergence of a laser beam substantially.

- If there are N atoms in a source, each emitting light with intensity I , then the total intensity produced by an ordinary source is proportional to NI , whereas in a laser source, it is proportional to N^2I . Considering that N is very large, we see that the light from a laser can be much stronger than that from an ordinary source.
- When astronauts of the Apollo missions visited the moon, they placed a mirror on its surface, facing the earth. Then scientists on the earth sent a strong laser beam, which was reflected by the mirror on the moon and received back on the earth. The size of the reflected laser beam and the time taken for the round trip were measured. This allowed a very accurate determination of (a) the extremely small divergence of a laser beam and (b) the distance of the moon from the earth.

What is the Bohr's correspondence principle?	<p>As we know, Bohr's atom model has been replaced by quantum mechanical model. According to this model, electrons in an atom do not move around the nucleus in definite orbits. However, the probability of finding electron is high near the Bohr orbit radius, and at the same time, the probability of finding the electron between these orbits is not zero. According to Bohr's correspondence principle, the predictions of quantum theory must correspond to the predictions of classical theory in the regions of sizes where classical theory holds.</p> <p>For large sizes wherein classical theory holds good, quantum number n become large. We may therefore rewrite Bohr's correspondence principle as</p> $\text{Limit [quantum physics]} = (\text{Classical Physics})$ $n \rightarrow \infty$ <p>For example, quantum condition for emission of radiation $hf = E_i - E_f$</p> <p>And Maxwell's classical theory says that an electron revolving with orbital frequency f must radiate light waves of frequency f. Calculations show that for quantum number n as large as 10000, the difference in frequency is < 0.015%. Thus Bohr's correspondence principle is established.</p>					
What are the basic characteristics of Lasers? Mention some of their applications.	<ul style="list-style-type: none"> ➤ Basic characteristics of Lasers: <ul style="list-style-type: none"> ○ Laser light is highly monochromatic ○ Laser light is highly coherent ○ Laser light is highly directional. ○ Laser light can be sharply focussed. ➤ Applications: <ul style="list-style-type: none"> ○ Performing surgery of many kinds ○ Voice and data transmission ○ Surveying ○ Welding automobiles ○ Manufacturing and reading CDs and DVDs ○ Garment industry (cutting several hundred layers of cloth at a time) ○ Generating holograms. 					
What is Orbital?	<p>An orbit of an electron in the Bohr model is the circular path of motion of an electron around the nucleus. But according to quantum mechanics, we cannot associate a definite path with the motion of electrons in an atom. We can talk about the probability of finding an electron in a certain region of space around the nucleus. This probability is inferred from the one electron wave function called the orbital. This orbital has no resemblance whatsoever with the orbit.</p>					
L and h	<p>Planck's constant (h) and Angular momentum (L) have same units and dimensions. $h = 6.626 \times 10^{-34} \text{ Js}$; Taking just units, $Js = (Fd)s = (ma)ds = (kg \text{ ms}^{-2}) m \text{ s} = \text{Kg m}^2 \text{ s}^{-1}$ $L = mvr = \text{kg ms}^{-1} \text{ m} = \text{Kg m}^2 \text{ s}^{-1}$</p>					
Ground state Energy	<p>What is the ground state energy of electron in case of 7_3Li ?</p> <p>➤ Here Z = 3, therefore n = 2 (why n = 2, see next page)</p> $E_n = -\frac{Z^2 \times 13.6}{n^2} eV = -\frac{9 \times 13.6}{4} = -\frac{122.4}{4} = -30.6 \text{ eV}$ <p>➤ A_ZX; Where A= Mass number (protons + neutrons in atom → called nucleons); Z = Atomic number (number of protons in atom); X is the atomic symbol (abbreviation used to represent atom in chemical formulae).</p> <p>➤ Number of neutrons = A – Z</p> <p>➤ Number of electrons = number of protons = Z (since atom as a whole is electrically neutral)</p> <p>➤ The lithium atom has a closed n=1 shell with two electrons and then one electron outside. Hence ground state is therefore taken as n = 2.</p>					
Name	symbol	Atomic Number (Z)	Protons	Neutrons	Electrons	Mass Number (A)
Hydrogen	H	1	1	0	1	1.01 (1)
helium	He	2	2	2	2	4.00 (4)
lithium	Li	3	3	4	3	6.94 (7)
beryllium	Be	4	4	5	4	9.01 (9)
boron	B	5	5	6	5	10.18 (11)
carbon	C	6	6	6	6	12.01 (12)

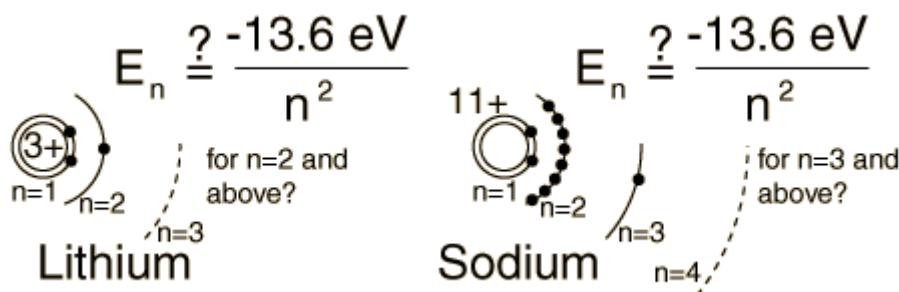
What Causes Electron Energies to Depend Upon the Orbital Quantum Number?

From the Bohr model or the hydrogen Schrodinger equation, the solution for the electron energy levels gives:

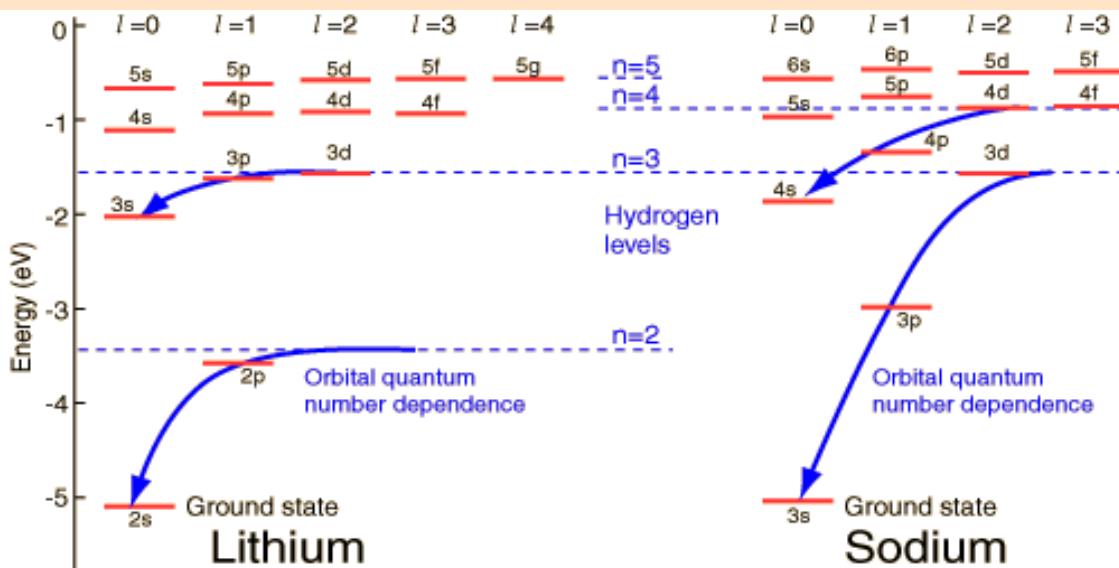
$$E_n = \frac{-13.6 \text{ eV}}{n^2}$$

This fits the hydrogen spectrum unless you take a high resolution look at fine structure or the structure produced by external magnetic fields (Zeeman effect), etc.

Hydrogen-like atoms such as lithium and sodium might be expected to exhibit similar energy levels. They consist of closed shells with a single electron outside. Envisioning a Bohr-type shell structure with just a single electron in the outer shell, the net charge inside that shell is just one net positive charge. This leads to the following expectation:



However, when data from spectra are used to build energy level diagrams for these atoms, a strong orbital dependence of the energy is found for the electrons of low angular momentum as shown below.



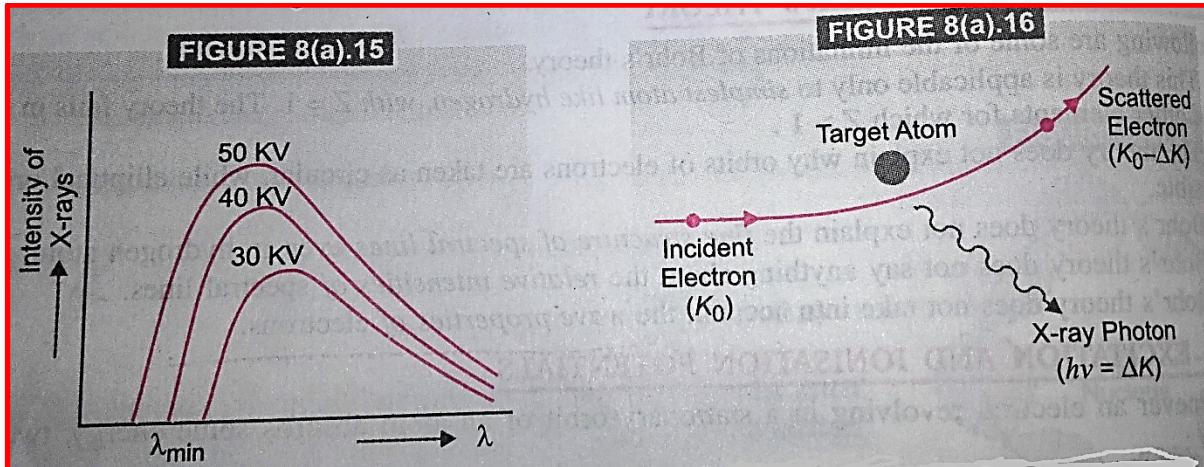
X-Ray Spectra: (Not in NCERT Syllabus) : only for info since X-rays also produces line spectra

There are 2 types of X-ray spectra:

- Continuous X-ray spectrum
- Characteristic spectrum or Line spectrum (superimposed on Continuous spectrum)

➤ Continuous X-ray spectrum

- Continuous X-ray spectrum is that which consists of all wavelengths larger than a certain minimum wavelength, λ_{\min} . The intensity of X-rays forming Continuous spectrum varies with the voltage applied across the cathode and target of X-ray tube as shown in Fig. 8(a).15. This spectrum does not depend on the nature of material of the target.
- Consider an electron of initial KE = K_0 that interacts (collides) with one of the target atoms, as shown in Fig. 8(a).16. The electron may lose a small amount of energy ΔK , which would appear in the form of X-ray photon. This is radiated from the site of the collision.

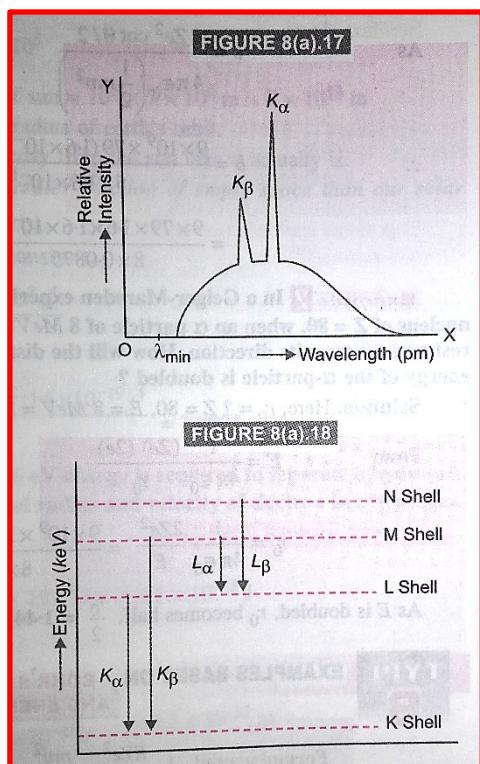


- If we ignore the energy transferred to the recoiling target atom, the energy of scattered electron would be ($K_0 - \Delta K$).
- The scattered electron may have a second collision with a target atom generating another X-ray photon and so on. This electron scattering process continues till electron is approximately stationary. All the photons generated by such electron collisions form part of continuous X-ray spectrum.
- If incident electron were to lose all its initial KE (K_0) in a single head-on collision with a target atom, a single X-ray photon of maximum energy / frequency (or minimum λ) would be emitted.

$$\circ \quad K_0 = h f_{\max} = \frac{hc}{\lambda_{\min}} ; \text{ Therefore } \lambda_{\min} = \frac{hc}{K_0} ; \text{ this is the cut off } \lambda \text{ of continuous X-ray spectrum, which does not depend upon the target material.}$$

Characteristic X-ray spectrum:

- Characteristic X-ray spectrum is that which consists of a few particular wavelengths superposed on the continuous X-ray spectrum in the form of peaks as shown in Fig 8(a).17. These wavelengths are Characteristic of the target material of X-ray tube.
- The peaks arise when an energetic electron strikes an atom of the target and knocks out one of the atom's deep lying electron, creating a vacancy or hole, in this shell (say K shell, $n = 1$). An electron in one of the outer shells having higher energy jumps to K shell, filling the vacancy/hole. During this jump, the atom emits characteristic X-ray photon. If the jump is from L shell ($n = 2$), the emitted radiation is K_α line. If the jump is from M shell, the emitted radiation is K_β line and so on.
- Similarly, we obtain L_α , L_β lines when electron jumps to L shell from M shell and N shell respectively. Some of the spectral lines are shown in Fig. 8(a).18. Their wavelengths would depend upon nature of the target material of X-ray tube.



Moseley's Law and Atomic Number

The square root of the frequency of a given spectral line (say K_{α}) emitted by an element is directly proportional to the atomic number of the element i.e.,

$$\sqrt{v} \propto Z \quad \text{or} \quad v \propto Z^2$$

The graph between \sqrt{v} and Z is shown in Fig. 7.

When K_{α} line is emitted, electron jumps from $n = 2$ to $n = 1$. The frequency of K_{α} line emitted by an element of atomic number is given by $v = 2.45 \times 10^{15} (Z - 1)^2$ Hz.

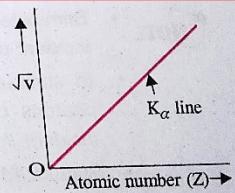


Figure 7

Importance of Moseley's law

1. Moseley's law (i.e., $\sqrt{v} \propto Z$) provided a guideline to place the elements in the periodic table. Before the investigation of this law, elements were placed in the periodic in the increasing order of the atomic mass of the elements. But Moseley suggested that the characteristic properties of the element are determined by the atomic number (Z) of the element. Hence, after Moseley's work, the elements were placed in the periodic table in the increasing order of the atomic number of the elements.

For example, before the discovery of Moseley's law, nickel ($_{28}\text{Ni}^{58.7}$) was placed earlier to cobalt ($_{27}\text{Co}^{58.9}$) in the periodic table according to increasing order of atomic mass. However, after the discovery of Moseley's law, cobalt is placed one position earlier to nickel in the periodic table according to increasing order of atomic number.

2. Moseley's law determined the atomic numbers of rare earth elements and their position in the periodic table.