02

Atomic Structure

IN THIS CHAPTER ....

The discovery of radioactivity, Faraday's law of electrolysis and other observations provided sufficient evidence to prove that atom is not indivisible. It can further be broken down into certain constituents or subatomic particles, such as electron, proton, neutron, meson, neutrino etc. Out of these, only electron, proton and neutron are of great importance and hence, are called **fundamental particles.**

Various experiments that lead to the discovery of these fundamental particles are as follows

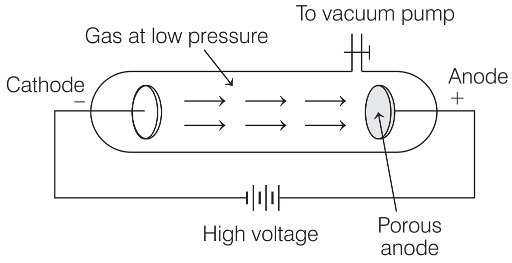
Cathode Rays and Discovery of Electron

When a high voltage electric current is passed through a gas filled evacuated tube following results are observed.

(i) **At normal pressure 760 mm of Hg** The gas remain non-conducting even at very high voltage ≈ 10,000V.

(ii) **At a pressure range of 10^{-2}-10^{-3} mm of Hg** The gas become conducting and some rays are visible which cause certain materials (including glass) to glow.

(iii) **At a pressure ≈ 10^{-4} mm of Hg** The gas remain conducting and the previous glow gets fainted. A new green glow behind anode at the walls of glass tube is observed.



A cathode ray discharge tube

All the above results indicate the presence of certain sources rays. These rays were emerged from cathode hence called **cathode rays**.

Later following distinctive properties were observed about these rays.

- Cathode rays travel in straight line path from cathode towards anode and cast shadows of metallic objects placed in their path.
- These rays can penetrate through thin layers of matter.
- They produce fluorescence when strike the glass wall of the discharge tube.
- These cause mechanical motion of a small pin wheel placed in their path. Thus, cathode rays possess kinetic energy and must contain material particles.
- These rays show deflection by electric and magnetic field both.
- X-rays are produced when cathode rays strike a metallic target.
- Cathode rays can produce chemical changes and thus, affect photographic plate.
- The nature of the cathode rays is independent of
  - (i) the nature of the cathode and
  - (ii) the gas in the discharge tube.
- Thus, we can say that **cathode rays contain negatively charged particles**. These particle were called **electrons** by Stoney.

  Certain formulae related with cathode ray particles are

  (i) **Parabolic path of cathode ray particles** in an electric field is given by

$$y = \frac{eE}{2mv^2}x$$

  (ii) **Radius of the circular path of cathode ray particl**e within the magnetic field is given by

$$r = \frac{mv}{eB}$$

Here, y = deflection in the path of cathode ray particle along the y axis
e = charge on cathode ray particle
m = mass of cathode ray particle
v = velocity of cathode ray particle
E = intensity of applied electric field
B = intensity of applied magnetic fied
x = distance between 2 parallel electric plates or electrodes.

Charge on Cathode Rays Particles

The first precise measurement of the charge on the electron was made by **Robert A. Millikan** in 1909 in his oil drop experiment. He measured the terminal velocity of a charged spherical oil-drop which is made stationary between two electrodes on which a very high potential is applied.

The formula used for calculating the charge on an electron was 'q' $= \frac{6\pi\eta r}{E}(v_1 + v_2)$

where, η = coefficient of viscosity of the gas medium
v_1, v_2 = terminal velocities
E = electric field strength
r = radius of the oil drop $= \sqrt{\frac{9\eta v_1}{2(f - \sigma)g}}$

(f = density of oil; σ = density of gas: g = gravitational force)

By oil drop experiment, the charge (e) on cathode rays particles was determined as -1.602×10^{-19}C or -4.803×10^{10} esu. Since, an electron has the smallest charge known, it was, thus, termed as unit negative charge.

Mass on Cathode Rays Particles

JJ Thomson in 1897 determined e/m, i.e. charge/mass, value of cathode ray particles by studying their deflections under electric and magnetic fields.

He gave the relation,

$$\frac{e}{m} = \frac{E}{rB^2} = -1.7588 \times 10^{11}\,\text{C kg}^{-1}$$

where, all the terms have usual significance.

Rest and Moving Mass

Thomson also showed that e/m value for the electrodes of different materials will always remains same. It confirmed that the constituent particles of cathode rays are common universal constituents of all atoms.

After knowing the charge, the mass of cathode rays particles can thus, be derived by

$$m = \frac{e}{e/m} = \frac{-1.602 \times 10^{-19}}{-1.76 \times 10^{11}}$$
$$= 9.108 \times 10^{-31}\text{kg}$$

This is termed as the **rest mass** of the cathode ray particles.

The mass of a moving cathode rays particle may be calculated by applying the following formula,

$$\frac{\text{Rest mass of cathode rays particle}}{\sqrt{1 - \left(\frac{v}{c}\right)^2}}$$

where, v is the velocity of the cathode rays particle and c is the velocity of light.

Infinity and Imaginary Mass

When v becomes equal to c, mass of the moving cathode rays particle becomes **infinity** and when the velocity of the cathode rays particle becomes greater than c, mass of the cathode rays particle becomes **imaginary**.

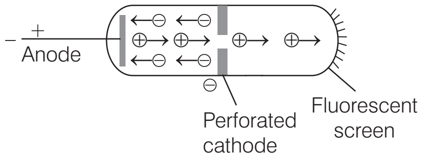
Electrons can also be produced by the action of ultraviolet light of X-rays on metal and from heated filaments. β-particles emitted by radioactive materials are also electrons.

Remember that all electrons carry the same charge. If they did not, they would be deflected by different magnitudes on passing through electric or magnetic fields.

Positive Rays and Discovery of Proton

In 1886, **Eugen Goldstein** used a discharge tube with a hole at cathode. He observed that while cathode rays were streaming away from the cathode, there were coloured rays produced simultaneously which passed through the perforated cathode and caused a glow on the wall opposite to the anode. Thomson observed that these rays consisted of positively charged particles and named them as positive rays.

These rays are also known as **canal rays** or **anode rays.**



Production of positive rays

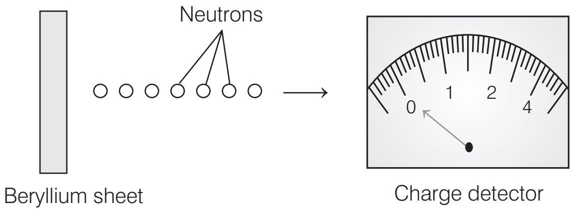
The properties of these rays were more or less similar to those of cathode rays.

The specific charge (e/m) of positive rays particles was found to vary with nature of gas and was maximum if H_2 is used.

Thus, the positive rays particles were infact positively charged gaseous atoms left after the removal of electron. These particles were given the name **proton**. These are fundamental constituents of all matter having a mass 1.673×10^{-27} kg and charge $+1.602\times 10^{-19}$ C.

Discovery of Neutrons

Chadwick (in 1932) bombarded beryllium (Be) and boron (B) sheet with high speed alpha (α) particles and noticed the emission of neutral particles, i.e. neutrons of mass nearly equal to protons and with no charge.



Ejection of neutron (Chadwick experiment)

Neutron is, therefore, having a mass 1.675×10^{-27} kg and no net charge. These are usually represented as ${}_0n^1$.

$$_4\text{Be}^9 + {}_2\text{He}^4 \longrightarrow {}_6\text{C}^{12} + \underset{\text{Neutron}}{{}_0n^1}$$

Properties of Fundamental Particles

Particles	Mass in			Charge in		Charge in units	Symbol	Discoverer	Location
	CGS	SI (kg)	amu (u)	esu	SI (Coulomb)				
Electron	9.1×10^{-28}	9.1×10^{-31}	0.000549	4.8×10^{-10}	1.602×10^{-19}	–1	${}_{-1}e^0$	JJ Thomson	Outside the nucleus
Proton	1.6×10^{-24}	1.672×10^{-27}	1.00727	—	1.6×10^{-19}	+1	${}_{+1}p^1$ or ${}_{+1}\text{H}^1$	Rutherford	In the nucleus
Neutron	1.6×10^{-24}	1.674×10^{-27}	1.00867	0	0	0	${}_0n^1$	Chadwick	In the nucleus

Today we all known that an atom consists of many other subatomic particles as well. On the basis of mass evaluations, these can be categorised as

(i) **Leptons Lightest**, e.g. electron, muon, tou and their anti-particles.

(ii) **Mesons** with intermediate masses pion, kaon, eta etc. and their anti-particle

(iii) **Baryons** with relatively large masses, e.g. proton, neutron, sigma, lambda etc. and their anti-particles.

Out of these baryons and mesons are collectively called as **hardons**. These hardons further consists of smaller particles called **quarks**, e.g. both neutron and proton are made up of 3 quarks each.

Thomson Atomic Model

JJ Thomson proposed a model in 1898, according to which an atom consists of a uniform positively charged sphere of radius 10^{-10} m approx. The electrons are embedded in it, so as to give most stable electrostatic arrangement.

He visualised atom as a pudding or cake of positive charge with electrons embedded into it. This model is often called **raisin pudding model** (raisin = electrons) or **plum pudding** or **water melon model.**

This model could account for the electrical neutrality of atom but it could not explain the results of gold foil scattering experiments of Rutherford.

Rutherford Atomic Model

Rutherford along with Marsden gave the model which was based upon his famous **alpha particle scattering experiment.**

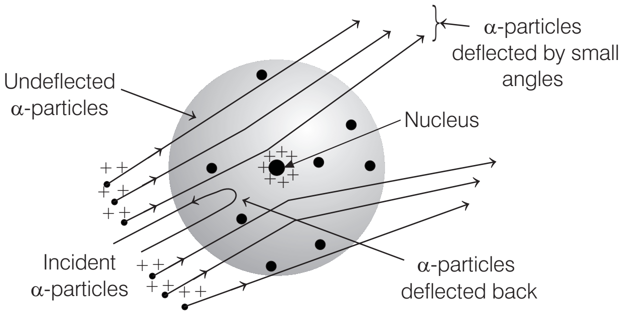
Alpha Particle Scattering Experiment

In this experiment, Rutherford bombarded the gold foil of thickness ≈ 100 nm with high energy positively charged helium ions (charge +2, mass 4u). The gold foil had a circular fluorescent ZnS screen around it. Whenever an α-particle struck the screen, a tiny flash of light was produced at that point.

Observation

The results of such an experiment were, however, quite unexpected as he observed that

- most of the α-particles passed through undeflected.



Scattering of α-particles by a dense, positively charged nucleus

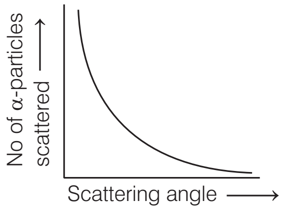
- a small fraction of α-particles was deflected by small angles.
- a very few α-particles (1 in 20000 approximate) bounced back, i.e. were deflected by nearly 180°.

Conclusions

On the basis of above observations, Rutherford concluded and gave his famous "Planetary model." According to which

- tom consists of a heavy and positively charged part at its centre, called the **nucleus** (diameter $= 10^{-14}$ m).
- the entire mass of an atom resides in its nucleus and is equal to the sum of masses of protons and neutrons. The mass of electron is negligible.
- the volume occupied by nucleus is very less as compared to the total volume of atom.
- the atom consists of lot of empty space around nucleus.
- electrons revolve around the nucleus in closed orbits, like planets around the sun, in the diameter of about 10^{-10} m. Almost all the space around nucleus is occupied by revolving electrons.

The graph between scattering angle and the number of α-particles scattered in the corresponding direction is shown in the figure given below



Informations of Rutherford's scattering equation can be memorised in the form of following relations

(i) Kinetic energy of α-particles

$$N = K_1 / [(1/2)mv^2]^2$$

(ii) Scattering angle 'θ'

$$N = K_2 / [\sin^4(\theta/2)]$$

(iii) Nuclear charge

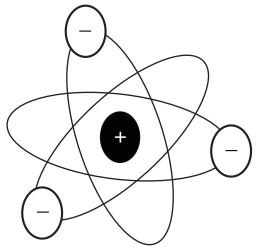
$$N = K_3 (Ze)^2$$

Here, N = number of α-particles striking the screen and K_1, K_2 and K_3 are the constants.

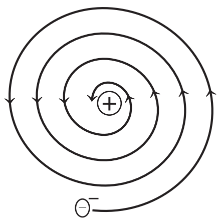
Drawbacks of the Model

The main weakness of Rutherford's model was its compliance with classical theory of electromagnetism. According to this theory if a charged particle revolves around another particle having opposite charge, it will radiate energy. This results in decrease of its orbiting radius.

The circular orbit becomes spiral gradually and electron finally fall on the nucleus as shown below.



(a) Rutherford's model of atom; electrons orbiting around nucleus



(b) Orbiting electron would radiate energy and spiral into the nucleus

Another weakness of this model was that it tells nothing about the electronic structure of atom.

In other words, it does not tell about the distribution of electrons around the nucleus.

Example 1. *If Rutherford performed his experiment using β-rays, what would have been his observations?*

(a) Most part of β-particles would have passed undeflected.

(b) A sharply defined pencil of β-rays, produced by passing the rays through pinhole, would had become more focussed (contracted) after passing through metal foil.

(c) A very few β-particles would had been completely absorbed.

(d) All of the above

Sol. (*d*) In case of β-rays, all the given observations are true because β-rays are infact negatively charged and hence, attracted towards nucleus.

Representation of Atom and Atomic Species

An atom is generally represented by the symbol, $_{Z}X^{A}$.

In this symbol, Z represents the atomic number which generally equals to the number of protons. A represents mass number. It is the sum of number of protons and number of neutrons in an atom.

In case of a neutral atom, number of protons and number of electrons are equal.

Atomic Species

Following species are common in relation to atoms.

(i) **Isotopes** These are the atoms that have same atomic number (Z) but different mass number (A).

e.g. $_{1}H^{1}, {}_{1}H^{2}, {}_{1}H^{3}$ are three isotopes of hydrogen.

Successive emission of one α and two β-particles from an element give its isotope.

(ii) **Isobars** These are the atoms of different elements that have same mass number (A) but different atomic number.

e.g. $_{18}Ar^{40}, {}_{19}K^{40}$.

Emission of one β-particle from an element results to its isobar.

(iii) **Isoelectronic** These species have same number of electrons.

e.g. $N^{3-}, O^{2-}, F^{-}, Ne, Na^{+}, Mg^{2+}$ all have 10 electrons.

(iv) **Isotones** These are the species in which atomic number as well as mass number are different but number of neutrons are same.

e.g. $_{1}H^{3}$ and $_{2}He^{4}$ both have 2 neutrons. Similarly, $_{14}Si^{30}$ and $_{15}P^{31}$ are isotones.

(v) **Isodiaphers** These species have same isotopic number, which is obtained by subtracting double of atomic number from atomic mass (or mass number), i.e. isotopic number

$$= \text{mass number} - 2 \times \text{atomic number}.$$

e.g. $_{19}K^{39}$ and $_{9}F^{19}$ are isodiaphers.

Developments Leading to the Bohr's Model of Atom

During the early 19th century, two developments in particular played a major role in the formulation of Bohr's model of atom. There were

- dual character of electromagnetic radiation.
- spectroscopic studies related to the emission and absorption of electronmagnetic radiation by atom.

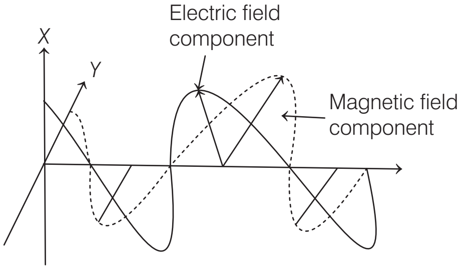
Dual Nature of Electromagnetic Radiations

Light, X-rays and γ rays are the examples of radiant energy. These are considered as various modes for the transference of energy. The nature of these modes carry the properties of wave and the particle both.

Wave Nature

Clark Maxwell in 1856 showed that radiant energy has wave properties and called them **electromagnetic waves** or **electromagnetic radiations**. All these radiations travel with the speed of light and do not require any medium for their propagation or transmission.

These radiation cantain oscillating electric and magnetic fields perpendicular to each other as shown below.



Depiction of electric and magnetic field association in an electromagnetic wave

A wave is a periodic disturbance in space or in a medium that involves a periodic change in some physical quantities. These include temperature, pressure, electric potential, electromagnetic field etc.

Thus, wave motion represents propagation of a periodic disturbance carrying energy from different sources.

Characteristics of Wave

(i) **Wavelength** It is the distance between two successive crests or troughs of a wave, i.e. distance between successive points of equal phase. It is denoted by the Greek letter 'λ'. It is expressed in centimetres, metres or in angstrom units.

(ii) **Frequency** It is the number of waves which pass through a given point in one second or unit time. It is denoted by the letter 'ν' (nu) and is expressed in hertz (Hz) or cycles per second (cps).

(iii) **Velocity** It is defined as the distance covered in one second by any wave. It is denoted by the letter 'c'. All the electromagnetic waves travel with the same velocity, i.e. 3×10^{10} cm/s.

The relation between velocity, wavelength and frequency is given as $\nu = \frac{c}{\lambda}$.

(iv) **Wave number** This is inverse of the wavelength and is shown by symbol '$\bar{\nu}$' (nu bar).

$$\bar{\nu} = \frac{1}{\lambda}$$

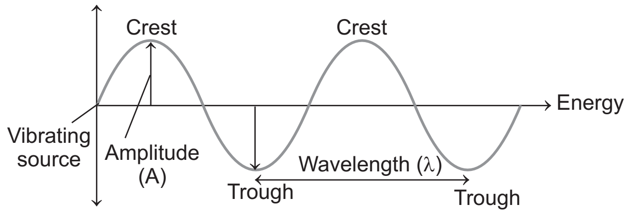
In simple words, the wave number is the number of wavelength per unit of length covered. Its unit is cm^{-1} or m^{-1}.

(v) **Amplitude** It is defined as the height of the crest or depth of the trough of a wave. It is denoted by the letter 'a' and determines the intensity of the radiation.

(vi) **Time period** Time taken by the wave for one complete cycle or vibration is called its time period. It is denoted by T and expressed in second per cycle.

$$T = \frac{1}{\nu}$$

All these characteristics are depicted in the figure given below.



Light wave

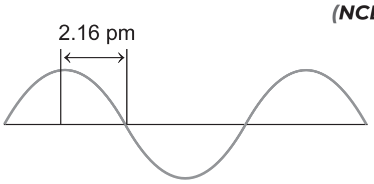
Electromagnetic radiations are of various types depending upon their wavelength (λ) or frequency (ν). These radiations constitute the electromagnetic spectrum.

The various regions of electromagnetic radiations are identified by different names and are summarised in the following table.

Characteristics of Various Electromagnetic Radiations

Name	Wavelength (Å)	Frequency (Hz)	Source	Uses
Radiowave	$3 \times 10^{14} - 3 \times 10^{7}$	$1 \times 10^{5} - 1 \times 10^{9}$	Alternating current of high frequency	Signal transmission
Microwave	$3 \times 10^{7} - 6 \times 10^{6}$	$1 \times 10^{9} - 5 \times 10^{11}$	Klystron tube	Cooking radar
Infrared (IR) waves	$6 \times 10^{6} - 7600$	$5 \times 10^{11} - 3.95 \times 10^{14}$	Incandescent objects	Heating
Visible	7600 – 3800	$3.95 \times 10^{14} - 7.9 \times 10^{14}$	Electric bulb, sun rays	Illumination
Ultraviolet wave (UV)	3800 – 150	$7.9 \times 10^{14} - 2 \times 10^{16}$	Sun rays, mercury vapour	Germisidal lamps
X-rays	150 – 0.1	$2 \times 10^{16} - 3 \times 10^{19}$	Cathode rays striking metal plate	Medical pictures, material testing
γ-rays	0.1 – 0.01	$3 \times 10^{19} - 3 \times 10^{20}$	Radioactive decay	Cancer treatment
Cosmic rays	0.01 –Zero	3×10^{20} – infinity	Outer space	

Example 2. *A hypothetical electromagnetic wave is shown in the figure. Find out the wavelength of the radiation.* ***(NCERT Exemplar)***



(a) 2.16 pm (b) 4.32 pm (c) 6.48 pm (d) 8.64 pm

Sol. (*d*) Wavelength is the distance between two successive peaks or two successive troughs of a wave. So, the wavelength will be 4 times of the distance shown, i.e. $\lambda = 4 \times 2.16 \text{ pm} = 8.64 \text{ pm}$

Particle Nature

The phenomenon like diffraction, interference can be easily well explained by wave nature of EMR.

However it fails to explain the other phenomenon like black body radiation, photoelectric effect etc.

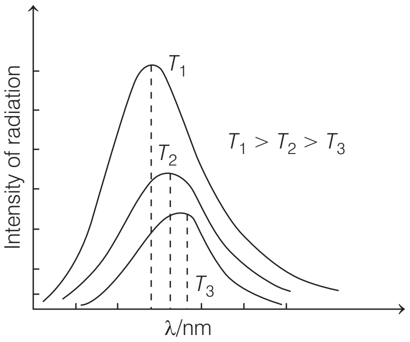
Black Body Radiation

The ideal body, which emits and absorbs all possible frequencies is called a **black body** and the radiations emitted by this body are called **black body radiations.**

Such bodies when hot are known to emit radiations over a wide range of wavelengths and in doing so, they show colour change as shown below.

$$\text{Dull red} \xrightarrow{\Delta} \text{Red} \xrightarrow{\Delta} \text{White} \xrightarrow{\Delta} \text{Blue}$$

At a given temperature, the relation of intensity of emitted radiation and its wavelength is shown below.



Intensity of radiation *vs* wavelength curve

These curves can not be explained satisfactorily on the basis of wave theory.

Planck's Quantum Theory

In 1900, Max Planck provided an explanation to this behaviour, according to which

- **atoms** and **molecules** could emit or absorb energy in discrete quantities or packets only, which are called **quantum.**
- the energy of a **quantum** is proportional to its frequency as $E = h\nu$. where, h is the proportionality constant, called the Planck's constant with the value 6.626×10^{-34} Js.
- energy is always gained or lost in integral multiples of $h\nu$ as $2h\nu$, $3h\nu$ etc. In other words, energy is quantised. Planck was unable to explain the reason behind quantisation of energy. However, **Einstein** explained the quantised nature of light while explaining the phenomenon of photoelectric effect.

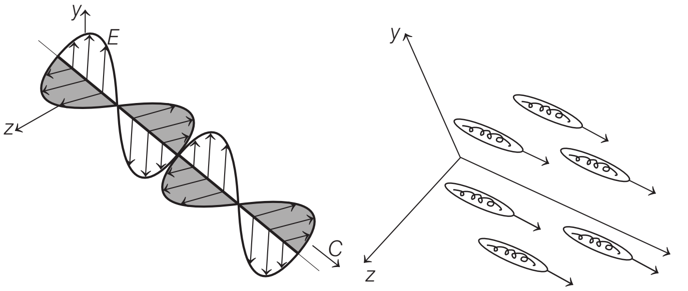
Photoelectric Effect

When a light of certain frequency strikes the surface of a metal, electrons are ejected or given out from the metal surface. This phenomenon of ejection of the electrons from the metal surface under the influence of incident radiation is called photoelectric effect. The electrons ejected from a substance in this manner are called **photoelectrons.**

Einstein Explanation

The photoelectric effect is only shown by a few metals under the influence of visible light. However, most of the metals exhibit this effect under the influence of more energetic radiations.

According to wave theory of light, both the number of electrons ejected and their energies should depend upon the intensity of incident light. However, in practice, it is found that only the number of ejected electrons depends upon incident light intensity while their energies do not. Einstein suggested that light consists of streams of particles, called photons which move with the speed of light.



(a) A classical view (b) Einstein's photon picture

Picture of a travelling light wave

Using Planck's quantum theory of radiation as a starting point, he deduced that each photon possess energy, E which is equal to

$$E = h\nu = \frac{hc}{\lambda} \qquad \left(\because \ \nu = \frac{c}{\lambda}\right)$$
$$= hc\bar{\nu}$$

where, ν = frequency of light.

Thus, shooting a beam of light on a metal surface means shooting a beam of photons. An electron is ejected when a photon strikes that electron and transfers all of its energy to electron.

So, as this energy is frequency dependent, hence energy of ejected electrons will also depend on frequency of light.

Threshold Frequency and Work Function

There is a characteristic minimum frequency for each metal, called **threshold frequency** (ν_0) below which the 'photoelectric effect' does not occur.

We can calculate, minimum amount of energy required to remove an electron from the metal surface, with the help of this frequency as,

$$E = h\nu_0$$

This is also called **work function** (W) of metal.

Kinetic Energy of Ejected Photoelectrons

Since, the striking photons have energy equal to $h\nu$ and the minimum energy required to eject an electron is $h\nu_0$, then $h\nu - h\nu_0$ will be transformed as KE of photoelectron, i.e. $\frac{1}{2} m_e v^2$, and as the total energy has to be conserved.

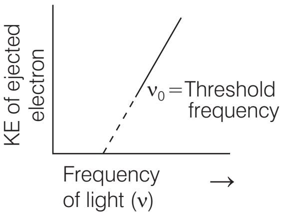
We can write Einstein equation as,

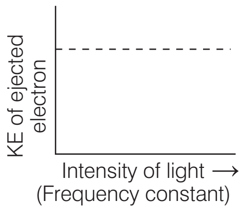
$$\frac{1}{2} m_e v^2 = h\nu - h\nu_0$$

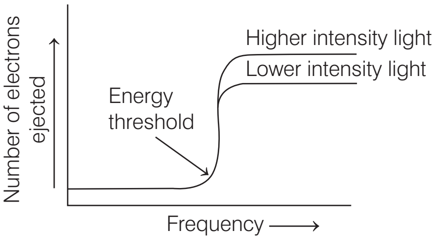
$$\boxed{\frac{1}{2} m_e v^2 = h(\nu - \nu_0)}$$

So, the maximum kinetic energy (KE_{max}) of photoelectrons is directly proportional to the frequency of incident light and is independent of its intensity.

All the curves associated with photoelectric effect are given below.







Stopping Potential

The phenomenon of photoelectric effect in a discharge tube is coherent with stopping potential (V_0). This potential is defined as the *minimum potential of anode required to reduce the* KE *of photoelectrons to zero*.

Both KE and V_0 are independent of the intensity of incident radiation.

Always remember for a photoelectron,

$$\frac{1}{2}mv^2 = eV_0$$

Example 3. *If P is the momentum of the fastest electron ejected from a metal surface after the irradiation of light having wavelength λ, then for* 1.5 P *momentum of the photoelectron, the wavelength of the light should be*
(Assume kinetic energy of ejected photoelectron to be very high in comparison to work function) ***(JEE Main 2019)***

(a) $\frac{4}{9}\lambda$ (b) $\frac{3}{4}\lambda$ (c) $\frac{2}{3}\lambda$ (d) $\frac{1}{2}\lambda$

Sol. (a) The expression of kinetic energy of photo electrons,

$$\text{KE} = \frac{1}{2}mv^2 = E - E_0$$

When, KE >> E_0, the equation becomes, $\text{KE} = \frac{1}{2}mv^2 = E$

$$\Rightarrow \quad \frac{1}{2}mv^2 = \frac{hc}{\lambda} \Rightarrow \frac{P^2}{2m^2} = \frac{hc}{\lambda}$$

$$\Rightarrow \quad \lambda = hc \times 2m^2 \times \frac{1}{P^2} \Rightarrow \lambda \propto \frac{1}{P^2}$$

$E = \frac{hc}{\lambda}$ = energy of incident light.

E_0 = threshold energy or work functions,

$$\frac{1}{2}mv^2 = \frac{1}{2} \times \frac{(mv)^2}{m^2} = \frac{1}{2} \times \frac{P^2}{m^2}$$

$\because \quad P$ = momentum $= mv$

As per the given condition, $\frac{\lambda_2}{\lambda_1} = \left(\frac{P_1}{P_2}\right)^2$

$$\Rightarrow \quad \frac{\lambda_2}{\lambda} = \left(\frac{P}{1.5 \times P}\right)^2 = \left(\frac{2}{3}\right)^2 = \frac{4}{9}$$

$$\Rightarrow \quad \lambda_2 = \frac{4}{9}\lambda \qquad \begin{bmatrix} \because \lambda_1 = \lambda \\ P_1 = P \end{bmatrix}$$

Example 4. *Threshold frequency* ν_0 *is the minimum frequency which a photon must possess to eject an electron from a metal. It is different for different metals. When a photon of frequency* $1.0 \times 10^{15}\,\text{s}^{-1}$ *was allowed to hit a metal surface, an electron having* 1.988×10^{-19} J *of kinetic energy was emitted. If a photon with a wavelength equal to* 600 nm *hits the metal surface,* ***(NCERT Exemplar)***

(a) the electrons will be ejected
(b) no electron will be emitted
(c) four electrons will be emitted
(d) cannot say anything

Sol. (b) We know that, $h\nu = h\nu_0 + \text{KE}$ or $h\nu - \text{KE} = h\nu_0$

$$= (6.626 \times 10^{-34}\,\text{Js} \times 1 \times 10^{15}\,\text{s}^{-1}) - 1.988 \times 10^{-19}\,\text{J}$$

$$h\nu_0 = 6.626 \times 10^{-19} - 1.988 \times 10^{-19}\,\text{J}$$

$$h\nu_0 = 4.638 \times 10^{-19}\,\text{J}$$

$$\nu_0 = \frac{4.638 \times 10^{-19}\,\text{J}}{6.626 \times 10^{-34}\,\text{Js}} = 0.669 \times 10^{15}\,\text{s}^{-1}$$

when, $\lambda = 600\text{nm} = 600 \times 10^{-9}\text{m}$

$$\nu = \frac{c}{\lambda} = \frac{3.0 \times 10^8\,\text{ms}^{-1}}{6.0 \times 10^{-7}\,\text{m}} = 0.5 \times 10^{15}\,\text{s}^{-1}$$

Thus, $\nu < \nu_0$.

Hence, no electron will be emitted.

Example 5. *The work function of sodium metal is* 4.41×10^{-19} J. *If photons of wavelength 300* nm *are incident on the metal, the kinetic energy of the ejected electrons will be* ($h = 6.63 \times 10^{-34}$ J s; $c = 3 \times 10^8$ m/s) .... $\times 10^{-21}$ J. ***(JEE Main 2020)***

Sol. (222) For photoelectrons, its kinetic energy will be

$$\text{KE} = E - E_a = \frac{hc}{\lambda} - E_0$$

λ = Wavelength of photon
$= 300\text{ nm} = 300 \times 10^{-9}$ m
E_0 = Threshold energy
= Work function of sodium metal
$= 4.41 \times 10^{-19}$ J

$$\text{So, KE} = \frac{6.63 \times 10^{-34} \times 3 \times 10^8}{300 \times 10^{-9}} - 4.41 \times 10^{-19}\,\text{J}$$

$$= 222 \times 10^{-21}\,\text{J}$$

Spectrum

A spectrum can be defined as "*pictorial representation of arrangement of radiations in increasing order of wavelength or decreasing order of frequency*". The spectrum may be emission or absorption spectrum on the basis of energy absorbed or emitted.

Emission and Absorption Spectra

Atom, molecule and ions emit radiations after absorbing energy. The spectrum of such emitted radiations is called **emission spectra.**

An **absorption spectra** is like the photographic negative of an emission spectra. Here, a continum of radiations is passed through a sample which absorbs the radiations of certain wavelengths. The missing wavelengths or radiations absorbed, leave dark spaces in bright continuous spectrum.

Band and Line Spectra

The spectra can be continuous or discontinuous also. In continuous spectra there is no sharp boundaries, thus it is also called as **band spectra**. Discontinuous spectra have sharp boundaries and is also called **line spectra.**

Bohr's Model

Both the explanations which proved dual nature of light and side wise development of spectroscopy concept were very useful in shaping the first theoritical model of atomic structure. This model was proposed by Neils Bohr a Danish Physicist. He tried to rectify the problem points of Rutherford model.

The essential features and main postulates of this improved form of Rutherford's model are as follows

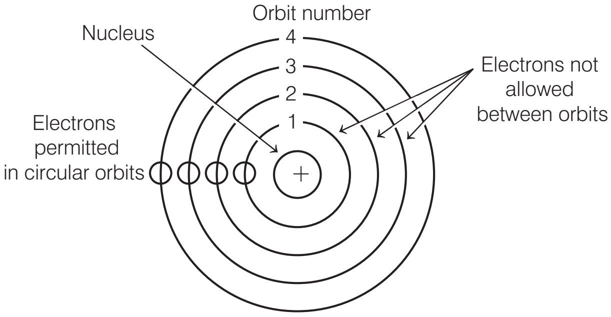
Essential Features

- Presence of a positively charged nucleus at the centre with all protons and neutrons. Thus, most of the mass and complete positive charge of the nucleus is concentrated within the nucleus.
- Revolution of negatively charged electrons around the nucleus.

Major Postulates

- The revolution of electrons around nucleus occur in circular paths of fixed radius and energy.
- These paths are called **orbits** or **stationary states** or energy **shells** or **stationary energy orbits** and are arranged concentrically around the nucleus.
- These are designated either as K, L, M, N etc., or 1, 2, 3 ……… The integers (1, 2, 3…) were designated as n or principal quantum numbers by Bohr.
- Only those orbits are valid in which the angular momentum is quantised, i.e. have the value as an integral multiple of $\frac{h}{2\pi}$.

  Thus, angular momentum $(m_e vr)$ of these orbitals can be $\frac{nh}{2\pi}$ where $n = 1, 2, 3, 4$ ……



Circular electron orbits or stationary levels in an atom

- The energy of an electron with in the orbit does not changes with time, i.e. during its course of revolution, the electron neither looses energy nor gains energy.
- An electron can move from one energy level to another through quantum or photon jumps only. When it resides in an orbit with lowest energy, it is said to be in **ground state.**
- It can jump from its lower energy level to higher energy level after absorbing energy. Here, at higher energy level, it is said to be in **excited state.**

  So, an electron can move only from its ground state to its excited state after absorbing energy or from its excited state to ground state after releasing energy.
- During transition between two stationary states of different energy, the frequency of radiation absorbed or emitted is given by

  $$\nu = \frac{E_2 - E_1}{h}$$

  This expression is called **Bohr's frequency rule.**

Bohr Calculations

Bohr made following calculations through his postulates.

1. Radii of Various Orbits

With the help of some classical laws of Physics and his postulates Bohr was able to calculate the radius of each orbit and gave the following formula for an electron

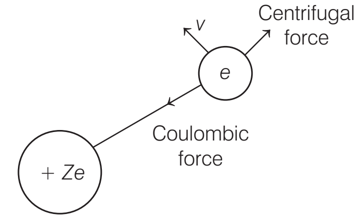
$$r_n = \frac{n^2h^2}{4\pi^2kme^2Z}$$

where, mass (m) and charge of an electron are constant along with Plank's constant (h) and Coulomb's constant (k), n is principal quantum or orbit number and Z is atomic number of atom concerned.

The above written formula was derived by equating electrostatic force of attraction with centrifugal force as,

$$\frac{Ze^2}{r^2} = mv^2/r$$

It is so because both of these forces act in opposite direction on an revolving electron and required to keep it revolving in its orbit as shown below.



Revolution of electron around the nucleus

Hence, only certain orbits whose radii are given by the above equation are available for the electron. The greater the value of n, i.e. farther level from the nucleus i.e. the greater is the radius. The radius of the smallest orbit $(n = 1)$ for hydrogen atom $(Z = 1)$ is considered as r_0.

For hydrogen atom if we put the values of all the constants in the given formula, we get

$$r_0 = 5.29 \times 10^{-11} \text{ m or } 0.529\text{Å}$$

Radius of nth orbit for an atom with atomic number Z is simply written as,

$$\boxed{r_n = r_0 \frac{n^2}{Z} = 0.529 \times \frac{n^2}{Z} \text{Å}}$$

Example 6. *The radius of hydrogen atom in the ground state is* 0.53 Å. *The radius of* Li^{2+} *in the similar state is*

(JEE Main 2020)

(a) 1.06 Å (b) 0.53 Å (c) 0.265 Å (d) 0.17 Å

Sol. (*d*) $r_{Li} = \frac{r_H \times n^2}{Z}$

($n = 1$, because state is same as hydrogen, i.e. ground state for Li, $Z = 3$)

$$r_{Li} = \frac{0.53 \times (1)^2}{3} = 0.17 \text{ Å}$$

2. Energy of Revolving Electron

The total energy, E of the electron is the sum of its kinetic and potential energy.

Substituting for r, gives us $E = -\frac{2\pi^2 m Z^2 e^4 K^2}{n^2 h^2}$

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

This expression shows that only certain energies are permissible for an electron.

After putting the values of constants in the fomula we get following simplified expressions.

$$\boxed{\begin{aligned} E &= -21.8 \times 10^{-12} \times \frac{Z^2}{n^2} \text{ erg/atom} \\ &= -21.8 \times 10^{-19} \times \frac{Z^2}{n^2} \text{ J/atom} \end{aligned}}$$

$$E_n = -13.6 \times 10^{-19} \times \frac{Z^2}{n^2} \text{ eV/atom} \quad \text{or} \quad -13.6 \times \frac{Z^2}{n^2} \text{ eV}$$

$$[\because 1 \text{eV} = 3.83 \times 10^{-23} \text{ kcal} = 1.602 \times 10^{-12} \text{erg} = 1.602 \times 10^{-19} \text{J}]$$

$$E = -313.6 \times \frac{Z^2}{n^2} \text{ kcal/mol} \qquad (\therefore 1 \text{ cal} = 4.18 \text{ J})$$

Remember the negative sign in all formulae of energy does not have any numerical implication. This sign only signifies that the energy of electron in an atom is lower than the energy of a free electron at infinity. The highest negative value is given for $n = 1$ corresponding to most stable orbit.

When $n = \infty, E = 0$, which corresponds to an ionised atom, i.e. the electron and nucleus are infinitely separated.

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

Example 7. *The ratio of the difference between the energy of 1st and 2nd Bohr's orbits to that between 2nd and 3rd orbit is*

(a) $\frac{1}{2}$ (b) $\frac{1}{3}$

(c) $\frac{27}{5}$ (d) $\frac{5}{27}$

Sol. (c) $\Delta E_{1,2} = E_2 - E_1 = \frac{E_H}{(n_2)^2} - \frac{E_H}{(n_1)^2}$

$$= E_H\left(\frac{1}{(2)^2} - \frac{1}{(1)^2}\right) = -\frac{E_H \times 3}{4}$$

$$\Delta E_{2,3} = E_3 - E_2 = -E_H \times \frac{5}{36}$$

$$\frac{\Delta E_{1,2}}{\Delta E_{2,3}} = E_H \times \frac{3}{4} \times \frac{36}{E_H \times 5} = \frac{27}{5}$$

Example 8. *If the energy of electron is* −0.850 eV, *then its distance from the nucleus will be*

(a) 2.39 Å (b) 5.69 Å

(c) 8.46 Å (d) 9.38 Å

Sol. (c) $E_n = -\frac{Z^2}{n^2} \times 21.8 \times 10^{-19}$

$\therefore \qquad -\frac{Z^2}{n^2} \times 21.8 \times 10^{-19} = -0.85 \times 1.6 \times 10^{-19}$

Or $\qquad n = 4 \qquad (\therefore Z = 1)$

$$r = \frac{n^2}{Z} \times 0.529$$

$$= \frac{16}{1} \times 0.529 = 8.46 \text{Å}$$

3. Bohr Velocity or Velocity of Electron

The formula for the velocity of an electron within the orbit is

$$v = \frac{2\pi K Z e^2}{nh}$$

where, except n and Z all are constants. So, after putting the values of all the constants in the formula, we get

$$v = 2.18 \times 10^8 \frac{Z}{n} \text{ cm/s}$$

Thus, the velocity of an electron in nth orbit of H-atom,

$$V_n = \frac{2\pi e^2}{nh}$$

$$= \frac{2.1847 \times 10^8}{n} \text{ cm s}^{-1}$$

Example 9. *Determine the number of revolutions made by electron in one second in the* 2^{nd} *Bohr orbit of hydrogen atom. (Take* $r_0 = 0.53 \times 10^{-10}$ m*)*

(a) 6.29×10^{12} (b) 5.29×10^{13}

(c) 2.39×10^{15} (d) 8.23×10^{14}

Sol. (*d*) If v is the speed of moving electron in the said Bohr orbit then, the number of revolutions made by electron in one second would be

$$rps = \frac{v}{2\pi r}$$

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

$\Rightarrow \qquad rps = \frac{nh}{4\pi^2 mr^2}$

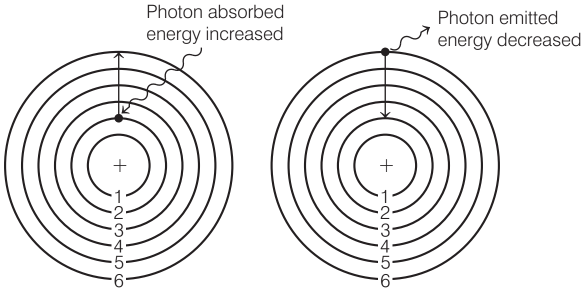
$$= \frac{nh}{4\pi^2 m\left(\frac{r_0 n^2}{Z}\right)^2} = \frac{h\cdot Z^2}{4\pi^2 m r_0^2 n^3}$$

$$= \frac{6.626\times 10^{-34}\times (1)^2}{4\times (3.14)^2\times 9.1\times 10^{-31}\times (0.53\times 10^{-10})^2\times (2)^3}$$

$$= 8.23\times 10^{14}\text{ Revolution/s}$$

Interpretation of Hydrogen Spectrum by Bohr's Model

According to Bohr's model, although electrons revolve in stationary energy orbits, but these can undergo transitions as shown below



An electron absorbs a photon of light while it jumps from a lower energy orbit and a photon is emitted while it returns to the original lower energy level.

These transitions were proved responsible for the sepecturm of an atom. Infact, Bohr explained the spectrum of hydrogen through these transitions.

The Spectrum

The spectrum of hydrogen can be obtained by passing the light through spectrograph. This light being emitted from the discharge tube contain hydrogen at low temperature.

Actually the electric discharge dissociates H_2 molecules and energetically excited hydrogen atoms are produced. These hydrogen atoms emit electromagnetic radiations of discrete frequencies.

The Interpretation

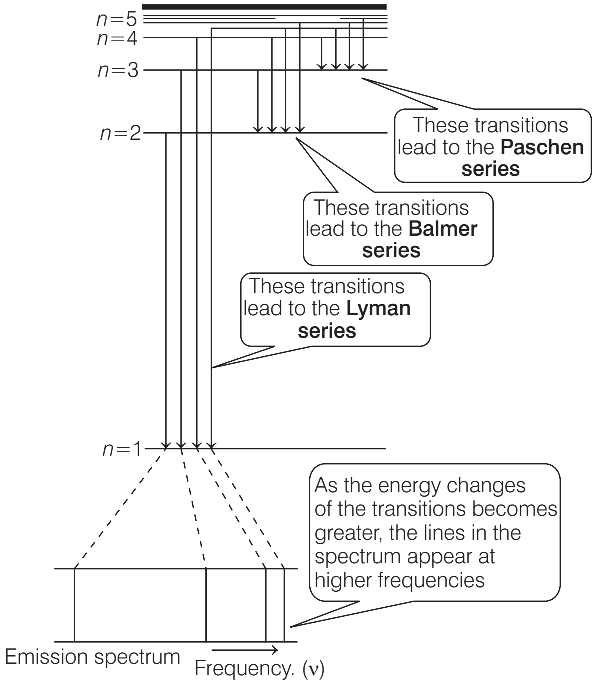
The spectrum obtained consists of large number of sharp lines each of which corresponds to a particular frequency. These lines are present in UV, visible and infra-red regions of electromagnetic spectrum.

The lines in emission spectrum of hydrogen are classified into following six series

1. Lyman series]—UV region
2. Balmer series]—Visible region
3. Paschen series
4. Brackett series } — IR region
5. Pfund series
6. Humphery series — Far IR region

All these lines were named after their discoverers. Humphrey series is the latest addition of the group.

The energy levels in the hydrogen atom and transitions of electrons between them is shown below.



Spectral lines in the hydrogen atom

The lines observed in above atomic spectrum are formed due to electronic transitions between energy levels.

Each of these transitions corresponds to a line in emission spectrum of hydrogen. The difference in energy between two levels is equal to the energy of resultant spectral line.

Balmer and Rydberg Formula

Balmer, in 1885 showed that if spectral lines are expressed in terms of wave number $\bar{\nu}$, then the visible lines of hydrogen spectrum obey the following formula

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

here, n = an integer equal to or greater than 3.

Swedish spectroscopist **Rydberg** gave above formula in more generalised form which is applicable to all the series of hydrogen spectrum and can be written as

$$\bar{\nu}_{\text{H}}(\text{cm}^{-1}) = R_{\text{H}}\left(\frac{1}{n_1^2}-\frac{1}{n_2^2}\right)$$

Here, R_{H} = 1,09,677 cm^{-1} and n_1 and n_2 are integers where $n_2 > n_1$.

This is called **Rydberg formula** and R_{H} is called as Rydberg constant.

For a particular series n_1 is constant. The values of n_1 and n_2 for different series of hydrogen spectrum are

(i) Lyman series, $n_1 = 1, \quad n_2 = 2, 3, 4, \ldots$
(ii) Balmer series, $n_1 = 2, \quad n_2 = 3, 4, 5, \ldots$
(iii) Paschen series, $n_1 = 3, \quad n_2 = 4, 5, 6, \ldots$
(iv) Brackett series, $n_1 = 4, \quad n_2 = 5, 6, 7, \ldots$
(v) Pfund series, $n_1 = 5, \quad n_2 = 6, 7, 8, \ldots$
(vi) Humphery series, $n_1 = 6, \quad n_2 = 7, 8, 9 \ldots$

For elements *except hydrogen*, the formula is written as,

wave number, $\bar{\nu} = R_{\text{H}} \cdot Z^2 \left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$

where, $R_{\text{H}} = 109677 \text{ cm}^{-1}$, Z = atomic number of element

The Balmer series of lines is the only series which appears in the visible region of EM spectrum.

The first, second and third lines of a spectral series are called α, β and γ respectively, e.g. H_α has the wavelength 4101.7Å similarly H_β and H_γ have 4340.5Å and 4861.3Å wavelengths respectively.

The maximum number of lines that can be emitted for a transition from $n_2 \to n_1$ (with $n_2 > n_1$) is given by

$$\frac{(n_2 - n_1 + 1)(n_2 - n_1)}{2}$$

While solving problems based on this topic inter-relate the quantity you have to calculate with the formula you know or divide the question in two steps. For example see the sample problem given below.

Example 10. *Calculate the energy and frequency of the radiation emitted when an electron jumps from n = 3 to n = 2 in a hydrogen atom.*

(a) $3.028 \times 10^{-9}, 4.57 \times 10^{12}$ (b) $3.028 \times 10^{-19}, 2.89 \times 10^{14}$
(c) $3.028 \times 10^{-19}, 4.57 \times 10^{14}$ (d) $2.128 \times 10^{-19}, 4.57 \times 10^{12}$

(NCERT Exemplar)

Sol. (*c*) Here we divide the question into two parts (i) we calculate wavelength or wave number (ii) with the help of wavelength or wave number we calculate energy and frequency.

$$\text{Wave number}, \bar{\nu} = 109677 \text{cm}^{-1} \left(\frac{1}{2^2} - \frac{1}{3^2}\right)$$

$$\bar{\nu} = 109677 \times \frac{5}{36} = 15232.9 \text{ cm}^{-1}$$

$$\bar{\nu} = \frac{1}{\lambda} \text{ or } \lambda = \frac{1}{\bar{\nu}} = \frac{1}{15232.9} = 6.564 \times 10^{-5} \text{ cm}$$

$\therefore$ Wavelength, $\lambda = 6.564 \times 10^{-7} \text{m}$

$$\text{Energy}, E = \frac{hc}{\lambda}$$

$$= \frac{6.626 \times 10^{-34} \text{Js} \times 3.0 \times 10^8 \text{ms}^{-1}}{6.564 \times 10^{-7} \text{m}}$$

$$= 3.028 \times 10^{-19} \text{ J}$$

$$\text{Frequency}, \nu = \frac{c}{\lambda} = \frac{3.0 \times 10^8 \text{ms}^{-1}}{6.564 \times 10^{-7} \text{m}} = 0.457 \times 10^{15} \text{ s}^{-1}$$

$$\nu = 4.57 \times 10^{14} \text{s}^{-1}$$

Alternate We first inter-relate the two formulae and then put the values: e.g.

$$\bar{\nu} = \frac{1}{\lambda} = R_{\text{H}} \left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

$$= \frac{c}{\lambda} = R_{\text{H}} c \left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) = \nu \text{ (frequency)}$$

Now by putting the value, we directly calculate the frequency. Similarly,

$$\nu = \frac{c}{\lambda} = R_{\text{H}} c \left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) = \frac{hc}{\lambda} = R_{\text{H}} hc \left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

$$\therefore \quad E = R_{\text{H}} hc \left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

By putting the values in the above formula, you can calculate E directly.

Example 11. *Find the wavelengths of the first line of* He^+ *ion spectral series whose interval between extreme lines is* $\frac{1}{\lambda_1} - \frac{1}{\lambda_2} = 2.7451 \times 10^4 \text{ cm}^{-1}$ *[*$R_{\text{H}} = 109677.76 \text{ cm}^{-1}$*]*

(JEE Main 2020)

(a) 8968 Å (b) 4689 Å
(c) 9378 Å (d) 2345 Å

Sol. (*b*) Extreme lines means first and last.

$$\frac{1}{\lambda_1} - \frac{1}{\lambda_2} = R_{\text{H}} Z^2 \left[\frac{1}{n_1^2} - \frac{1}{\infty^2}\right] - R_{\text{H}} Z^2 \left[\frac{1}{n_1^2} - \frac{1}{(n_1 + 1)^2}\right] = \frac{RZ^2}{(n_1 + 1)^2}$$

$$2.7451 \times 10^4 = \frac{109677.76 \times 2^2}{(n_1 + 1)^2}$$

$$(n_1 + 1) = 4$$

$$n_1 = 3$$

Wavelength of first line

$$\frac{1}{\lambda} = 109677.76 \times 2^2 \times \left[\frac{1}{3^2} - \frac{1}{4^2}\right]$$

$$\lambda = 4689 \times 10^{-8} \text{cm} = 4689 \text{ Å}$$

Remember For *shortest wavelength* or *maximum energy* or *maximum frequency*, *n* **has to be maximum** and for *longest wavelength* or *minimum energy* or *minimum frequency*, *n* **has to be minimum**. This can be best understood by the example given below.

Example 12. *For any given series of spectral lines of atomic hydrogen, let* $\Delta\bar{\nu} = \bar{\nu}_{\text{max}} - \bar{\nu}_{\text{min}}$ *be the difference in maximum and minimum frequencies in* cm^{-1}*. The ratio* $\Delta\bar{\nu}_{\text{Lyman}} / \Delta\bar{\nu}_{\text{Balmer}}$ *is*

(JEE Main 2019)

(a) 27 : 5 (b) 5 : 4
(c) 9 : 4 (d) 4 : 1

Sol. (*c*) For any given series of spectral lines of atomic hydrogen. Let $\Delta\bar{\nu} = \bar{\nu}_{\text{max}} - \bar{\nu}_{\text{min}}$ be the difference in maximum and minimum frequencies in cm^{-1}.

For Lyman series,

$$\Delta\bar{\nu} = \bar{\nu}_{\max} - \bar{\nu}_{\min}$$

General formula:

$$\bar{\nu} = 109677\left[\frac{1}{n_i^2} - \frac{1}{n_f^2}\right]$$

For Lyman $n_1 = 1, n_2 = 2, 3, \ldots$

$$\bar{\nu}_{\max} = 109{,}677\left(\frac{1}{1} - \frac{1}{\infty}\right) = 109{,}677\left(\frac{1}{1} - 0\right) = 109{,}677$$

$$\bar{\nu}_{\min} = 109{,}677\left(\frac{1}{1} - \frac{1}{(2)^2}\right) = 109{,}677\left(\frac{3}{4}\right)$$

$$\Delta\bar{\nu}_{\text{Lyman}} = \bar{\nu}_{\max} - \bar{\nu}_{\min} = 109{,}677 - \left[\frac{109{,}677 \times 3}{4}\right] = \frac{109{,}677}{4}$$

For Balmer series,

$$\bar{\nu}_{\max} = 109{,}677\left(\frac{1}{(2)^2} - \frac{1}{\infty}\right) \Rightarrow \frac{109677}{4}$$

$$\bar{\nu}_{\min} = 109{,}677\left(\frac{1}{(2)^2} - \frac{1}{(3)^2}\right) \Rightarrow \frac{109677 \times 5}{36}$$

$$\Delta\bar{\nu} = \bar{\nu}_{\max} - \bar{\nu}_{\min}$$

$$\Delta\bar{\nu}_{\text{Balmer}} = \frac{109{,}677}{4} - \left[\frac{109{,}677}{36} \times 5\right] = 109{,}677\left(\frac{1}{9}\right)$$

$$\frac{\Delta\bar{\nu}_{\text{Lyman}}}{\Delta\bar{\nu}_{\text{Balmer}}} = \frac{109{,}677/4}{109{,}677/9}$$

$$\frac{\Delta\bar{\nu}_{\text{Lyman}}}{\Delta\bar{\nu}_{\text{Balmer}}} = \frac{9}{4}$$

$\therefore$ The ratio of $\dfrac{\Delta\bar{\nu}_{\text{Lyman}}}{\Delta\bar{\nu}_{\text{Balmer}}}$ is 9 : 4.

You have to remember the value of n, for different series. (There is no need to remember the value of n_2 because n_2 is always greater than n_1 and it reaches upto ∞ . For example see solved sample problem given below.

Example 13. *Heat treatment of muscular pain involves radiation of wavelength of about* 900 nm. *Which spectral line of H-atom is suitable for this purpose?* [$R_H = 1 \times 10^5$ cm^{-1}, $h = 6.6 \times 10^{-34}$ Js, $c = 3 \times 10^8$ ms^{-1}] ***(JEE Main 2019)***

(a) Paschen, $5 \to 3$

(b) Paschen, $\infty \to 3$

(c) Lyman, $\infty \to 1$

(d) Balmer, $\infty \to 2$

Sol. (*b*) By using the formula,

$$\Delta E = \frac{hc}{\lambda} \qquad \left[\text{Here, } \frac{1}{\lambda} = R_H\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right] \times Z^2\right]$$

So, $\Delta E = hc \times R_H\left[\dfrac{1}{n_1^2} - \dfrac{1}{n_2^2}\right] \times Z^2$

or $hc \times \dfrac{1}{\lambda} = hc \times R_H\left[\dfrac{1}{n_1^2} - \dfrac{1}{n_2^2}\right] \times Z^2$

or $\dfrac{hc}{hc \times R_H \times Z^2 \times \lambda} = \left[\dfrac{1}{n_1^2} - \dfrac{1}{n_2^2}\right]$ or $\left[\dfrac{1}{n_1^2} - \dfrac{1}{n_2^2}\right]$.

$$= \frac{1}{(1 \times 10^7 m^{-1}) \times (900 \times 10^{-9}\,\text{m})} \qquad (Z \text{ for H} = 1)$$

or $\left[\dfrac{1}{n_1^2} - \dfrac{1}{n_2^2}\right] = \dfrac{1}{9}$

from option (b), or

$$\left[\frac{1}{3^2} - \frac{1}{\infty}\right] = \frac{1}{9} \quad \text{or} \quad n_1 = 3 \text{ and } n_2 = \infty$$

Experimental Evidences in Favour of Bohr's Model

It was found that

- The values of ionisation enthalpies, radii etc., for hydrogen atom, as calculated by Bohr, came closer to their experimental value.
- For hydrogen atom the calculated values of wavelength belonging to different spectral lines agrees with their experimental values. This observation is made by spectrophotometer.

  Both the above written points are considered as the experimental evidences in favour of Bohr model.

Remember The Bohr's model is applicable only to hydrogen atom and similar species, i.e. to the one-electron systems, e.g. He^+, Li^{2+}, Be^{3+}, B^{4+} etc.

Limitations of Bohr's Model

Bohr left the following facts unexplained

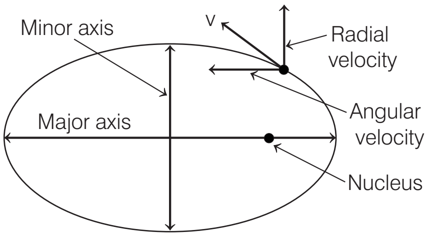
- Fine structure of atom.
- Spectrum of multi-electron systems.
- **Zeeman effect**, i.e. effect of magnetic field on an excited atom.
- **Stark effect**, i.e. effect of electric field on an excited atom.
- **Splitting**, i.e. resolution of spectral lines occur in both the effects.
- Three dimensional existence of atom.
- Dual nature of matter and especially electron.

Bohr Sommerfeld Model

Bohr along with **Sommerfeld** (1915) suggested the existence of elliptical orbits alongwith circular orbits. This had the situation of nuclei at one of the foci of ellipse and was used to explain the fine structure in hydrogen spectrum.

Radial and Azimuthal Components in Elliptical Orbits

When an electron revolves around the nucleus in elliptical orbits, the distance between the electron and the nucleus is called **radius vector** and the angle of revolution is called **azimuthal angle** as shown below.



An ellipse with electron showing radial and angular velocities

Due to the presence of such orbits, the tangential velocity of an electron at any instance can also be resolved into two components, i.e.

- the **radial velocity** means the one along the radius vector and
- the **transverse** or **angular velocity** means the one perpendicular to the radius vector.

These two velocities give rise to **radial** and **angular** or **azimuthal momentum** as,

$$\text{Radial momentum} = n_r \times \frac{h}{2\pi}$$

$$\text{Azimuthal momentum} = n_\phi \times \frac{h}{2\pi}$$

Here, n_r = radial quantum number

n_ϕ = azimuthal quantum number

These, n_r and n_ϕ are related to principal quantum number of Bohr (n) as

$$n = n_r + n_\phi$$

$$\frac{n}{n_\phi} = \frac{n_r + n_\phi}{n_\phi}$$

$$= \frac{\text{length of major axis}}{\text{length of minor axis}}$$

Always remember that for a certain value of *n*,

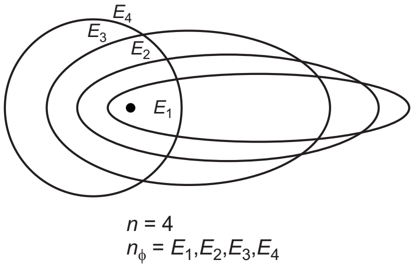
(i) **The value of n_ϕ can never be zero,** because if $n_\phi = 0$, that means the minor axis of ellipse will also be zero.

So the electron is showing straight line motion which is impossible inside an atom.

(ii) n_ϕ **cannot be greater than *n*** because in such cases the path will not be elliptical as minor axis of ellipse exceeds its major axis.

(iii) n_ϕ **equal to *n* is possible** but in that case the orbit will be circular. Usually circular orbit is considered as the special case of ellipse, where major axis equals the minor axis.

(iv) n_ϕ **smaller than *n* is possible** and in all such cases the orbit will remain elliptical.



Correlation between the values of n and n_ϕ

Energy of Moving Electron

Sommerfeld also modified the expression of energy of moving electron in elliptical orbit for hydrogen as,

$$E_n = -\frac{2\pi^2 me^4}{(n_\phi + n_r)^2 h^2}$$

Experimental and theoretical observations based on wave mechanics show different values of n_ϕ (azimuthal quantum number) as $0, 1, 2, 3, \ldots$, till $(n-1)$, in the place of 1, 2, 3, … till n as given by Sommerfeld.

This new quantum number beginning with zero and ending at $(n-1)$ has been represented by l to avoid the confusion with n_ϕ. This l is related to n as l = zero to $(n-1)$

Drawbacks of Sommerfeld Model

The weak points of Bohr-Sommerfeld model were

- This theory cannot give the exact idea of number of lines observed in fine spectrum.
- The information about the relative intensities of these lines is also not given.
- The exact definition of position and momentum of electron can be given by this theory which is contrary to Heisenberg's uncertainty principle.

Modern Structure of an Atom

The modern structure of atom is based upon dual nature of matter and waves & 3D quantised approach.

Dual Nature of Matter: de-Broglie Equation

The French physicist **Lewis de-Broglie,** in 1924, proposed that matter like radiation also possesses dual nature, i.e. has wave as well as particle nature. In other words, he said that electrons also has momentum as well as wavelength just like photons.

The wave associated with matter waves is called **de-Broglie matter wave**. He also derived an expression for it, with the help of Plank's equation and Einstein's mass energy relationship. This expression is given below

$$\boxed{\lambda = \frac{h}{mc} = \frac{h}{P}} \quad \text{where, } P = mc \text{ (momentum)}$$

The given relation between wavelength (λ) and momentum (p) correlates the wave—matter duality of electron and known as **de-Broglie equation**. It is very clear from the above expression that Planck's constant (h) provides connecting link between particle and wave nature.

It is also very clear from the given expression that de-Broglie wavelength is independent of the nature of matter. Secondly, the **dual nature of matter is considered to be visible in motion** only.

After applying de-Broglie equation to large particle (mass 10^{-3} kg) and hydrogen atom (mass $\approx 10^{-31}$ kg) separately, it was found that the equation is applicable to all objects. However, de Broglie concluded that every object in motion has wave character but the wavelengths associated with large masses are so small that these can be neglected easily.

Remember As waves in nature show delocalisation hence, the wave character puts some restrictions on exact position of electron and other similar particles.

In case kinetic energy, E of the particle is given, the de-Broglie wavelength can be calculated by the formula.

$$\lambda = \frac{h}{\sqrt{2mE}} \qquad [\because P = \sqrt{2mE}]$$

For a charged particle of charge q following modification in de-Broglie equation is visible.

$$\boxed{\lambda = \frac{h}{\sqrt{2eVm}}}$$

de-Broglie waves are always associated with electron and other microscopic particles. Thus, for various sub-atomic particles the value of λ can be give by the following expressions

(i) **For electron**, $\lambda = \frac{12.27}{\sqrt{V}}$ Å

(ii) **For proton**, $\lambda = \frac{0.268}{\sqrt{V}}$ Å

(iii) **For α-particles**, $\lambda = \frac{0.101}{\sqrt{V}}$ Å

where, V = accelerating potential of these particles,

(iv) **For neutrons**, $\lambda = \frac{h}{\sqrt{2Em}} = \frac{0.286}{\sqrt{E(eV)}}$ Å

(v) **For gaseous molecules**,

$$\lambda = \frac{h}{m \times v_{\text{rms}}} \text{Å} = \frac{h}{\sqrt{3mkT}}$$

where, k = Boltzmann constant,

The number of de-Broglie wavelengths in a given Bohr's orbit is always equal to the orbit number as,

$$mvr = \frac{nh}{2\pi} \Rightarrow \boxed{2\pi r = \frac{nh}{mv} = n\lambda}$$

Example 14. *The de-Broglie wavelength of an electron in the 4th Bohr orbit is* ***(JEE Main 2020)***

(a) $6\pi a_0$ (b) $2\pi a_0$

(c) $8\pi a_0$ (d) $4\pi a_0$

Sol. (c) The de-Broglie wavelength of an electron,

$$\lambda = \frac{h}{p}, \text{ or } \frac{h}{mv}$$

But, from the Bohr's postulate of quantisation of angular momentum of electrons, $= mvr = \frac{nh}{2\pi}$,

$$\therefore \qquad mv = \frac{nh}{2\pi r}$$

Upon substitution, $\lambda = \frac{h}{\left(\frac{nh}{2\pi r}\right)} = \frac{2\pi r}{n}$,

where, r is the radius of orbits in Bohr model $= \frac{n^2 a_0}{Z}$

$$\therefore \qquad \lambda = \frac{2\pi \times n^2 \times a_0}{n \times Z} = \frac{2\pi n a_0}{Z} = 8\pi a_0 \qquad \begin{pmatrix} Z = 1 \text{ for hydrogen} \\ n = 4 \text{ (given)} \end{pmatrix}$$

Example 15. *The de-Broglie wavelength (λ) associated with a photoelectron varies with the frequency (ν) of the incident radiation as, [ν_0 is threshold frequency]* ***(JEE Main 2019)***

(a) $\lambda \propto \frac{1}{(\nu - \nu_0)^{\frac{1}{4}}}$ (b) $\lambda \propto \frac{1}{(\nu - \nu_0)^{\frac{3}{2}}}$

(c) $\lambda \propto \frac{1}{(\nu - \nu_0)}$ (d) $\lambda \propto \frac{1}{(\nu - \nu_0)^{\frac{1}{2}}}$

Sol. (*d*) de-Broglie wavelength (λ) for electron is given by

$$\lambda = \frac{h}{\sqrt{2m\,\text{K.E}}} \qquad \ldots\text{(i)}$$

Also, according to photoelectric effect

$$\text{KE} = h\nu - h\nu_0$$

On substituting the value of KE in Eq. (i), we get

$$\lambda = \frac{h}{2m \times (h\nu - h\nu_0)}$$

$$\lambda \propto \frac{1}{(\nu - \nu_0)^{1/2}}$$

de-Broglie concept was the beginning of wave nature duality for matter particles. It was further strengthen by the experiments of (Davisson and Germer) and (Thomson and Reid).

The final break through in matter wave duality was the uncertainty principle.

Heisenberg's Uncertainty Principle

Werner Heisenberg of Germany, gave the principle of uncertainty in which he stated that *the exact position and exact velocity* (or momentum) *of a sub- atomic particle* can not be measured simultaneously. This principle was exactly opposite to Bohr's theory of fixed position of electron and definite energy of orbits. The principle can be expressed mathematically as,

$$\boxed{\Delta P \cdot \Delta x \geq \frac{h}{4\pi}}$$

Here, ΔP = uncertainty in momentum,

Δx = uncertainty in position,

h = Planck's constant

Now since, $P = mv$; hence, $\Delta P = m\Delta v$

Interpretation of Formula

Above formula can be interpreted as,

Whenever, the position and momentum (velocity) of a subatomic particle be measured simultaneously, then always a minimum error of $\frac{h}{4\pi}$ magnitude will occur.

By putting the value of Δp in the above expression, we get

$$m \cdot \Delta v \times \Delta x \geq \frac{h}{4\pi}$$

or $$\boxed{\Delta v \times \Delta x \geq \frac{h}{4\pi \times m}}$$

Likewise $$\Delta E \, \Delta t \geq \frac{h}{4\pi} \quad \text{(for energy and time)}$$

Similarly, $$\Delta\phi \Delta\theta \geq \frac{h}{4\pi} \quad \text{(for angular motion)}$$

The above expression also tell us about following points

- Uncertainty in velocity or position varies inversely with mass, thus it is negligible for macroscopic objects.
- We cannot draw a trajectory of a microparticles in contrast to a macroparticle and hence, in light of the Heisenberg's principle, the Bohr's concept of the orbit of an electron becomes untenable.

  Thus, for an electron within the atom the best we can think of in terms of probability of locating electron with a probable velocity in a given region of space at a given time.

Remember Heisenberg's uncertainty principle is applicable only when the location and momentum are along the same axis, i.e. if Δx is uncertainty in position along the z-axis then ΔP must also be uncertainty in momentum along the z-axis.

Example 16. *If uncertainty in the measurement of position and momentum are equal then uncertainty in the measurement of velocity is equal to*

(a) $\frac{1}{2m}\sqrt{\frac{2h}{\pi}}$ (b) $\frac{1}{2m}\sqrt{\frac{h}{\pi}}$ (c) $\frac{1}{4m}\sqrt{\frac{h}{\pi}}$ (d) $\frac{1}{2m}\sqrt{\frac{h}{2\pi}}$

Sol. (*b*) By Heisenberg's uncertainty principle for minimum uncertainty,

$$\Delta x \cdot \Delta P = \frac{h}{4\pi}$$

Given, $$\Delta x = \Delta P$$

So, $$(\Delta P)^2 = (\Delta x)^2 = \frac{h}{4\pi}$$

$\therefore$ $$\Delta P = \sqrt{\frac{h}{4\pi}}$$

or $$m\Delta v = \frac{1}{2}\sqrt{\frac{h}{\pi}}$$

$$\Delta v = \frac{1}{2m}\sqrt{\frac{h}{\pi}}$$

Quantum Mechanical Model

de-Broglie concept of matter waves and Heisenberg's uncertainity principle were the land mark in the history of atomic structure. Both of these led the foundation of probability concept of electron within an atom.

On the basis of dual nature of matter and Heisenberg uncertainty principle, Erwin Schrodinger, an Austrian physicist, in 1926 developed a new branch of science, called the **quantum mechanics** or **wave mechanics** and gave a model for atom, called **'wave mechanical** or **quantum mechanical model'** of atom.

In his model he visualised electron as a three dimensional wave in the electronic field of a positively charged nucleus inside the atom.

The quantum mechanical study of any system consists of

- writing Schrodinger equation for the system.
- solving Schrodinger equation for the meaningful solutions of the wave functions and corresponding energies.
- the meaningful solutions of wave function must follow the conditions, i.e. they have to be single valued, continuous and finite.
- calculation of all the observable properties of the system from wave function.

Schrodinger Equation

Schrodinger derived an equation for an electron which describes the wave motion of an electron along any of the three cartesian axis, i.e. x, y and z. This equation is

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

Here, ψ = wave function,

h = Planck's constant

E = total energy of electron, i.e. KE + PE for electron

V = potential energy of electron.

The Schrodinger wave equation can also be written as,

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

Here, $$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

i.e. the differential (Laplacian) operator.

In quantum mechanics, there is an operator corresponding to every observable property. It is like a mathematical command which act on a mathematical function.

Infact, Schrodinger gave a generalised equation, for a system, such as, an atom or a molecule, whose energy does not change with time, i.e. time independent which is written as

$$\hat{H}\psi = E\psi$$

Here, $\hat{H}$ is the total energy operator for electron, called **hamiltonian.**

The hamiltonian is the sum of kinetic energy operator $\hat{T}$ and potential energy operator $\hat{V}$, i.e.

$$\hat{H} = \hat{T} + \hat{V}$$

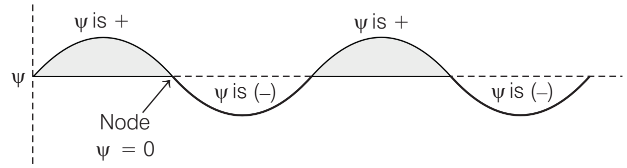
Thus, above equation can be written as, $(\hat{T} + \hat{V})\psi = E\psi$

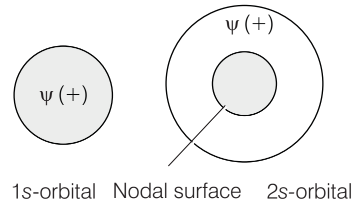
Here, E = total energy of the system.

Wave Function

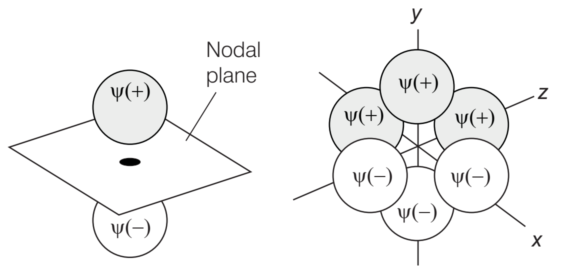
The wave function, ψ (psi) may be regarded as the amplitude function expressed in terms of coordinates *x, y* and *z.*

The wave function values may be positive or negative depending upon the values of coordinates. Its comparison with a wave is given below





(a) In *s*-orbital



2*p*-orbital

Three mutually perpendicular (orthogonal) 2*p*-orbital

(b) In *p*-orbital

The visualisation of wave function in orbitals as compared with a wave

Eigen Functions

The acceptable solutions of Schrodinger wave equation are called **eigen functions.**

Schrödinger equation for electron wave is the differential equation of second order, hence has several solutions or eigen functions for any ψ. Many of these solutions are imaginary and not valid.

Only those values of ψ are valid which satisfy following conditions

- The wave function must be finite and continuous.
- The solution must be single valued, i.e. at a given point there can never be more than one value for amplitude ψ.
- $\frac{\partial\psi}{\partial x}$, $\frac{\partial\psi}{\partial y}$ and $\frac{\partial\psi}{\partial z}$ must be continuous functions of *x, y* and *z* respectively.
- The probability of finding the electron over all spaces from plus infinity to minus infinity must be equal to one.

The Schrodinger wave equation when fully solved with the help of advanced mathematics gives the same expression as given by Bohr for the energy of an electron.

For several wave functions, (e.g. $\psi_1, \psi_2, \psi_3, \ldots$) several corresponding energies were calculated as $E_1, E_2, E_3, \ldots$ Each of these wave functions is called an '**orbital**'as these are functionally similar with Bohr's orbit.

Thus, orbitals can be visualised as diffused negatively charged clouds of different shapes, sizes and orientations around the nucleus.

Three key words to be used in "**wave mechanical model**" with their crispy elaboration are given below

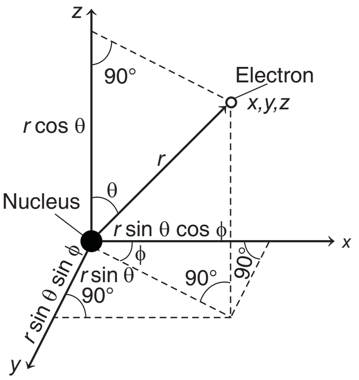
(i) **Orbit** It is a two dimensional imaginary space around the nucleus, where probability of finding electrons is maximum. An orbit can contain 2 to 32 electrons of variable energy but of same family.

(ii) **Orbital** It is a three dimensional real space around the nucleus where probability of finding a particular electron is maximum. An orbital can accommodate maximum 2 electrons of exactly equal energy.

(iii) **Subshells** Aggregation or group of orbitals of exactly equal energy which combine to form an orbit. These are named as *s,p,d* and *f.*

Concept of Sperical Atom

As the atom has spherical symmetry so, the Schrodinger wave equation can also be written in the form of spherical polar coordinates (r, θ and ϕ) instead of cartesian coordinates *x, y* and *z* with respect to nucleus. The relationships between the two coordinate systems are shown below in the figure.



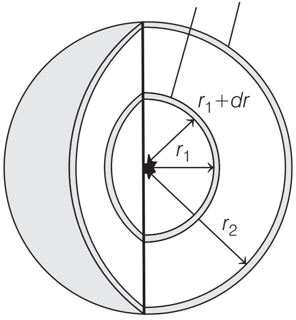
Relationship between cartesian (x, y, z) and polar coordinates (r, θ, φ)

Conceptual understanding of correlation between both these systems helps in finding radial and angular distribution of electrons within an atom.

Radial Distribution of Radial Wave Functions (R)

To know most probable distance of electron from the nucleus, radial distribution functions are very important. Since, the atoms has spherical symmetry, it is more useful to discuss this probability in a spherical shell between the spheres of radius $(r_1 + dr)$ and r_1 as shown below.

The thicknes of the shells is *dr*



Spherical shell of thickness *dr*

Volume of thin shell of thickness dr at the radius r_1

= area of surface of sphere × $dr_1 = 4\pi r^2 dr_1$

The volume of the thin shell at radius r_2 is greater than that at r_1.

Thus, the radial electron probability function,

$$(R) = 4\pi r^2 dr \psi^2$$

This can be defined as "the probability of finding the electron at a distance r from the nucleus regardless of direction."

Remember ψ is not to be confused with probability factor, ψ^2 which describles the probability of finding an electron within a small space.

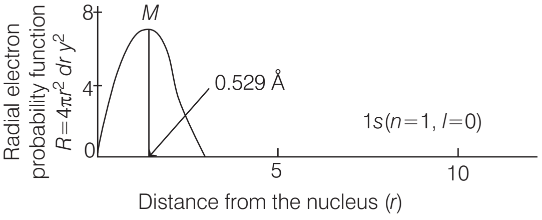
All these factors along with radial distribution help in the formation of radial probability distribution curves.Through these curves, we can interpret the variation in probability of finding an electron at different radial distances from the nucleus without any reference to its direction.

Radial Distribution Curves and their Interpretation

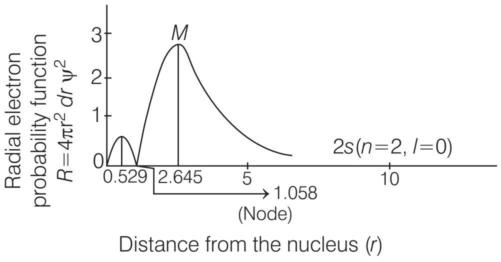
Radial distribution curves are drawn between radial electron probability function and distance of electron from the nucleus.

These curves tells us about following points.

- In each case the probability of finding the electrons at the origin (nucleus) is zero, i.e. electron will never be found at the nucleus.
- The distance for maximum probability in an orbital increases with the value of n or principal quantum number, e.g. this distance for 1s, 2s and 3s subshells follows the order $1s < 2s < 3s$.
- The total number of peaks appearing in the curves for s, p and d orbitals is equal to $n, (n-1)$ and $(n-2)$ respectively where n = principal quantum number.
- The curve of 1s-electron is given below. In this curve, we can interpret the value of R is zero at nucleus where r is also zero. It then increases as r increases, passes through a maximum (peak) at $r = 0.529$ Å which is equal to the radius of Bohr's first orbit and then falls to zero as r tends to inifinity. Thus, for 1s electron $R = 0$ (minimum) at $r = 0$ and ∞ while it is maximum at $r = 0.529$ Å.



- For 2s electron the value of R is zero at $r = 0$. The value of R increases as r increases. It then passes through a lower maximum at $r = 0.529$ Å and falls to zero again at $r = 1.058$ Å. R reaches second maximum at $r = 5 \times 0.529$ Å and then finally approaches zero as r tends to infinity. The distance, i.e. 1.058 Å at which the probability of finding electron is zero is called **node** or **nodal plane** or **nodal surface**.



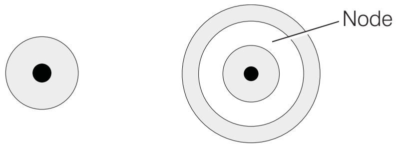
Nodes

These are the points or spaces within the orbital where probability of findling an electron is zero. Thus, we can say that electron density is not maximum at all the places in an orbital. It may also be zero at some places.

The quantity of these nodes is fixed for a particular orbital and can be calculated in following manner.

(i) For *s*-orbital, number of nodes = $(n - 1)$, so

- 1*s* orbital contains no node,
- 2*s* orbital contains one node,
- 3*s* orbital contains 2 nodes and so on.



1*s*-orbital 2*s*-orbital

Spherical *s* orbital, symmetrically disposed about the nucleus

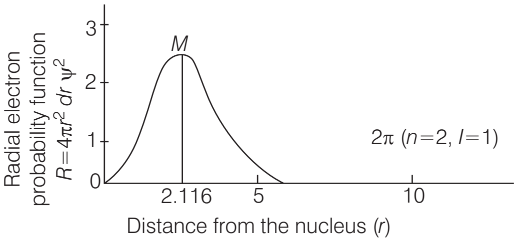
(ii) Similarly, for a *p*-orbital, number of nodes = $(n - 2)$. In both the above cases n = principal quantum number.

These nodes can be spherical or non-spherical. Spherical nodes are called Radial Nodes while non-spherical nodes are called angular nodes.

For any atom, raidal and angular nodes can be calculated by using following formulae.

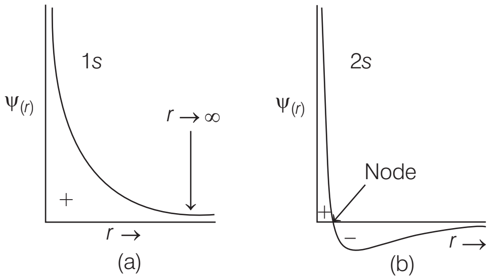
- No. of angular nodes = azimuthal quantum no. = l
- No. of radial nodes = $(n - l - 1)$
- No. of total nodes = $(n - 1)$

- On comparing 2*s* and 2*p*-orbitals, we find that the 2*s*-electron spends most of its time close to the nucleus than does the 2*p*-electron. In other words, 2*s*-electron is bound more tightly to the nucleus than does the 2*p*-electron. Radial distribution curve for 2*p*-orbital is given below.



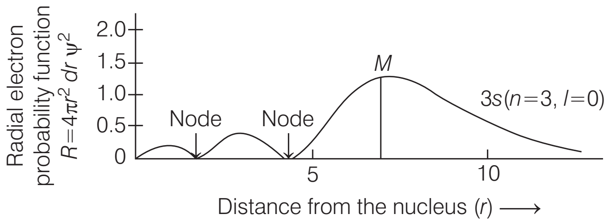
So the energy 2*s*-electron is less than the energy of 2*p*-electron, although both the electrons are of the same energy level (orbit).

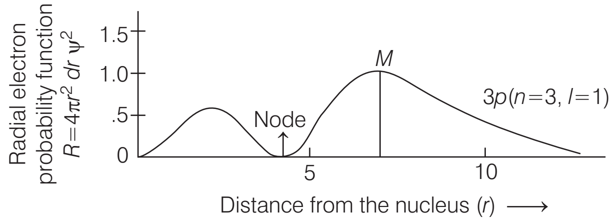
- Similar findings are seen in the curves between orbital wave function (ψ) and r with the difference that here negative values of wave function are also visible (because ψ can be negative or positive but ψ^2 can only be positive). For 1*s* and 2*s* these curves looks like

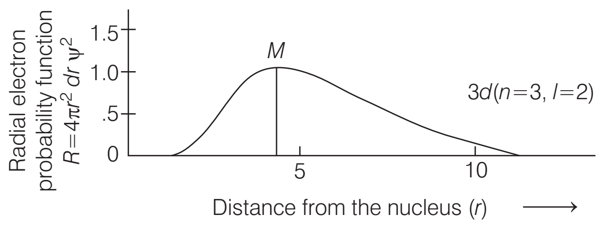


(a) (b)

- Similar properties are visible in the radial probability distribution curves of 3*s*, 3*p* and 3*d* orbitals are shown below.

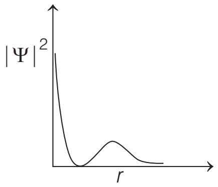






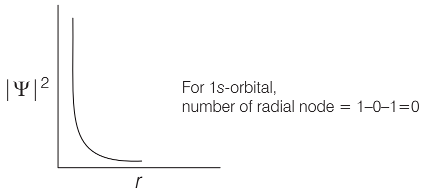
The point M in each curves represents the maximum distance.

Example 17. *The graph between $|\psi|^2$ and r (radial distance) is shown below. This represents* ***(JEE Main 2019)***

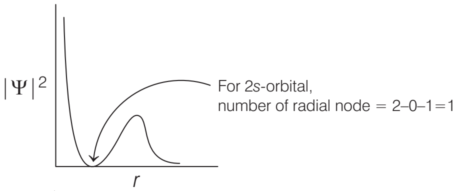


(a) 1*s*-orbital (b) 2*p*-orbital
(c) 3*s*-orbital (d) 2*s*-orbital

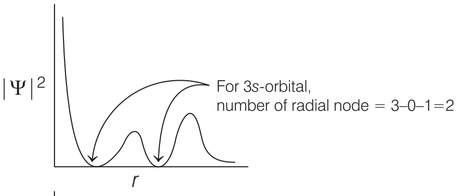
Sol. (*d*) The graphs between $|\psi|^2$ and *r* are radial density plots having $(n-l-1)$ number of radial nodes. For 1s, 2s, 3s and 2 *p*-orbitals these are respectively.



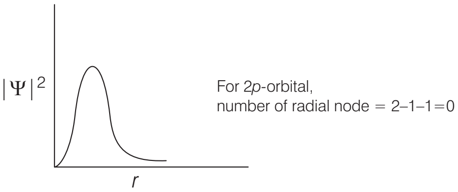
For 1*s*-orbital, number of radial node = 1–0–1=0



For 2*s*-orbital, number of radial node = 2–0–1=1



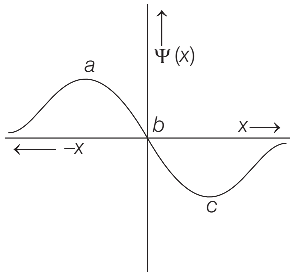
For 3*s*-orbital, number of radial node = 3–0–1=2



For 2*p*-orbital, number of radial node = 2–1–1=0

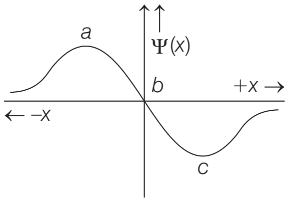
Thus, the given graph between $|\psi|^2$ and *r* represents 2*s*-orbital.

Example 18. *The electrons are more likely to be found* ***(JEE Main 2019)***



(a) in the region *a* and *c*
(b) in the region *a* and *b*
(c) only in the region *a*
(d) only in the region *c*

Sol. (*a*) The given graph is between orbital wave function and *r*. So, the electrons are more likely to be found in the region *a* and *c*. At *b*, wave function becomes zero and is called radial nodal surface or simply node.



These graphs of wave function (ψ) and distance (*r*) from the nucleus helps in determining the shape of orbital.

Angular Distribution or Angular Wave Function $(\theta\phi)$

These wave functions give the probability of finding an electron at certain angle from the nucleus. Thus, angular wave functions are independent of *n* and show their independency on *l* and m_l. Here, n, l and m_l are called quantum numbers.

Quantum Numbers

These are the numbers which basically define an electron within an atom. There are in all four quantum numbers, out of these three, i.e. n, l and m are needed to define the orbital and the 4th one defines the spin of electron within the orbital. These are discussed below

Principal Quantum Number (n)

It defines the principal shell in which the electron is revolving around the nucleus. It designates the average distance of the electron from the nucleus. Hence, *this quantum number represents the size of the electron orbits.*

- The electron that has a higher principal quantum number is at a higher energy level.
- An electron with $n=1$ has the lowest energy and is bound most firmly to the nucleus.
- There is a limited number of electrons in an atom which can have the same principal quantum number and is given by $2n^2$, where n is the principal quantum number concerned. Thus,

Principal quantum number	$(n) \longrightarrow$	1	2	3	4
Letter designation	$\longrightarrow$	K	L	M	N
Maximum number of electrons	$(2n^2) \longrightarrow$	2	8	18	32

Azimuthal Quantum Number (l)

This quantum number was first described by **Sommerfeld**. It is also known as the **second**, **subsidiary**, **lesser** or the **orbital** quantum number. It is represented by letter 'l'. This quantum number describes the name of subshell and the shape of orbital present in it. It is related to orbital angular momentum by the following relation,

$$mvr = \frac{h}{2\pi}\sqrt{[l(l+1)]}$$

l can have values ranging from 0 to $(n-1)$.

(i) When $l = 0$, the subshell is s and orbital is spherical in shape.

(ii) When $l = 1$, the subshell is p and orbital is dumb-bell shaped.

(iii) When $l = 2$, the subshell is d and orbital is double dumb-bell shaped.

(iv) When $l = 3$, the subshell is f and orbital is complicated in shape.

Energy of an electron in an orbit depends upon the principal quantum number (n) for systems with only one electron. For multielectron systems, energy depends both on principal quantum number (n) and azimuthal quantum number (l).

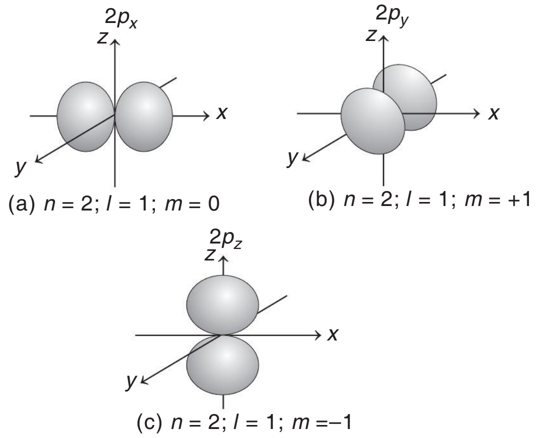
Magnetic Quantum Number (*m*)

This quantum number was introduced by **Lande** to describe the Zeeman effect. It is denoted by letter "*m*". The magnetic quantum number is also called **orientation quantum number** because it gives the orientation or distribution of the electron cloud.

For each value of azimuthal quantum number, the magnetic quantum number, may assume all the integral values between $+l$ to $-l$ through zero. e.g.

(i) When $l = 0$, m has only one value, i.e. 0; hence, there occur only one spherical orbital for each value of n.

(ii) When $l = 1$, m has 3 values, i.e. +1, 0 and –1; hence, there occur 3 orbitals in p subshell namely p_x, p_y and p_z along the x-axis, y-axis and z-axis respectively.

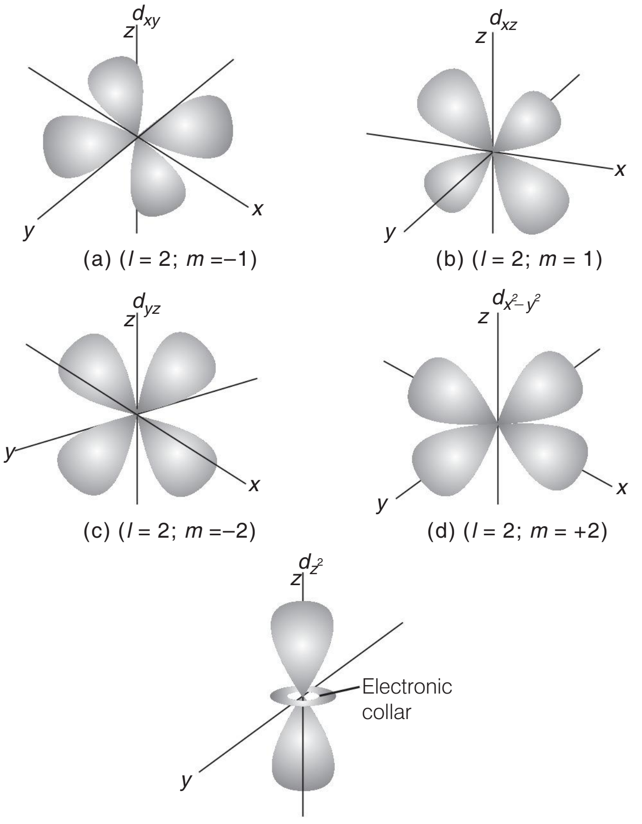


(a) $n = 2$; $l = 1$; $m = 0$ (b) $n = 2$; $l = 1$; $m = +1$ (c) $n = 2$; $l = 1$; $m = -1$

Orientation of *p*-orbitals along *x*, *y* and *z* axis

These orbitals of a subshell are identical in energy, shape and size. They differ only in their direction in space. Orbitals with identical energy are called **degenerate orbitals**.

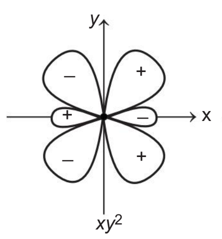
(iii) For $l = 2$, i.e. d subshell, m has 5 values namely +2, +1, 0, –1, –2 representing 5 such orbitals namely d_{xy}, d_{yz}, d_{zx}, $d_{x^2-y^2}$, d_{z^2}. Out of these only d_{xy} and $d_{x^2-y^2}$ lie in xy plane.

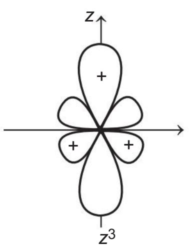


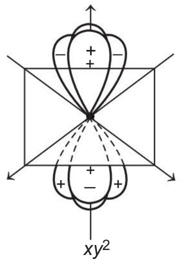
(a) ($l = 2$; $m = -1$) (b) ($l = 2$; $m = 1$) (c) ($l = 2$; $m = -2$) (d) ($l = 2$; $m = +2$) (e) ($l = 2$; $m = 0$)

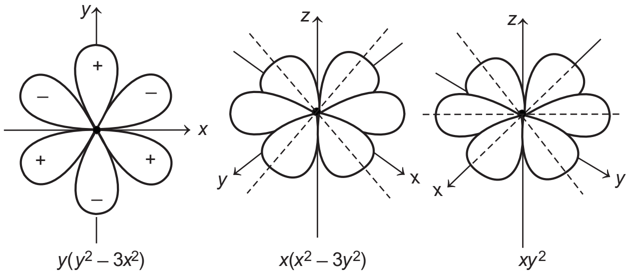
Orientation of *d*-orbitals

(iv) For $l = 3$, i.e. f subshell, m has 7 values namely +3, +2, +1, 0, –1, –2, –3. These orbitals have representation difficulties that's why we consider their shape as "diffused" in generalised way. There is no unique way of representing all the seven orbitals.
According to one opinion these orbitals can be represented as f_{z^3}, f_{xz^2}, f_{yz^2}, f_{xyz}, $f_{x(x^2-3y^2)}$, $f_{y(3x^2-y^2)}$ and $f_{z(x^2-y^2)}$, while according to another view these can be represented as f_{x^3}, f_{y^3}, f_{z^3}, $f_{x(z^2-y^2)}$, $f_{y(z^2-x^2)}$, $f_{z(x^2-y^2)}$ and f_{xyz}.









Orientation of *f*-orbitals

- Total value of m for a given value of $n = n^2$
- Total value of m for a given value of $l = (2l + 1)$

Spin Quantum Number (s)

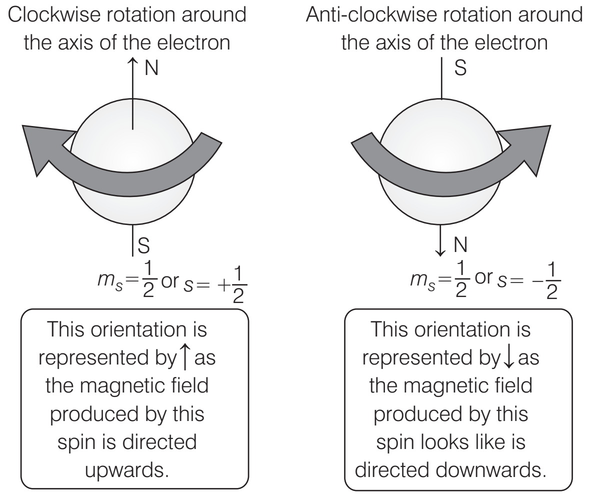
This quantum number was given by **Ullenback** and **Gold Smith**. This quantum number is also called magnetic spin quantum number and denoted by m_s or s. It is assigned arbitary values of $+\frac{1}{2}$ and $-\frac{1}{2}$.

The commonly called spin is actually **spin angular momentum** which is normally constant and cannot be changed. It is a vector quantity and can have only two orientations relative to the chosen axis, i.e. clockwise and anti-clockwise.

This spin angular momentum can be calculated as,

$$s = \frac{h}{2\pi}\sqrt{s(s+1)}. \text{ Here, } s = \pm\frac{1}{2}$$

The clockwise and anticlockwise spin of electrons is responsible for the production of magnetic fields in mutually opposite directions. The attraction between these fields is responsible for the creation of stable condition within an orbital as shown below.



This orientation is represented by ↑ as the magnetic field produced by this spin is directed upwards.

This orientation is represented by ↓ as the magnetic field produced by this spin looks like is directed downwards.

Rotation of electrons and direction of magnetic field produced.

This attraction is responsible for overcoming the repulsive forces between 2 electrons while residing inside an orbital.

The spin magentic moment can be calculate by the following formula

$$\text{Magnetic moment} = \sqrt{n(n+2)} \text{ B.M. or } \sqrt{s(s+1)}\,\frac{h}{2\pi mc}$$

where, $n =$ number of unpaired electrons, $s = \pm\frac{1}{2}$ and

B.M = Bohr magneton (a unit of magnetic moment)

Remember When m_s is written for spin quantum number the sign (+) and (–) are not used which are otherwise used in case of s.

Structure of Atom on the Basis of Wave Mechanical Model

According to wave mechanical model, the structure of atom can be summarised as

- The electron in an atom are arranged in shells or in different energy levels or in orbits which are indicated by numbers, 1, 2, 3, ... or letters *K, L, M*, ...
- With in each shell, there are subshells or in sub levels which are designated as *s, p, d* and *f*.
- Electrons of different energy levels are present in **discrete volumes** of different shapes, sizes and orientations in the sub-levels around the nucleus.
- Each of such discrete volume is called an **orbital** which has the maximum probability of finding a particular electron of a particular energy level.
- Each orbital may hold up two electrons of exactly equal energy provided they have opposite spins.
- The number of orbitals in a subshell is fixed, e.g.
  - s-subshell has one orbital.
  - p has 3, i.e. p_x, p_y and p_z
  - d has 5, i.e. d_{xy}, d_{yz}, d_{zx}, $d_{x^2-y^2}$ and dz^2
  - f subshell has 7 orbitals.
- Just like the number, the shape of orbitals is also fixed e.g.
  - s has spherical shape.
  - p has dumb bell shape.
  - All d orbitals except d_{z^2} have double dumb bell shapes. d_{z^2} has single dumb bell with one electric collar.
  - f orbitals are considered to contain diffused shape.
- There are in all four quantum numbers to define an electron in an atom. Out of these first three, i.e. *n, m* and *l* are needed to define the **orbital** and the 4th one defines the spin of electron in it.

Finding Quantum Numbers

In order to find all the four quantum number for an electron following steps are suggested

***Step* I** First find the value of n (principal quantum number) for the given electron from the electronic configuration of the element. e.g. For 17th electron of Cl, $1s^2, 2s^2, 2p^6, 3s^2, 3p^5$ the 17th electron enters in $3p$ orbital, so $n = 3$

***Step* II** The known values of l are 0, 1, 2 and 3 respectively for s, p, d and f orbitals. Since in case of 17^{th} electron, the orbital is p , so the value of $l = 1$

***Step* III** Values of m varies from $-\ l$ to $+\ l$ including 0.

Thus, for $l = 1,\ m = -1,\ 0,\ +1$

$$\overset{-1}{p_x} \quad \overset{0}{p_y} \quad \overset{+1}{p_z}$$

Since, the fifth electron enters in $p_y,\ m = 0$

***Step* IV** Value of s may be $+\frac{1}{2}$ or $-\frac{1}{2}$

So for 17th electron it may by ± 1/2

Thus, the correct set of quantum numbers for 17^{th} electron is

$$n = 3, l = 1, m = 0 \text{ and } s = \pm\frac{1}{2}.$$

Example 19. *Which of the following sets of quantum numbers is not possible?*

(a) $n = 4, l = 1, m = 0, s = +\frac{1}{2}$ (b) $n = 4, l = 3, m = -3, s = -\frac{1}{2}$

(c) $n = 4, l = 0, m = 0, s = -\frac{1}{2}$ (d) $n = 4, l = 1, m = +2, s = -\frac{1}{2}$

Sol. (*d*) m has values $-l$ to $+l$ including 0. Thus, if $l = 1$, the possible values of $m = -1, 0, +1$ but not $+2$ as given in set (d). Thus, set (d) is not possible.

Example 20. *The number of orbitals associated with quantum numbers* $n = 5,\ m_s = +\frac{1}{2}$ *is* ***(JEE Main 2020)***

(a) 25 (b) 50 (c) 15 (d) 11

Sol. (*a*) According to quantum mechanical atom model, for each value of n, there are 'n' different values of l, i.e. $l = 0, 1, 2, \ldots, (n-1)$. And, for each value of l, there are $2l + 1$ different values of m_l, i.e. $m_l = 0, \pm1, \pm2 \ldots \pm l$.

$\therefore$ Total number of possible combinations of n, l and m_l, for a given value of n is n^2, and each such combination is associated with an orbital. Each orbital can occupy a maximum of two electrons, having a different value of spin quantum number (m_s), which are $+\frac{1}{2}$ or $-\frac{1}{2}$.

$\therefore$ Number of orbitals associated with $n = 5$ is $n^2 = 25$. Each of those orbitals can be associated with $m_s = \frac{1}{2}$ as well as $m_s = -\frac{1}{2}$.

$\therefore$ Answer = 25

Example 21. *The quantum number of four electrons are given below*

I. $n = 4, l = 2, m_l = -2, m_s = -\frac{1}{2}$

II. $n = 3, l = 2, m_l = 1, m_s = +\frac{1}{2}$

III. $n = 4, l = 1, m_l = 0, m_s = +\frac{1}{2}$

IV. $n = 3, l = 1, m_l = 1, m_s = -\frac{1}{2}$

The correct order of their increasing energies will be

(a) IV < III < II < I (b) I < II < 1III < IV

(c) IV < II < III < I (d) I < III < II < IV

(JEE Main 2019)

Sol. (*c*) Smaller the value of $(n + l)$, smaller the energy. If two or more sub-orbits have same values of $(n + l)$, sub-orbits with lower values of n has lower energy. The $(n + l)$ values of the given options are as follows :

I. $n = 4, l = 2 ; n + l = 6$ II. $n = 3, l = 2; n + l = 5$

III. $n = 4, l = 1, n + l = 5$ IV. $n = 3, l = 1, n + l = 4$

Among II and III, $n = 3$ has lower value of energy. Thus, the correct order of their increasing energies will be

IV < II < III < I

Pauli Exclusion Principle

Pauli, in 1925 proposed that no two electrons in an atom can be represented by same values of all the four quantum numbers. It is true for 2 electrons of same orbital even an orbital can accommodate a maximum of 2 electrons with opposite spin. These two electrons have same values of principal (n), azimuthal (l) and magnetic quantum numbers (m) but the value of spin quantum number will be different in them always as they possess opposite spins.

e.g. In oxygen (atomic number = 8) : $1s^2, 2s^2, 2p^4$

	$1s$	$2s$	$2p_x$	$2p_y$	$2p_z$
Principal Q.N.	1	2	2	2	2
Azimuthal Q.N.	0	0	1	1	1
Magnetic Q.N.	0	0	+1	–1	0
Spin Q.N.	$+\frac{1}{2} - \frac{1}{2}$	$+\frac{1}{2} - \frac{1}{2}$	$+\frac{1}{2} - \frac{1}{2}$	$+\frac{1}{2}$	$+\frac{1}{2}$

Electronic Configuration of Elements

The arrangement of electrons in various shells, sub-shells and orbitals in an atom is termed as electronic configuration.

It is written in terms of $\boldsymbol{nl^x}$.

where, n indicates the order of shell, l indicates the subshell and x indicates the number of electrons present in the subshell.

Rules for Filling of Electrons in Orbitals

Following rules have to be followed while filling electrons in orbitals

Aufbau Principle

Aufbau is a German word meaning "building up". The principle related to this word gives us an idea about the filling of orbitals by electrons. The rule states that *orbitals are filled up according to the increase in their energy.'*

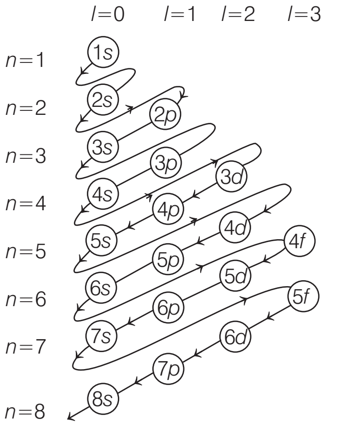
The order of increase of energy can be calculated from $(n + l)$ rule which states that

- The lower the value of $(n + l)$ for an orbital, the lower is its energy, e.g. between $3d$ and $4s$, the $4s\,(4 + 0 = 4)$ will be filled before $3d(3 + 2 = 5)$.

  Similarly between $4f$ and $6s$, the $6s\,(6 + 0 = 6)$ will be filled first than $4f(4 + 3 = 7)$.
- If two orbitals have same value of $(n + l)$, the orbital with lower value of n will be filled first, e.g. between $2p$ and $3s$, $2p(2 + 1 = 3)$ will be filled first than $3s(3 + 0 = 3)$.

The order in which electrons are filled in the orbitals, according to this rule is

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



Increasing order of energy or order of filling of electron

Extra Stability of Completely Filled and Half-Filled Orbitals

The ground state electronic configuration of atom corresponds to the lowest energy state and gives higher stability. The electronic configuration of most of the atoms follows the basic rules. However, certain elements such as Cr or Cu do not follow the rules.

In such elements, the two sub-shells $4s$ and $3s$ slightly differ in energy. i.e. $4s$ is slightly lower in energy than $3d$ orbital.

In such case, the electron from lower energy sub-shell may jump to higher energy sub-shell provided such a shift results in either completely filled or half-filled condition of all the orbitals of subshell. For example,

- **Cr** atomic number – 24 → $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^5, 4s^1$
- **Cu** atomic number – 29 → $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^{10}, 4s^1$
- **Nb** atomic number – 41 → $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^{10}$ $4s^2, 4p^6, 4d^4, 5s^1$
- **Mo** atomic number – 42 → $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^{10}$ $4s^2, 4p^6, 4d^5, 5s^1$
- **Ru** atomic number – 44 → $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^{10}$ $4s^2, 4p^6, 4d^7, 5s^1$

The extra stability of half-filled and full-filled electronic configuration can be explained in terms of symmetry and exchange energy with the help of Hund's rule.

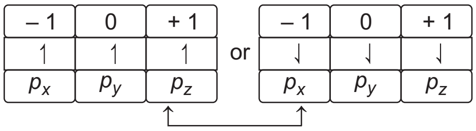
Hund's Rule of Maximum Multiplicity

The rule states that *pairing of electrons in the orbitals of a particular sub-shell (p, d, or f) does not take place until all the orbitals of a sub-shell are singly occupied.*

Moreover, the singly occupied orbitals must have the electrons with parallel spin.

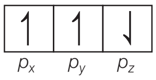
The basis of this rule is that two electrons in a particular orbital feel greater repulsion and hence, while filling orbitals of equal energy, pairing of electrons is avoided as long as it is possible.

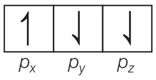
e.g. Suppose there are three electrons to be filled in a p-orbital. So, according to Hund's rule the correct possible representations are

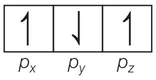


Both are correct electronic representations since both obey the Hund's rule

Other possible representations are like







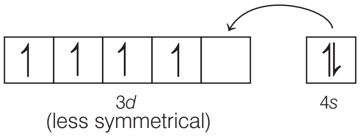
All of these are violating Hund's rule of maximum multiplicity.

Remember If the orbitals are only singly occupied, all electrons must have same spin quantum number spinning in the same direction.

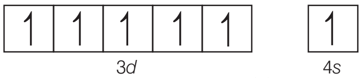
Symmetrical Distribution of Electrons

This is the another aspect of Hund's rule. According to this, the electronic configurations in which all the orbitals of the same sub-shell are either completely filled or half filled have relatively more symmetrical distribution of electrons.

Consequently, their shielding of one another is relatively small and the electrons are more strongly attracted by the nucleus. This leads to more stability of the atom. e.g. The expected configuration of Cr is $3d^4 4s^2$.

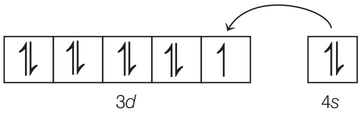


But shifting of one electron from $4s$ to $3d$ orbital makes the configuration more symmetrical and hence, more stable.

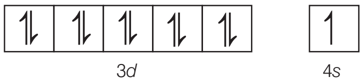


(more symmetrical and half-filled)

Similarly in copper, shifting of one electron from 4*s* to 3*d* makes the configuration more stable.



(less symmetrical)



(more symmetrical and completely filled)

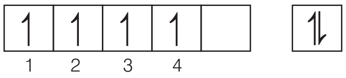
Exchange Energy

For the practical evaluation of this rule, the term "maximum multiplicity" is added in the rule. This term is used to explain the extra stability of half-filled or fully-filled orbitals due to exchange energies

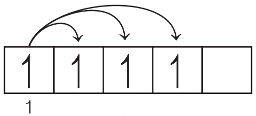
The exchange energy means hypothetical energy evolved on shifting of electrons from one orbital to another within the same sub-shell.

In simplified terms the configuration with more exchange energies is considered as more stable.

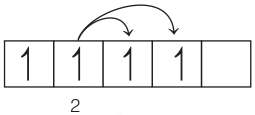
Let us compare the number of exchanges in $3d^4 4s^2$ (expected electronic configuration of Cr) and $3d^5 4s^1$ (actual electronic configuration of Cr).



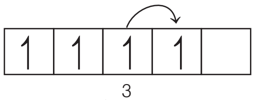
($3d^4$ configuration)
Total exchanges
= 3 + 2 + 1 = 6



3 exchanges for electron 1

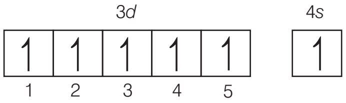


2 exchanges for electron 2

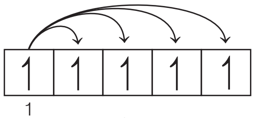


1 exchange for electron 3

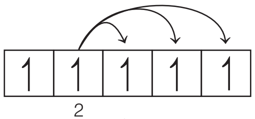
In the above arrangement electron exchanges are six which implies that there are 6 arrangements possible with parallel spin in $3d^4 4s^2$ configuration.



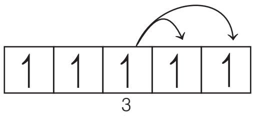
($3d^5$ configuration)
Total exchanges
= 4 + 3 + 2 + 1 = 10



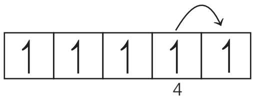
4 exchanges for electron 1



3 exchanges for electron 2



2 exchanges for electron 3



1 exchange for electron 4

Here, total 10 exchanges are possible, thus it involves more exchange energy and hence, is more stable.

Practice Exercise

ROUND I Topically Divided Problems

Sub-atomic Particles, Early Atomic Models and Atomic Species

1. Which of the following statements about the electron is incorrect? *(NCERT Exemplar)*

(a) It is a negatively charged particle
(b) The mass of electron is equal to the mass of neutron
(c) It is a basic constituent of all atoms
(d) It is a constituent of cathode rays

2. Which of the following will not show deflection from the path on passing through an electric field? *(NCERT Exemplar)*

(a) Proton
(b) Cathode rays
(c) Electron
(d) Neutron

3. Which of the following conclusions could not be derived from Rutherford's α-particle scattering experiment? *(NCERT Exemplar)*

(a) Most of the space in the atom is empty
(b) The radius of the atom is about 10^{-10} m while that of nucleus is 10^{-15} m
(c) Electrons move in a circular path of fixed energy, called orbits
(d) Electrons and the nucleus are held together by electrostatic forces of attraction

4. Find the total number of protons in 34 mg of NH_3 at STP. (Mass of 1 $p = 1.6726 \times 10^{-27}$ kg). *(NCERT)*

(a) 12.044×10^{23}
(b) 12.044×10^{22}
(c) 12.044×10^{21}
(d) 12.044×10^{20}

5. The diameter of zinc atom is 2.6 Å. Calculate the number of atoms present in a length of 1.6 cm if the zinc atoms are arranged side by side lengthwise. *[NCERT Exemplar]*

(a) 6.023×10^{23}
(b) 6.15×10^{7}
(c) 1.62×10^{19}
(d) 6.15×10^{12}

6. Two atoms are said to be isobars if *(NCERT Exemplar)*

(a) they have same atomic number but different mass number
(b) they have same number of electrons but different number of neutrons
(c) they have same number of neutrons but different number of electrons
(d) sum of the number of protons and neutrons is same but the number of protons is different

7. Rutherford scattering formula fails for very small scattering angles because

(a) the kinetic energy of α-particles is larger
(b) the gold foil is very thin
(c) the full nuclear charge of the target atom is partially screened by its electron
(d) All of the above

8. Choose the arrangement which shows the increasing value of e/m for e, p, n and α-particles.

(a) $n < \alpha < p < e$
(b) $e < p < \alpha < n$
(c) $n < p < e < \alpha$
(d) $p < n < \alpha < e$

9. Which of the following pairs have identical values of e/m ?

(a) A proton and a neutron
(b) A proton and deuterium
(c) A deuterium and an α-particle
(d) An electron and γ-rays

10. Hydrogen has three isotopes (A), (B) and (C). If the number of neutron(s) in (A), (B) and (C) respectively, are (x), (y) and (z), the sum of (x), (y) and (z) is *(JEE Main 2020)*

(a) 4
(b) 3
(c) 2
(d) 1

Dual Nature of Light, Black-body Radiation, Photoelectric Effect and Plank's Quantum Theory

11. The work function of a metal is 4.2 eV. If radiations 2000Å fall on the metal, then the kinetic energy of the fastest photoelectron is

(a) 1.6×10^{-19} J
(b) 16×10^{10} J
(c) 3.2×10^{-19} J
(d) 6.4×10^{-10} J

12. A certain metal when irradiated to light ($\nu = 3.2 \times 10^{16}$ Hz) emits photoelectrons with twice kinetic energy as did photoelectrons when the same metal is irradiated by light ($\nu = 2.0 \times 10^{16}$ Hz). The ν_0 (threshold frequency) of metal is

(a) 1.2×10^{14} Hz (b) 8×10^{15} Hz
(c) 1.2×10^{16} Hz (d) 4×10^{12} Hz

13. If the threshold wavelength (λ_0) for ejection of electron from metal is 330 nm, then work function for the photoelectric emission is

(a) 1.2×10^{-18} J (b) 1.2×10^{-20} J
(c) 6×10^{-19} J (d) 6×10^{-12} J

14. The kinetic energy of the photoelectrons does not depend upon

(a) Intensity of incident radiation
(b) Frequency of incident radiation
(c) Wavelength of incident radiation
(d) Wave number of incident radiation

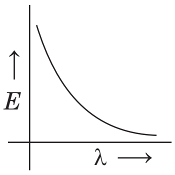
15. The ratio of the energy of a photon of 2000 Å wavelength radiation to that of 4000 Å wavelength radiation is

(a) $\frac{1}{4}$ (b) 4 (c) $\frac{1}{2}$ (d) 2

16. The ejection of the photoelectron from the silver metal in the photoelectric effect experiment can be stopped by applying a voltage of 0.35 V when the radiation 256.7 nm is used. Calculate the work function for silver metal.

(a) 4.83 eV (b) 0.35 eV (c) 4.48 eV (d) 3.21 eV

17. Which graph shows how the energy E of a photon of light is related to its wavelength (λ)?

(a)


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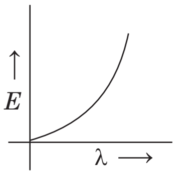
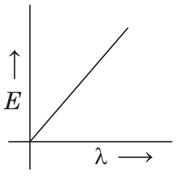
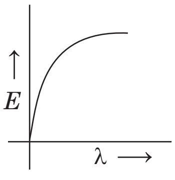


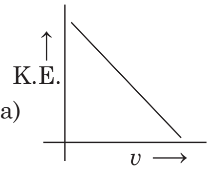
(c)


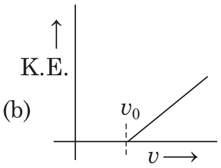
(d)


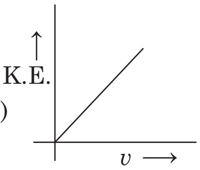
18. In photoelectric effect, the kinetic energy of photoelectron increase linearly with the

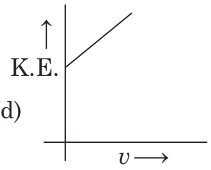
(a) wavelength of incident light
(b) velocity of incident light
(c) frequency of incident light
(d) atomic mass of an element

19. According to Einstein's photoelectric equation, the graph between kinetic energy of photoelectrons ejected and the frequency of the incident radiation is

(a)


(b)


(c)


(d)


20. The momentum (in kg-m/s) of photon having 6 MeV energy is

(a) 3.2×10^{-20} (b) 1.6×10^{-21}
(c) 2.0×10^{-20} (d) 3.2×10^{-21}

21. The number of photons of light having wave number $\bar{\nu}$ in 10 J of energy is

(a) $\frac{h}{10c\bar{\nu}}$ (b) $\frac{10}{hc\bar{\nu}}$ (c) $\frac{hc}{10\bar{\nu}}$ (d) $10h\bar{\nu}c$

22. If the photon of the wavelength 150 pm strikes an atom and one of its inner bound electrons is ejected out with a velocity of 1.5×10^7 ms^{-1}, the energy with which it is bound to the nucleus is ***(NCERT)***

(a) 1.222×10^{-16} J (b) 7.63×10^{3} eV
(c) 1.22×10^{-19} kJ (d) All of these

23. Lifetimes of the molecules in the excited states are often measured by using pulsed radiation source of duration nearly in the nanosecond range. If the radiation source has the duration of 2*ns* and the number of photons emitted during the pulse source is 2.5×10^{15}, calculate the energy of the source.

(a) 8.28×10^{-10} J (b) 8.28×10^{-10} kJ ***(NCERT)***
(c) 8.28×10^{-10} eV (d) None of these

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

(a) 189.51 kJ mol^{-1}
(b) 199.51 kJ mol^{-1}
(c) 198.52 kJ mol^{-1}
(d) 201.51 kJ mol^{-1}

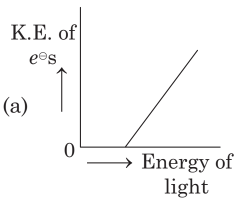
25. A 100 Watt bulb emits monochromatic light of wavelength 400 nm. Calculate the number of photons emitted per second by the bulb

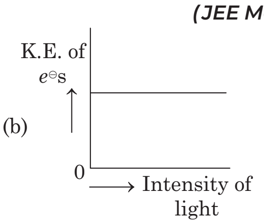
(a) 2.012×10^{20} s^{-1} (b) 3.012×10^{20} s^{-1}
(c) 4.012×10^{20} s^{-1} (d) 2.112×10^{20} s^{-1}

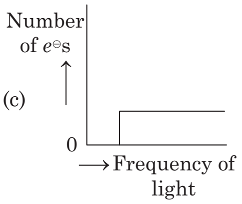
26. Calculate the number of protons emitted in 10 hours by a 60 W sodium lamp
(λ of photon = 5893Å)

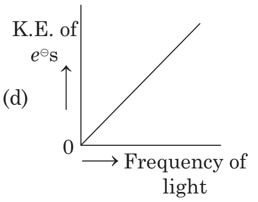
(a) 6.52×10^{23} (b) 7.52×10^{24}
(c) 6.41×10^{24} (d) 8.41×10^{24}

27. Which of the graphs shown below does not represent the relationship between incident light and the electron ejected from metal surface? ***(JEE Main 2019)***









28. Light of wavelength 5000 Å falls on a metal surface of work 1.9 eV. The energy of photons and the kinetic energy of of photoelectrons respectively are

(a) 2.48 eV, 5.7×10^{-20} J (b) 3.48 eV, 5.7×10^{-20} J
(c) 2.48 eV, 6.8×10^{-20} J (d) 7.59 eV, 5.9×10^{-18} J

29. When electromagnetic radiation of wavelength 300 nm falls on the surface of sodium, electrons are emitted with a kinetic energy of 1.68×10^{5} J mol^{-1}. What is the minimum energy needed to remove an electron from sodium?

(a) 8.43×10^{-19} J mol^{-1} (b) 4.83×10^{-19} J mol^{-1}
(c) 3.84×10^{-19} J mol^{-1} (d) 8.43×10^{-21} J mol^{-1}

30. A photon of 300 nm is absorbed by a gas, which the re-emits two photons. One re-emitted photon has a wavelength of 400 nm. Calculate the energy of the other re-emitted photon.

(a) 1.656×10^{-19} J (b) 1.892×10^{-20} J
(c) 1.656×10^{-24} J (d) 1.76×10^{-20} J

31. When a certain metal was irradiated with light of frequency 4.0×10^{16} s^{-1}, the photoelectrons emitted has three times the kinetic energy as the kinetic energy of photoelectrons emitted when the metal was irradiated with light of frequency 2.0×10^{16} s^{-1} Calculate the critical frequency (v_0) of the metal.

(a) 1×10^{15} s^{-1} (b) 1×10^{16} s^{-1}
(c) 2×10^{16} s^{-1} (d) 3×10^{16} s^{-1}

32. A dye absorb light of λ = 4530Å and then fluorescence of 5080Å Assuming that under given conditions 47% C absorbed energy is re-emitted out as fluorescence, calculate ratio of quanta emitted out to the number of quanta absorb

(a) 0.527 (b) 1.527 (c) 2.324 (d) 5.629

33. Yellow light emitted from a sodium lamp has a wavelength (λ) of 580 nm. Calculate the frequency (ν) and wave number ($\bar{\nu}$) of the yellow light. ***(NCERT)***

(a) 5.17×10^{14} s^{-1}, 1.724×10^{4} cm^{-1}
(b) 4.27×10^{14} s^{-1}, 3.245×10^{4} cm^{-1}
(c) 1.26×10^{15} s^{-1}, 8.37×10^{3} cm^{-1}
(d) 51.7×10^{14} s^{-1}, 1.724×10^{5} cm^{-1}

34. What is the number of photons of light with a wavelength of 4000 pm that provide 1 J of energy? ***(NCERT)***

(a) 4.9695×10^{17} (b) 4.9695×10^{8}
(c) 2.0122×10^{15} (d) 2.0122×10^{16}

35. Arrange the following type of radiations in increasing order of frequency. ***(NCERT)***

(i) Radiation from microwave oven
(ii) Amber light from traffic signal
(iii) Radiation from FM radio
(iv) Cosmic rays from outer space and
(v) X-rays

The correct order is

(a) (i) < (iii) < (ii) < (iv) < v)
(b) (iii) < (i) < (v) < (ii) < (iv)
(c) (iii) < (i) < (ii) < (v) < (iv)
(d) (iii) < (v) < (i) < (ii) < (iv)

36. What is the minimum energy that photons must possess in order to produce photoelectric effect with platinum metal? The threshold frequency for platinum is 1.3×10^{15} s^{-1}

(a) 3.6×10^{-13} erg (b) 8.2×10^{-13} erg
(c) 8.2×10^{-14} erg (d) 8.6×10^{-12} erg

37. Two hydrogen atoms collide head-on and end up with zero kinetic energy. Each then emits a photon with a wavelength 121.6 nm. The transition that leads to this wavelength and the velocity of hydrogen atoms travelling before the collision are, respectively (Given, $R_H = 1.097\times10^{7}$ m^{-1} and $m_H = 1.67\times10^{-27}$ kg)

(a) $n_2 \rightarrow n_1$; 4.43×10^{4} ms^{-1}
(b) $n_4 \rightarrow n_3$; 4.43×10^{4} ms^{-1}
(c) $n_3 \rightarrow n_2$; 2.63×10^{7} ms^{-1}
(d) $n_2 \rightarrow n_3$; 4.43×10^{4} ms^{-1}

Bohr Model and Interpretation of Hydrogen Spectrum

38. Bohr's theory is applicable to

(a) He (b) Li^{2+}

(c) He^{2+} (d) None of these

39. The radius of which of the following orbit is same as that of the first Bohr's orbit of hydrogen atom?

(a) Li^{2+} $(n = 2)$ (b) Li^{2+} $(n = 3)$

(c) Be^{3+} $(n = 2)$ (d) He^{+} $(n = 2)$

40. According to Bohr's theory, the angular momentum for an electron of 3rd orbit is

(a) $3\,\hbar$ (b) $1.5\,\hbar$ (c) $9\,\hbar$ (d) $2\,\dfrac{h}{\pi}$

41. The energy associated with the first orbit in the hydrogen atom is $-\ 2.18 \times 10^{-18}$ J $atom^{-1}$. What is the energy associated with the fifth orbit? *(NCERT)*

(a) -0.43×10^{-18} J (b) -0.087×10^{-18} J

(c) -2.18×10^{-18} J (d) -3.16×10^{-15} J

42. Electromagnetic radiation of wavelength 242 nm is just sufficient to ionise the sodium atom. Calculate the ionisation energy of sodium in kJ mol^{-1}. *(NCERT)*

(a) 4.945×10^{5} kJ / mol (b) 4.945×10^{4} kJ / mol

(c) 4.945×10^{2} kJ / mol (d) 4.945×10^{3} kJ / mol

43. The potential energy of an electron present in the ground state of Li^{2+} ion is

(a) $+\dfrac{3e^2}{4\pi\varepsilon_0\, r}$ (b) $-\dfrac{3e}{4\pi\varepsilon_0\, r}$ (c) $-\dfrac{3e^2}{4\pi\varepsilon_0 r}$ (d) $-\dfrac{3e^2}{4\pi\varepsilon_0 r^2}$

44. The velocity of an electron placed in 3rd orbit of H atom, will be

(a) 2.79×10^{7} cm/s (b) 9.27×10^{27} cm/s

(c) 7.29×10^{7} cm/s (d) 92.7×10^{7} cm/s

45. The radius of the second Bohr orbit in terms of the Bohr radius, a_0, in Li^{2+} is *(JEE Main 2020)*

(a) $\dfrac{2a_0}{3}$ (b) $\dfrac{4a_0}{3}$ (c) $\dfrac{4a_0}{9}$ (d) $\dfrac{2a_0}{9}$

46. The difference between the radii of 3rd and 4th orbits of Li^{2+} is ΔR_1. The difference between the radii of 3rd and 4th orbits of He^{+} is ΔR_2. Ratio $\Delta R_1 : \Delta R_2$ is *(JEE Main 2020)*

(a) 3 : 2 (b) 8 : 3 (c) 2 : 3 (d) 3 : 8

47. Which one of the following about an electron occupying the 1*s*-orbital in a hydrogen atom is incorrect? (The Bohr radius is represented by a_0) *(JEE Main 2019)*

(a) The electron can be found at a distance $2a_0$ from the nucleus.

(b) The magnitude of the potential energy is double that of its kinetic energy on an average.

(c) The probability density of finding the electron is maximum at the nucleus.

(d) The total energy of the electron is maximum when it is at a distance a_0 from the nucleus.

48. Emission transitions in the Paschen series end at orbit $n = 3$ and start from orbit n and can be represented as $\nu = 3.29 \times 10^{15}\ (\text{Hz}) \left[\dfrac{1}{3^2} - \dfrac{1}{n^2}\right]$.

Calculate the value of n if the transition is observed at 1285 nm. Find the region of the spectrum. *(NCERT)*

(a) 4, Infra-red (b) 5, Infra-red

(c) 6, Visible (d) 3, Infra-red

49. Which of the following transitions are not allowed in the normal electronic emission spectrum of an atom?

(a) $2s \rightarrow 1s$ (b) $2p \rightarrow 1s$

(c) $3d \rightarrow 4p$ (d) $5p \rightarrow 3s$

50. The line spectra of two elements are not identical because

(a) the elements do not have the same number of neutrons

(b) they have different mass numbers

(c) their outermost electrons are at different energy levels

(d) All of the above

51. An emission transition starts from the orbit having radius 1.3225 nm and ends at 211.6 pm. Name the series to which this transition belongs and the region of the spectrum. *(NCERT)*

(a) Lyman, UV (b) Balmer, visible

(c) Paschen, IR (d) Brackett, IR

52. Which of the following electronic transition in hydrogen atom will require largest amount of energy?

(a) From $n = 1$ to $n = 2$ (b) From $n = 2$ to $n = 3$

(c) From $n = \infty$ to $n = 1$ (d) From $n = 3$ to $n = 5$

53. For emission line of atomic hydrogen from $n_i = 8$ to $n_f = n$, the plot of wave number $(\bar{\nu})$ against $\left(\dfrac{1}{n^2}\right)$ will be (The Rydberg constant, R_H is in wave number unit) *(JEE Main 2019)*

(a) non linear

(b) linear with slope $-R_H$

(c) linear with slope R_H

(d) linear with intercept $-R_H$

54. The frequency of light emitted for the transition $n = 4$ to $n = 2$ of He^{+} is equal to the transition in H atom corresponding to which of the follwing? *(AIEEE 2011)*

(a) $n = 3$ to $n = 1$ (b) $n = 2$ to $n = 1$

(c) $n = 3$ to $n = 2$ (d) $n = 4$ to $n = 3$

55. The region in the electromagnetic spectrum where the Balmer series lines appear is *(JEE Main 2020)*

(a) infrared (b) ultraviolet

(c) microwave (d) visible

56. For the Balmer series in the spectrum of H atom, $\bar{v} = R_H \left\{\frac{1}{n_1^2} - \frac{1}{n_2^2}\right\}$, the correct statements among I to IV are

I. As wavelength decreases, the lines in the series converge.

II. The integer n_1 is equal to 2.

III. The lines of longest wavelength corresponds to $n_2 = 3$.

IV. The ionisation energy of hydrogen can be calculated from wave number of these lines. *(JEE Main 2020)*

(a) I, II, IV (b) II, III, IV (c) I, III, IV (d) I, II, III

57. The shortest wavelength of H atom in the Lyman series is λ_1. The longest wavelength in the Balmer series of He^+ is *(JEE Main 2020)*

(a) $\frac{36\lambda_1}{5}$ (b) $\frac{5\lambda_1}{9}$ (c) $\frac{9\lambda_1}{5}$ (d) $\frac{27\lambda_1}{5}$

Modern Structure of Atom
(de-Broglie and Heisenberg's Principle)

58. The wave nature of electron is verified by

(a) de-Broglie (b) Davisson and Germer

(c) Rutherford (d) All of these

59. Table-Tennis ball has a mass 10 g and a speed of 90 m/s. If speed can be measured within an accuracy of 4%, what will be the uncertainty in position? *(NCERT Exemplar)*

(a) 3.6×10^{-23} m (b) 1.46×10^{-33} m

(c) 2.8×10^{-30} m (d) 1.00×10^{-34} m

60. Similar to electron diffraction, neutron diffraction microscope is also used for the determination of the structure of molecules. If the wavelength used here is 800 pm, calculate the characteristics velocity associated with the neutron (mass of neutron $= 1.675\times10^{-27}$ kg). *(NCERT)*

(a) $4.92\times10^2\ \text{ms}^{-1}$ (b) $2.46\times10^3\ \text{ms}^{-1}$

(c) $9.84\times10^2\ \text{ms}^{-1}$ (d) $0.246\times10^3\ \text{ms}^{-1}$

61. If the de-Broglie wavelength of the electron in n^{th} Bohr orbit in a hydrogenic atom is equal to $1.5\ \pi a_0$ (a_0 is Bohr radius), then the value of n/Z is *(JEE Main 2019)*

(a) 1.0 (b) 0.75 (c) 0.40 (d) 1.50

62. According to de-Broglie, matter should exhibit dual behaviour, that is both particle and wave like properties. However, a cricket ball of mass 100 g does not move like a wave when it is thrown by a bowler at a speed of 100 km/h. Calculate the wavelength of the ball. *(NCERT Exemplar)*

(a) 2.385×10^{-36} m (b) 23.85×10^{-36}m

(c) 238.5×10^{-36} m (d) 2385×10^{-36} m

63. Out of electron, proton, neutron and α-particle which one will have a higher velocity to produce matter wave of the same wavelength? *(NCERT Exemplar)*

(a) Electron (b) Proton

(c) Neutron (d) α-particle

64. Which of the following particles moving with same velocity would be associated with smallest de-Broglie wavelength?

(a) Helium molecule

(b) Oxygen molecule

(c) Hydrogen molecule

(d) Carbon molecule

65. The mass of an electron is *m,* its charge is *e* and it is accelerated from rest through a potential difference, *V.* The velocity of electron will be calculated by formula

(a) $\sqrt{\frac{V}{m}}$ (b) $\sqrt{\frac{eV}{m}}$

(c) $\sqrt{\left(\frac{2eV}{m}\right)}$ (d) None of these

66. A stream of electrons from a heated filament was passed between two charged plates kept at a potential difference *V* esu. If *e* and *m* are charge and mass of an electron, respectively, then the value of h/λ (where, λ is wavelength associated with electron wave) is given by *(JEE Main 2016)*

(a) $2\ meV$ (b) $\sqrt{meV}$

(c) $\sqrt{2meV}$ (d) meV

67. What is the wavelength of an α-particle having mass 6.6×10^{-27} kg moving with a speed of 10^5 cm s^{-1}? ($h = 6.6\times10^{-34}$ kg m^2- s)

(a) 2×10^{-12} m (b) 3×10^{-10} m

(c) 1×10^{-10} m (d) 2×10^{-10} m

68. The de-Broglie wavelength relates to applied voltage for α-particles as

(a) $\lambda = \frac{12.3\ \text{Å}}{\sqrt{V}}$ (b) $\lambda = \frac{0.286}{\sqrt{V}}\ \text{Å}$

(c) $\lambda = \frac{0.101}{\sqrt{V}}\ \text{Å}$ (d) $\lambda = \frac{0.856}{\sqrt{V}}\ \text{Å}$

69. The uncertainty in momentum of an electron is 1×10^{-5} kg m / s. The uncertainty in its position will be ($h = 6.62 \times 10^{-34}$ kg m^2 / s)

(a) 2.36×10^{-28} m (b) 5.25×10^{-28} m
(c) 2.27×10^{-30} m (d) 5.27×10^{-30} m

70. If the kinetic energy of an electron is increased four times, the wavelength of the de-Broglie wave associated with it would becomes

(a) half times (b) $\frac{1}{4}$ times
(c) four times (d) two times

Wave Mechanical Model and Quantum Numbers

71. The two electrons in K-subshell will differ in

(a) principal quantum number
(b) azimuthal quantum number
(c) magnetic quantum number
(d) spin quantum number

72. Which of the following arrangement of orbitals is in the increasing order of energy? *(NCERT Exemplar)*

(a) $1s, 2s, 2p, 3s$ (b) $4s, 3s, 3p, 4d$
(c) $5p, 4d, 5d, 4f, 6s$ (d) $5f, 6d, 7s, 7p$

73. What is the lowest value of n that allows g orbitals to exist? *(NCERT)*

(a) 3 (b) 4 (c) 5 (d) 6

74. Which of the following has non-spherical shell of electron?

(a) He (b) B (c) Be (d) Li

75. Which of the following sets of quantum numbers are not possible ? *(NCERT)*

I. $n = 0, l = 0, m_l = 0, m_s = +\frac{1}{2}$
II. $n = 1, l = 0, m_l = 0, m_s = -\frac{1}{2}$
III. $n = 1, l = 1, m_l = 0, m_s = +\frac{1}{2}$
IV. $n = 2, l = 1, m_l = 0, m_s = -\frac{1}{2}$
V. $n = 3, l = 3, m_l = -3, m_s = +\frac{1}{2}$
VI. $n = 3, l = 1, m_l = 0, m_s = +\frac{1}{2}$

(a) I, II and III (b) I, III and V
(c) I, IV and VI (d) I, II, III and V

76. Total number of orbitals associated with third shell will be *(NCERT Exemplar)*

(a) 2 (b) 4 (c) 9 (d) 3

77. Number of angular nodes for $4\,d$ orbital is *(NCERT Exemplar)*

(a) 4 (b) 3 (c) 2 (d) 1

78. A certain orbital has no angular nodes and two radial nodes. The orbital is *(JEE Main 2021)*

(a) $2s$ (b) $3s$ (c) $3p$ (d) $2p$

79. The Z-component of angular momentum of an electron in an atomic orbital is governed by the

(a) magnetic quantum number
(b) azimuthal quantum number
(c) spin quantum number
(d) principal quantum number

80. Which of the following statements regarding an orbital is correct?

(a) An orbital is a definite trajectory around the nucleus in which electron can move
(b) An orbital always has spherical trajectory
(c) An orbital is the region around the nucleus where there is a 90 – 95% probability of finding all the electrons of an atom
(d) An orbital is characterised by 4 quantum numbers n, l, m and s

81. For a particular value of azimuthal quantum number, the total number of magnetic quantum number values are given by

(a) $l = \frac{m+1}{2}$ (b) $l = \frac{m-1}{2}$ (c) $l = \frac{2m+1}{2}$ (d) $m = \frac{2l+1}{2}$

82. Among the following sets of quantum numbers, which one is incorrect for $4d$-electron?

(a) $n = 4, l = 3, 2, m = +\frac{1}{2}$ (b) $n = 4, l = 2, 1, m = +\frac{1}{2}$
(c) $n = 4, l = 2, -2, m = +\frac{1}{2}$ (d) $n = 4, l = 2, 1, m = -\frac{1}{2}$

83. The quantum numbers $+\frac{1}{2}$ and $-\frac{1}{2}$ for an electron represent

(a) rotation of electron in clockwise and anticlockwise direction respectively
(b) rotation of electron in anticlockwise and clockwise direction respectively
(c) magnetic moment of electron pointing up and down respectively
(d) two quantum mechanical spin states which have no classical analogue

84. For an electron in a hydrogen atom, the wave function ψ is proportional to $\exp^{-t/a_0}$, where a_0 is the Bohr's radius. What is the ratio of the probability of finding the electron at the nucleus to the probability of finding it at a_0?

(a) e (b) e^2 (c) $\frac{1}{e^2}$ (d) Zero

85. Consider the following statements.

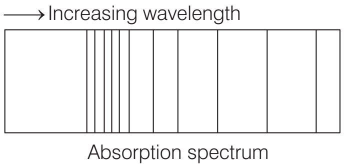
1. Electron density in xy plane in $3d_{x^2-y^2}$ orbital is zero
2. Electron density in xy plane in $3d_{z^2}$ orbital is zero
3. $2s$ orbital has only one spherical node
4. For $2p_z$ orbital yz is the nodal plane

The correct statements are

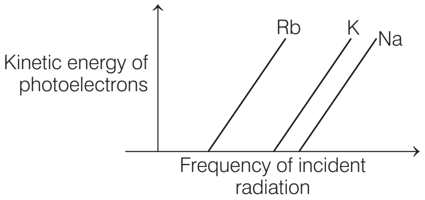
(a) 2 and 3 (b) 1, 2, 3, 4 (c) Only 2 (d) 1 and 3

86. The figure that is not a direct manifestation of the quantum nature of atoms is *(JEE Main 2020)*

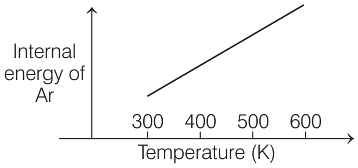
(a)



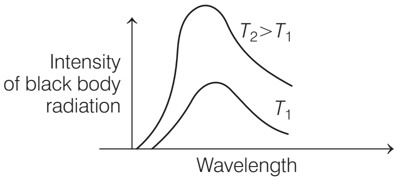
(b)



(c)



(d)



87. The number of subshells associated with $n = 4$ and $m = -2$ quantum numbers is *(JEE Main 2020)*

(a) 8 (b) 2 (c) 16 (d) 4

88. Consider the hypothetical situation where the azimuthal quantum number, l takes values 0, 1, 2, …… $n+1$, where n is the principle quantum number. Then, the element with atomic number

(a) 8 is the first noble gas *(JEE Main 2020)*
(b) 13 has a half-filled valence subshell
(c) 9 is the first alkali metal
(d) 6 has a $2p$-valence subshell

89. The correct statement about probability density (except at infinite distance from nucleus) is *(JEE Main 2020)*

(a) it can be zero for $1s$ orbital
(b) it can be negative for $2p$ orbital
(c) it can be zero for $3p$ orbital
(d) it can never be zero for $2s$ orbital

90. Which of the following combination of statements is true regarding the interpretation of the atomic orbitals?

I. An electron in an orbital of high angular momentum stays away from the nucleus than an electron in the orbital of lower angular momentum.
II. For a given value of the principal quantum number, the size of the orbit is inversely proportional to the azimuthal quantum number.
III. According to wave mechanics, the ground state angular momentum is equal to $\frac{h}{2\pi}$.
IV. The plot of ψ *vs* r for various azimuthal quantum numbers, shows peak shifting towards higher r value. *(JEE Main 2019)*

(a) I, III (b) II, III
(c) I, II (d) I, IV

91. The correct set of four quantum numbers for the valence electrons of rubidium atom $[Z = 37]$ is *(JEE Main 2014)*

(a) $5, 0, 0, +\frac{1}{2}$ (b) $5, 1, 0, +\frac{1}{2}$
(c) $5, 1, 1, +\frac{1}{2}$ (d) $5, 0, 1, +\frac{1}{2}$

Filling of Electrons in Orbitals and Related Principles

92. For the electrons of oxygen atom, which of the following statements is correct? *(NCERT Exemplar)*

(a) Z_{eff} for an electron in a $2s$-orbital is the same as Z_{eff} for an electron in a $2p$-orbital
(b) An electron in the $2s$-orbital has the same energy as an electron in the $2p$-orbital
(c) Z_{eff} for an electron in $1s$-orbital is the same as Z_{eff} for an electron in a $2s$-orbital
(d) The two electrons present in the $2s$-orbital have spin quantum numbers m_s but of opposite sign

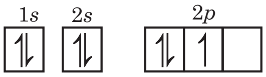
93. The pair of ions having same electronic configuration is *(NCERT Exemplar)*

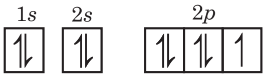
(a) Cr^{3+}, Fe^{3+}
(b) Fe^{3+}, Mn^{2+}
(c) Fe^{3+}, Co^{3+}
(d) Sc^{3+}, Cr^{3+}

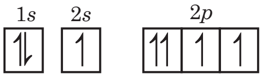
94. Which of the following options does not represent ground state electronic configuration of an atom? *(NCERT Exemplar)*

(a) $1s^2 2s^2 2p^6, 3s^2 3p^6, 3d^8, 4s^2$
(b) $1s^2 2s^2 2p^6, 3s^2 3p^6 3d^9, 4s^2$
(c) $1s^2 2s^2 2p^6, 3s^2 3p^6 3d^{10}, 4s^1$
(d) $1s^2 2s^2 2p^6, 3s^2 3p^6 3d^5, 4s^1$

95. Which of the following will violates Aufbau principle as well as Pauli's exclusion principle?

(a)


(b)


(c)


(d) None of the above

96. The electronic configuration with maximum exchange energy will be

(a) $3d_{xy}^1, 3d_{yz}^1, 3d_{zx}^1, 4s^1$
(b) $3d_{xy}^1, 3d_{yz}^1, 3d_{zx}^1, 3d_{x^2-y^2}^1, 3d_{z^2}^1, 4s^1$
(c) $3d_{xy}^2, 3d_{yz}^2, 3d_{zx}^2, 3d_{x^2-y^2}^2, 3d_{z^2}^1, 4s^1$
(d) $3d_{xy}^2, 3d_{yz}^2, 3d_{zx}^2, 3d_{x^2-y^2}^2, 3d_{z^2}^2, 4s^1$

97. A Mo atom in its ground state has $4d^5, 5s^1$ configuration and a Ag atom has $4d^{10}, 5s^1$ configuration. This is because a shell which is half-filled or completely filled is particularly

(a) strongly exchange stabilised
(b) weakly exchange stabilised
(c) weakly exchange destabilised
(d) strongly exchange destabilised

98. In a set of degenerate orbitals, the electrons distribute themselves to retain like spins as far as possible. This statement belongs to

(a) Pauli's exclusion principle
(b) Aufbau principle
(c) Hund's rule of maximum multiplicity
(d) Slater's rule

ROUND II Mixed Bag

1. Chlorophyll present in green leaves of plants absorbs light at 4.620×10^{14} Hz. Which part of the electromagnetic spectrum does it belong to? *(NCERT Exemplar)*

(a) UV (b) IR (c) Far IR (d) Visible

2. If an electron has spin quantum number of $+\frac{1}{2}$ and a magnetic quantum number of –1, it cannot be represented in an

(a) *s*-orbital (b) *p*-orbital (c) *d*-orbital (d) *f*-orbital

3. How many electrons in an atom may have the following quantum number? *(NCERT)*

(i) $n = 4, m_s = \frac{1}{2}$ (ii) $n = 3, l = 0$

(a) 32 and 2 respectively (b) 16 and 2 respectively
(c) 16 and 1 respectively (d) 32 and 1 respectively

4. If the light of wavelength, λ is used to observe an electron then uncertainty in position of the electron would be

(a) less than λ (b) more than λ
(c) equal to λ (d) equal to or greater than λ

5. In the ground state of Cu^+, the number of shell occupied, sub-shells occupied, filled orbitals and unpaired electrons respectively are

(a) 4, 8, 15, 0 (b) 3, 6, 15, 1
(c) 3, 6, 14, 0 (d) 4, 7, 14, 2

6. The electronic configuration of the oxide ion is more similar to the electronic configuration of the

(a) sulphide ion (b) nitride ion
(c) oxygen atom (d) nitrogen atom

7. In Rutherford's experiment, generally the thin foil of heavy atoms, like gold, platinum, etc., have been used to be bombarded by the α-particles. If the thin foil of light atoms like aluminium, etc., is used, what difference would be observed from the above results? *(NCERT)*

(a) All the α-particles pass through without much effect
(b) The number of α-particles deflected back becomes half
(c) The number of α-particles deflected increases
(d) The results are same in both the case

8. The work function (ϕ) of some metals is listed below. The number of metals which will show photoelectric effect when light of 300 nm wavelength falls on the metal is

Metal	Li	Na	K	Mg	Cu	Ag	Fe	Pt	W
ϕ (eV)	2.4	2.3	2.2	3.7	4.8	4.3	4.7	6.3	4.75

(a) 2 (b) 4 (c) 6 (d) 8

9. Which transition in the hydrogen atomic spectrum will have the same wavelength as the Balmer transition, $n = 4$ to $n = 2$ of He^+ spectrum? *[NCERT]*

(a) $n = 4$ to $n = 3$ (b) $n = 3$ to $n = 2$
(c) $n = 4$ to $n = 2$ (d) $n = 2$ to $n = 1$

10. The quantum numbers of six electrons are given below. Arrange them in the order of increasing energies.

I. $n = 4, l = 2, m_l = -2, m_s = -\frac{1}{2}$
II. $n = 3, l = 2, m_l = 1, m_s = +\frac{1}{2}$
III. $n = 4, l = 1, m_l = 0, m_s = +\frac{1}{2}$
IV. $n = 3, l = 2, m_l = -2, m_s = -\frac{1}{2}$
V. $n = 3, l = 1, m_l = -1, m_s = +\frac{1}{2}$
VI. $n = 4, l = 1, m_l = 0, m_s = +\frac{1}{2}$ *(NCERT)*

(a) I < II = IV < III = VI < V
(b) V < II = IV < III = VI < I
(c) V < III = VI < II = IV < I
(d) V < II = IV < III = VI < I

11. An electron, a proton and an alpha particle have KE of $16E$, $4E$ and E respectively. What is the qualitative order of their de-Broglie wavelengths?

(a) $\lambda_e > \lambda_p = \lambda_\alpha$ (b) $\lambda_p = \lambda_\alpha > \lambda_e$
(c) $\lambda_p < \lambda_e < \lambda_\alpha$ (d) $\lambda_\alpha < \lambda_e \approx \lambda_p$

12. Suppose 10^{-17} J of light energy is needed by the interior of a human eye to see an object. Calculate the number of photons of green light ($\lambda = 550$ nm) needed to generate this minimum amount of energy.

(a) 26 (b) 27 (c) 28 (d) 29

13. The incorrect statement about Bohr's orbit of hydrogen atom is

(a) $r = n^2 \dfrac{h^2}{4\pi^2 m\left(\dfrac{e^2}{4\pi\varepsilon_0}\right)}$

(b) KE of electron = PE of electron

(c) $E = -\dfrac{1}{n^2}\,\dfrac{2\pi^2 m\left(\dfrac{e^2}{4\pi\varepsilon_0}\right)^2}{h^2}$

(d) None of the above is incorrect

14. Calculate the total number of angular nodes and radial nodes present in $3p$-orbital. *(NCERT Exemplar)*

(a) 1, 1 (b) 2, 1
(c) 2, 2 (d) 1, 2

15. An ion with mass number 37 possesses one unit of negative charge. If the ion contains 11.1% more neutrons than the electrons, find the symbol of the ion. *(NCERT)*

(a) $^{35}_{17}Cl$ (b) $^{37}_{17}Cl^-$
(c) $^{37}_{19}K^+$ (d) None of these

16. Some energy is required to ionize a H-atom if the electron occupies $n = 5$ orbit. The ratio of the ionization enthalpy of H-atom (energy required to remove the electron from $n = 1$ orbit) with the energy required to ionise H-atom if electron occupies $n = 5$ orbit is *(NCERT)]*

(a) 1 : 25 (b) 25 : 1 (c) 1 : 5 (d) 5 : 1

17. What is the colour of light emitted when the electron in a hydrogen atom undergoes transition from an energy level with $n = 4$ to an energy level with $n = 2$? *(NCERT)*

(a) Blue (b) White (c) Green (d) Red

18. Which of the following is correctly matched?

(a) Momentum of H- atom when electrons return from $n = 2$ to $n = 1$: $\dfrac{3Rh}{4}$
(b) Momentum of photon : Independent of wavelength of light
(c) e/m ratio of anode rays : Independent of gas in the discharge tube
(d) Radius of nucleus : $(\text{Mass no.})^{1/2}$

19. The uncertainty in position of an electron ($m = 9.1 \times 10^{-28}$ g) moving with a velocity 3×10^4 cm/s accurate upto 0.001% will be

(a) 3.84 cm (b) 1.92 cm
(c) 7.68 cm (d) 5.76 cm

20. The number of photons emitted per second by a 60 W source of monochromatic light of wavelength 663 nm is ($h = 6.63 \times 10^{-34}$ Js).

(a) 4×10^{-20} (b) 1.54×10^{20}
(c) 3×10^{-20} (d) 2×10^{20}

21. An electron beam is accelerated through a potential difference of 10,000 volt. The de-Broglie wavelength of the electron beam is

(a) 0.123 Å (b) 0.356 Å
(c) 0.186 Å (d) 0.258 Å

22. I_2 molecule dissociates into atoms after absorbing light of 4500 Å. If one quantum of energy is absorbed by each molecule, the KE of iodine atoms will be (BE of I_2 = 240 kJ/mol)

(a) 240×10^{-19} J (b) 0.216×10^{-19} J
(c) 2.16×10^{-19} J (d) 2.40×10^{-19} J

23. A particle A moving with a certain velocity has the de-Broglie wavelength of 1 Å. For particle B with mass 25% of A and velocity 75% of A, calculate the de-Broglie wavelength.

(a) 3 Å (b) 5.33 Å
(c) 6.88 Å (d) 0.48 Å

24. If uncertainties in the measurement of position and momentum of an electron are equal, the uncertainty in the measurement of velocity is

(a) 8.0×10^{12} ms^{-1} (b) 4.2×10^{10} ms^{-1}
(c) 8.5×10^{10} ms^{-1} (d) 6.2×10^{10} ms^{-1}

25. The uncertainty in position for a dust particle ($m = 10^{-11}$ g; diameter = 10^{-4} cm and velocity = 10^{-4} cm/s) will be (The error in measurement of velocity is 1%)

(a) 5.27×10^{-4} cm (b) 5.27×10^{-5} cm
(c) 5.27×10^{-6} cm (d) 5.27×10^{-7} cm

26. The frequency of revolution of an electron in the second Bohr orbit in hydrogen atom is

(a) 8.18×10^{14} Hz (b) 2.39×10^{15} Hz
(c) 3.29×10^{16} Hz (d) 9.25×10^{14} Hz

Numeric Value Questions

27. In 7 mg of ^{14}C total mass of neutrons in kg will be 4.37×10^{-x}. Here, the value of x is .... (Assume that mass of a neutron = 1.675×10^{-27} kg. *(NCERT)*

28. A 25 watt bulb emits monochromatic yellow light of wavelength 0.57 μm. The rate of emission of quanta per second is 7.169×10^{x}. The value of x is .... *(NCERT)*

29. The maximum kinetic energy of the photoelectrons is found to be 6.63×10^{-19} J. When the metal is irradiated with a radiation of frequency 2×10^{15} Hz, the threshold frequency of the metal is about ......$\times 10^{15}$ s^{-1}.

30. When the excited electron of a H-atom in $n = 6$ drops to the ground state. The maximum number of emission line is .... *(NCERT)*

31. The number of spherical nodes in $4p$-orbital is ......

32. The radius of first Bohr orbit is x, then de-Broglie wavelength of electron in 3rd orbit is nearly ......πx.

33. Photoelectrons are liberated by ultraviolet light of wavelength 3000 Å from a metallic surface for which the photoelectric threshold is 4000 Å. The de-Broglie wavelength of electron emitted with maximum kinetic energy, is ...$a \times 10^{-9}$ m. The value of a will be ......

34. Maximum value of $(n + l + m)$ for unpaired electrons in second excited state of chlorine $_{17}Cl$ is ....

35. The degeneracy of the nth level of hydrogen atom that has the energy $\left(-\frac{R_H}{16}\right)$ is ....

36. The radius of the second Bohr orbit for hydrogen atom is x Å, the value of x will be ...... (Planck's constant (h) = 6.6262×10^{-34} Js; mass of electron = 9.1091×10^{-31} kg ; charge of electron (e) = 1.60210×10^{-19} C; permitivity of vacuum ($\in_0$) = 8.854185×10^{-12}kg^{-1}m^{-3}A^{2})

37. Energy of an electron is given by

$$E = -2.178 \times 10^{-18} \text{ J}\left(\frac{Z^2}{n^2}\right).$$

Wavelength of light required to excite an electron in an hydrogen atom from level $n = 1$ to $n = 2$ is 1.21×10^{-y} m.

The value of y is ....

($h = 6.62 \times 10^{-34}$ J s and $c = 3.0 \times 10^{8}$ ms^{-1})

38. ....eV is the energy of a possible excited state of hydrogen.

39. A certain orbital has $n = 4$ and $m_L = -3$. The number of radial nodes in this orbital is .... *(JEE Main 2021)*

40. The number of orbitals with $n = 5$, $m_l = +2$ is .... *(JEE Main 2021)*

Answers

Round I

1. (b)	**2.** (d)	**3.** (c)	**4.** (c)	**5.** (b)	**6.** (d)	**7.** (c)	**8.** (a)	**9.** (c)	**10.** (b)
11. (c)	**12.** (b)	**13.** (c)	**14.** (a)	**15.** (d)	**16.** (c)	**17.** (a)	**18.** (c)	**19.** (b)	**20.** (d)
21. (b)	**22.** (b)	**23.** (a)	**24.** (b)	**25.** (a)	**26.** (c)	**27.** (d)	**28.** (a)	**29.** (c)	**30.** (a)
31. (b)	**32.** (a)	**33.** (a)	**34.** (d)	**35.** (c)	**36.** (d)	**37.** (a)	**38.** (b)	**39.** (c)	**40.** (a)
41. (b)	**42.** (c)	**43.** (c)	**44.** (c)	**45.** (b)	**46.** (c)	**47.** (d)	**48.** (b)	**49.** (c)	**50.** (c)
51. (b)	**52.** (a)	**53.** (c)	**54.** (b)	**55.** (d)	**56.** (d)	**57.** (c)	**58.** (b)	**59.** (b)	**60.** (a)
61. (b)	**62.** (c)	**63.** (a)	**64.** (b)	**65.** (c)	**66.** (c)	**67.** (c)	**68.** (c)	**69.** (c)	**70.** (a)
71. (d)	**72.** (a)	**73.** (c)	**74.** (b)	**75.** (b)	**76.** (c)	**77.** (c)	**78.** (b)	**79.** (b)	**80.** (c)
81. (b)	**82.** (a)	**83.** (d)	**84.** (d)	**85.** (a)	**86.** (c)	**87.** (b)	**88.** (b)	**89.** (c)	**90.** (d)
91. (a)	**92.** (d)	**93.** (b)	**94.** (b)	**95.** (c)	**96.** (d)	**97.** (a)	**98.** (c)		

Round II

1. (d)	**2.** (a)	**3.** (b)	**4.** (a)	**5.** (c)	**6.** (b)	**7.** (a)	**8.** (b)	**9.** (d)	**10.** (d)
11. (a)	**12.** (c)	**13.** (b)	**14.** (a)	**15.** (b)	**16.** (b)	**17.** (a)	**18.** (a)	**19.** (b)	**20.** (d)
21. (a)	**22.** (b)	**23.** (b)	**24.** (a)	**25.** (c)	**26.** (a)	**27.** (6)	**28.** (19)	**29.** (1)	**30.** (15)
31. (2)	**32.** (6)	**33.** (1.2)	**34.** (25)	**35.** (16)	**36.** (2.12)	**37.** (7)	**38.** (3.4)	**39.** (0)	**40.** (3)

Solutions

Round I

1. Mass of electron $= 9.1 \times 10^{-31}$ kg

Mass of neutron $= 1.67 \times 10^{-27}$ kg

2. Neutron being neutral will not show deflection from the path on passing through an electric field.

4. 1 mole of NH_3 contains protons $= 7 + 3 = 10$ moles of protons (7 in N and 1 in each H atom)

$= 6.023 \times 10^{23} \times 10$ protons

34×10^{-3} g NH_3 will contain

$$= \frac{34 \times 10^{-3} \times 6.023 \times 10^{24}}{17} = 12.046 \times 10^{21} \text{ protons}$$

5. Diameter of Zn atom $= 2.6\ \text{Å} = 2.6 \times 10^{-10}$ m

Given, length $= 1.6$ cm $= 1.6 \times 10^{-2}$ m

Number of Zn atoms in 1.6×10^{-2} m

$$= \frac{1.6 \times 10^{-2}\ \text{m}}{2.6 \times 10^{-10}\ \text{m}} = 0.6154 \times 10^{8} \text{ atoms}$$

$$= 6.154 \times 10^{7} \text{ atoms}$$

6. Isobars have the same mass number (i.e. sum of protons and neutrons) but different atomic number (i.e. number of protons).

7. According to Rutherford

$$\text{Scattering angle} \propto \frac{1}{\sin^4(\theta/2)}$$

It fails for very small scattering angles because the full nuclear charge of the target atom is partially screened by its electron.

8.
Mass of electron $= 9.1 \times 10^{-31}$ kg,
Mass of proton $= 1.67 \times 10^{-27}$ kg
Mass of neutron $= 1.675 \times 10^{-27}$ kg
Mass of α-particle $= 6.67 \times 10^{-27}$ kg
Charge of neutrons $=$ zero
Charge for proton $= 1.6 \times 10^{-19}$ C
Charge for electron $= 1.6 \times 10^{-19}$ C
Charge for α-particle $= 2 \times 1.6 \times 10^{-19}$ C

So, from these data increasing order of e/m for e, p, n and α-particle is $e > p > \alpha > n$ ($\because$ neutron has no charge).

9.

	Deuterium	***α*-particle**
q	$+1e$	$+2e$
m	$1\,p + 1\,n$	$2\,p + 2n$
$\frac{e}{m}$	$\frac{1}{2m_p}$	$\frac{1}{2m_p}$

So, deuterium and an α-particle have identical value of e/m.

10. Number of neutrons in protium $({}^1_1\text{H})$ is zero (x).

Number of neutrons in deuterium $({}^2_1\text{H}$ or ${}^2_1\text{D})$ is 1 (y).

Number of neutrons in tritium $({}^3_1\text{H}$ or ${}^3_1\text{T})$ is 2 (z)

So, the sum of x, y and z is $x + y + z = 3$

11. KE = (Energy of radiation − Work function)

$$= \left(h \times \frac{c}{\lambda} - 4.2\right)$$

$$= \left(\frac{6.6 \times 10^{-34} \times 3 \times 10^{8}}{2000 \times 10^{-10}}\right) - (4.2 \times 1.602 \times 10^{-19})$$

$$= (9.9 \times 10^{-19}) - (6.7 \times 10^{-19}) = 3.2 \times 10^{-19} \text{ J}$$

12. $\text{K.E}_1 = h\nu_1 - h\nu_0$

$\text{K.E}_2 = h\nu_2 - h\nu_0$

As $(\text{K.E})_1 = 2\,(\text{K.E})_2$

$$\begin{aligned} h\nu_1 - h\nu_0 &= 2(h\nu_2 - h\nu_0) \\ &= h(\nu_1 - \nu_0) = 2h(\nu_2 - \nu_0) \\ \nu_1 - \nu_0 &= 2\nu_2 - 2\nu_0 \\ 2\nu_0 - \nu_0 &= 2\nu_2 - \nu_1 \\ \nu_0 &= 2\nu_2 - \nu_1 \\ &= 2(2.0 \times 10^{16}) - (3.2 \times 10^{16}) \\ &= 8 \times 10^{15}\,\text{s}^{-1} = 8 \times 10^{15} \text{ Hz} \end{aligned}$$

13. Work function = Threshold energy

$$\begin{aligned} &= h\nu_0 = \frac{hc}{\lambda_0} \\ &= \frac{6.6 \times 10^{-34} \text{ Js} \times 3 \times 10^{8} \text{ m}}{330 \times 10^{-9} \text{ m}} \\ &= 6 \times 10^{-19} \text{ J} \end{aligned}$$

14. The kinetic energy of photoelectrons does not depend upon intensity of incident radiation.

15. $E = \dfrac{hc}{\lambda}$

Ratio of energy of photon $\dfrac{E_1}{E_2} = \dfrac{\lambda_2}{\lambda_1}$

$$= \frac{4000 \text{ Å}}{2000 \text{ Å}} = 2$$

16. Energy of the incident radiation

= Work function + Kinetic energy of photoelectron

Energy of incident radiation (E)

$$= hv = h\frac{c}{\lambda} = \frac{(6.626 \times 10^{-34} \text{ Js})\,(3.0 \times 10^{8} \text{ ms}^{1})}{(256.7 \times 10^{-9} \text{ m})}$$

$= 7.74 \times 10^{-19}$ J = 4.83 eV (as 1 eV $= 1.602 \times 10^{-19}$ J)

The potential applied gives the kinetic energy to the electron.

Hence, kinetic energy of the electron = 0.35 eV

∴ Work function = 4.83 eV − 0.35 eV = 4.48 eV

17. The energy equation for a photon in term of wavelength (λ) is given by

$$E = \frac{hc}{\lambda}, \text{ i.e. } E \propto \frac{1}{\lambda}.$$

20. $E = mc^2 = (mc) \times c = p \times c$ or $p = \dfrac{E}{c}$ (p is momentum)

$$= \frac{6 \times 10^{6} \times 1.6 \times 10^{-19}}{3 \times 10^{8} \text{ m}} = 3.2 \times 10^{-21} \text{ kg-ms}$$

21. $E = \dfrac{nhc}{\lambda} = nhc\bar{v}$ $\quad\left(\because \bar{\nu} = \dfrac{1}{\lambda}\right)$

∴ $10 = nhc\bar{\nu}$ or $n = \dfrac{10}{hc\bar{\nu}}$

22. Energy of incident radiation, $h\nu = h\nu_0 + \dfrac{1}{2}mv^2$

$$E = h\nu = \frac{hc}{\lambda} = \frac{6.626 \times 10^{-34} \text{ Js} \times 3.0 \times 10^{8} \text{ ms}^{-1}}{150 \times 10^{-12} \text{ m}}$$

(1 pm $= 10^{-12}$ m)

$E = 13.25 \times 10^{-16}$ J

KE of ejected electron $= \dfrac{1}{2}mv^2$

$$\begin{aligned} &= \frac{1}{2} \times 9.11 \times 10^{-31} \text{ kg} \times (1.5 \times 10^{7} \text{ ms}^{-1})^2 \\ &= 1.025 \times 10^{-16} \text{ J} \end{aligned}$$

$$\begin{aligned} W_0 = h\nu_0 &= h\nu - \frac{1}{2}mv^2 \\ &= 13.25 \times 10^{-16} \text{ J} - 1.025 \times 10^{-16} \text{ J} \\ &= 12.225 \times 10^{-16} \text{ J} \\ &= \frac{12.225 \times 10^{-16}}{1.602 \times 10^{-19}} \text{ eV} = 7.63 \times 10^{3} \text{ eV} \end{aligned}$$

Note Energy with which the electron was bound to the nucleus = work function for the metal.

23. Frequency, $\nu = \dfrac{1}{\text{period}} = \dfrac{1}{2ns}$

$$= \frac{1}{2 \times 10^{-9}\text{s}} = 0.5 \times 10^{-9}\text{s}^{-1}$$

Energy of the source = energy of 1 photon × number of photons produced

$$\begin{aligned} E_{\text{source}} &= h\nu \times N \\ &= 6.626 \times 10^{-34} \text{ Js} \times 0.5 \times 10^{9} \text{ s}^{-1} \times 2.5 \times 10^{15} \\ &= 8.28 \times 10^{-10} \text{ J} \end{aligned}$$

24. $E = h\nu = (6.626 \times 10^{-34} \text{ Js})\,(5 \times 10^{14} \text{ s}^{-1})$

$= (3.313 \times 10^{-19})$

Energy of one mole of photons

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

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

25. Power of the bulb = 100 watt = 100 Js^{-1}

Energy of one photon,

$$\begin{aligned} E = h\nu &= \frac{hc}{\lambda} \\ &= \frac{6.626 \times 10^{-34} \text{ Js} \times 3 \times 10^{8} \text{ ms}^{-1}}{400 \times 10^{-19} \text{ m}} \\ &= 4.969 \times 10^{-19} \text{ J} \end{aligned}$$

Number of photon emitted

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

26. Energy emitted by sodium lamp in 1s.

= Watt × second = 60 × 1 J

Energy of photon emitted $= \dfrac{hc}{\lambda}$

$$\begin{aligned} &= \frac{6.626 \times 10^{-34} \times 3 \times 10^{8}}{5893 \times 10^{-10}} \\ &= 3.37 \times 10^{-19} \text{ J} \end{aligned}$$

$\therefore$ Number of photons emitted per second $= \dfrac{60}{3.37 \times 10^{-19}}$

$$= 17.8 \times 10^{19}$$

$\therefore$ Number of photons emitted in 10 hours

$$= 17.8 \times 10^{19} \times 10 \times 60 \times 60 = 6.41 \times 10^{24}$$

27. For photoelectric effect,

(i) KE $= E - E_0$

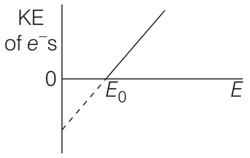
where, KE = kinetic energy of ejected electrons.

E = energy of incident light = $h\nu$

E_0 = threshold energy = $h\nu_0$

ν = frequency of incident light

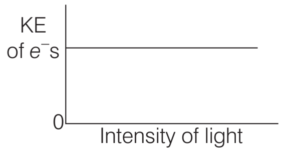
ν_0 = threshold frequency



Slope = ± 1, intercept = $- E_0$

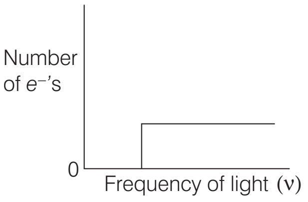
So, option (a) is correct.

(ii) KE of ejected electrons does not depend on the intensity of incident light.



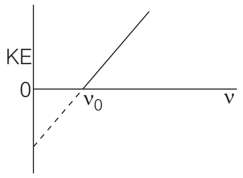
So, option (b) is correct.

(iii) When, number of ejected electrons is plotted with frequency of light, we get



So, option (c) is also correct.

(iv) KE $= h\nu - h\nu_0$



Slope = + h, intercept = $- h\nu_0$

So, option (d) is not correct.

28. Wavelength of light (λ) = 5000 Å = 5×10^{-7} m

Work function ($h\nu_0$) = 1.9 eV

$$= 1.9 \times 1.6 \times 10^{-19} \text{ J}$$
$$= 3.4 \times 10^{-19} \text{ J}$$

- Energy of photons

$$E = h\nu = \frac{hc}{\lambda}$$
$$= \frac{(6.626 \times 10^{-34} \text{ Js}) \times (3 \times 10^{8} \text{ ms}^{-1})}{5 \times 10^{-7} \text{ m}}$$
$$= 3.97 \times 10^{-19} \text{ J}$$
$$= \frac{3.97 \times 10^{-19} \text{ J}}{1.6 \times 10^{-19} \text{ J}}$$
$$= 2.48 \text{ eV} \qquad (\because 1.6 \times 10^{-19} \text{ J} = 1 \text{ eV})$$

- Kinetic energy of photoelectrons

$$\text{KE} = \frac{1}{2} mv^2$$
$$= h\nu - h\nu_0$$
$$= (3.97 \times 10^{-19} \text{ J}) - (3.4 \times 10^{-19} \text{ J})$$
$$= 5.7 \times 10^{-20} \text{ J}$$

29. Wavelength of radiation = 300 nm = 300×10^{-9} m

Energy of radiation, (E)

$$E = h\nu = \frac{hc}{\lambda}$$
$$= \frac{6.626 \times 10^{-34} \text{ Js} \times 3 \times 10^{8} \text{ ms}^{-1}}{300 \times 10^{-9} \text{ m}}$$
$$= 6.626 \times 10^{-19} \text{ J}$$

Energy of one mole of photons

$= N_A \times E$ (where N_A = Avogadro number)

$$= 6.022 \times 10^{23} \times 6.626 \times 10^{-19} \text{ J mol}^{-1}$$
$$= 3.99 \times 10^{5} \text{ J mol}^{-1}$$

The minimum energy needed to remove one mole of electrons from sodium $= (3.99 - 1.68) \times 10^{5}$ J mol^{-1} $= 2.31 \times 10^{5}$ J mol^{-1}

The minimum energy for one electron

$$= \frac{2.31 \times 10^{5} \text{ J mol}^{-1}}{6.022 \times 10^{23} \text{ electrons}}$$
$$= 3.84 \times 10^{-19} \text{ J mol}^{-1}$$

30. $E_{\text{total}} = \dfrac{hc}{\lambda} = \dfrac{6.626 \times 10^{-34} \text{ Js} \times 3 \times 10^{8} \text{ ms}^{-1}}{300 \times 10^{-9} \text{ m}}$

$$= 6.626 \times 10^{-19} \text{ J}$$
$$E_1 = \frac{6.626 \times 10^{-34} \text{ Js} \times 3 \times 10^{8} \text{ ms}^{-1}}{400 \times 10^{-9} \text{ m}}$$
$$E_2 = (E_{\text{total}} - E_1)$$
$$= 6.626 \times 10^{-19} \times \left(1 - \frac{3}{4}\right) = \frac{1}{4} \times 6.626 \times 10^{-19} \text{ J}$$
$$= 1.656 \times 10^{-19} \text{ J}$$

31. Using Einstein's photoelectron equation,

$$\text{KE} = h\nu - h\nu_0 = h(\nu - \nu_0)$$
$$\text{KE}_1 = h(\nu_1 - \nu_0) \qquad \text{...(i)}$$
$$\text{KE}_2 = h(\nu_2 - \nu_0) \qquad \text{...(ii)}$$

Dividing equation (ii) by (i), we get

$$\frac{\text{KE}_2}{\text{KE}_1}=\frac{h(\nu_2-\nu_0)}{h(\nu_1-\nu_0)}=\frac{(\nu_2-\nu_0)}{(\nu_1-\nu_0)}$$

But given that

$$\frac{\text{KE}_2}{\text{KE}_1}=3$$

$$\therefore\quad 3=\frac{\nu_2-\nu_0}{\nu_1-\nu_0}\Rightarrow 3(\nu_1-\nu_0)=\nu_2-\nu_0$$

$$\Rightarrow\ 3\nu_1-\nu_2=3\nu_0-\nu_0=2\nu_0$$

$$\Rightarrow 3\times 2.0\times 10^{16}-4\times 10^{16}=2v_0$$

$$\Rightarrow \nu_0=\frac{2\times 10^{16}}{2}=1\times 10^{16}\ \text{s}^{-1}$$

32. We now, energy of light absorbed in one photon

$$=\frac{hc}{\lambda_{\text{absorbed}}}$$

Let n_1 photons be absorbed.

Total energy absorbed $=\dfrac{n_1 hc}{\lambda_{\text{absorbed}}}$

Now, energy of light re-emitted out in one photon

$$=\frac{hc}{\lambda_{\text{emitted}}}$$

Let, n_2 photons are re-emitted the total energy re-emitted out $=n_2\times\dfrac{hc}{\lambda_{\text{emitted}}}$

$$\frac{h}{\lambda_{\text{absorbed}}}\times n_1\times\frac{47}{100}=n_2\times\frac{hc}{\lambda_{\text{emitted}}}$$

$$\frac{n_2}{n_1}=\frac{47}{100}\times\frac{\lambda_{\text{emitted}}}{\lambda_{\text{absorbed}}}$$

$$\frac{n_2}{n_1}=\frac{47}{100}\times\frac{5080}{4530}=0.527$$

33. Frequency, $\nu=\dfrac{c}{\lambda}$ $\qquad$ [1 nm $=10^{-9}$ m]

$\lambda=580\text{ nm}=580\times 10^{-9}\text{ m}=580\times 10^{-7}\text{ cm}$

$$\nu=\frac{3.0\times 10^{8}\ \text{ms}^{-1}}{580\times 10^{-9}\ \text{m}}=5.17\times 10^{14}\ \text{s}^{-1}$$

($\therefore$ Velocity of light $=3\times 10^{8}\ \text{ms}^{-1}$)

Wave number, $\bar{\nu}=\dfrac{1}{\lambda}=\dfrac{1}{580\times 10^{-7}\text{ cm}}$

$$=1.724\times 10^{4}\ \text{cm}^{-1}$$

34. Energy of one photon,

$$E=\frac{hc}{\lambda}=\frac{6.626\times 10^{-34}\text{Js}\times 3.0\times 10^{8}\ \text{ms}^{-1}}{4000\times 10^{-12}\ \text{m}}$$

(1 pm $=10^{-12}$ m)

$$=4.9695\times 10^{-17}\text{J}$$

Number of photons,

$$N=\frac{1\text{ J}}{4.9695\times 10^{-17}\text{J}}=2.0122\times 10^{16}\text{ photons}$$

35. The order of the given frequency is as follows : Radiation from FM radio < microwaves<amber colour < X-rays < cosmic rays.

36. The threshold frequency (ν_0) is the lowest frequency that photons may possess to produce the photoelectric effect. The energy corresponding to this frequency is the minimum energy (E).

$$E=h\nu_0$$

$$=(6.626\times 10^{-27}\text{erg-s})\ (1.3\times 10^{15}\text{s}^{-1})$$

$$=8.6\times 10^{-12}\text{ erg}$$

37. Wavelength is in UV region, thus n_1 will be 1.

$$\frac{1}{121.6\times 10^{-9}}=1.097\times 10^{7}\times 1^{2}\times\left(\frac{1}{1^{2}}-\frac{1}{n_2^{2}}\right)$$

On solving, $\quad n_2\approx 2$

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

$$\frac{1}{2}\times 1.67\times 10^{-27}\times v^{2}=\frac{6.626\times 10^{-34}\times 3\times 10^{8}}{121.6\times 10^{-9}}$$

$$v=4.43\times 10^{4}\ \text{ms}^{-1}$$

39. $r_{\text{H}}=0.529$ Å

$$r_n=r_{\text{H}}\times\frac{n^{2}}{Z}$$

For Li^{2+} ($n=2$),

$$r_{\text{Li}^{2+}}=r_{\text{H}}\times\frac{(2)^{2}}{3}=\frac{r_{\text{H}}\times 4}{9}$$

For Li^{2+} ($n=3$),

$$r_{\text{Li}^{2+}}=r_{\text{H}}\times\frac{(3)^{3}}{3}=3r_{\text{H}}$$

For Be^{3+} ($n=2$)

$$r_{\text{Be}^{3+}}=r_{\text{H}}\times\frac{(2)^{2}}{4}=r_{\text{H}}$$

For He^{+} ($n=2$)]

$$r_{\text{He}^{+}}=r_{\text{H}}\times\frac{(2)^{2}}{2}=2r_{\text{H}}$$

Thus, Be^{3+} ($n=2$) has same radius as that of the first Bohr's orbit of H-atom.

40. Angular momentum, $mvr=\dfrac{nh}{2\pi}=\dfrac{3\times h}{2\pi}=\dfrac{1.5h}{\pi}$

$$=3\hbar\qquad\left[\because\ \hbar=\frac{h}{2\pi}\right]$$

41. Energy in nth orbit, $E_n=\dfrac{-2.18\times 10^{-18}}{n^{2}}$ J

Energy in fifth orbit,

$$E_5=\frac{-2.18\times 10^{-18}}{5^{2}}\text{J}=-0.0872\times 10^{-18}\text{J}$$

42. Given, wavelength, $\lambda=242\text{ nm}=242\times 10^{-9}$ m

Energy, $E=h\nu=\dfrac{hc}{\lambda}=\dfrac{6.626\times 10^{-34}\text{Js}\times 3.0\times 10^{8}\ \text{ms}^{-1}}{242\times 10^{-9}\ \text{m}}$

$$E=0.0821\times 10^{-17}\text{ J/atom}$$

This energy is sufficient for ionisation of one Na atom, so it is the ionisation energy of Na.

$$E = 6.02\times 10^{23} \times 0.0821\times 10^{-17} \text{ J/mol}$$

$$E = 4.945\times 10^{5} \text{ J/mol} = 4.945\times 10^{2} \text{ kJ/mol}$$

43. P.E $= -\dfrac{1}{4\pi\varepsilon_0}\dfrac{Ze^2}{r}$

For Li^{2+}, $Z = 3$ so $E = -\dfrac{3e^2}{4\pi\varepsilon_0 r}$

44. $v = \dfrac{2.18\times 10^{8}\times Z}{n}$ cm s^{-1}

For H atom, $Z = 1$ and third orbit, $n = 3$,

$$v_3 = \frac{2.18\times 10^{8}\times 1}{3} = 7.26\times 10^{7}\text{cm s}^{-1}$$

45. According to Bohr model, radius of orbit

$r_n = \dfrac{a_0\times n^2}{Z}$, where a_0 = Bohr radius

(Radius of 1st orbit of H-atom)

For, Li^{2+}, $Z = 3$ and $n = 2$

$$\therefore \qquad r = \frac{2^2\times a_0}{3} = \frac{4a_0}{3}$$

46. We know that, $r = 0.529\,\dfrac{n^2}{Z}$ Å

For Li^{2+} $\quad (r_{\text{Li}^{2+}})_{n=4} - (r_{\text{Li}^{2+}})_{n=3}$

$$\Rightarrow \qquad \frac{0.529}{3}(16-9) = \Delta R_1 \qquad \text{...(i)}$$

For He^{+} $\quad (r_{\text{He}^{+}})_{n=4} - (r_{\text{He}^{+}})_{n=3}$

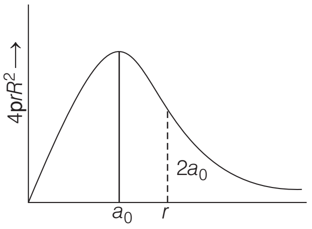
$$\Rightarrow \qquad \frac{0.529}{2}(16-9) = \Delta R_2 \qquad \text{...(ii)}$$

$$\frac{\Delta R_1}{\Delta R_2} = \frac{\frac{0.529}{3}(16-9)}{\frac{0.529}{2}(16-9)} = \frac{2}{3}$$

Hence, the ratio of $\Delta R_1 : \Delta R_2$ is 2 : 3.

47. Statement (d) is incorrect.

(a) The radial distribution curves obtained by plotting radial probability functions *vs* r for 1*s*-orbital is



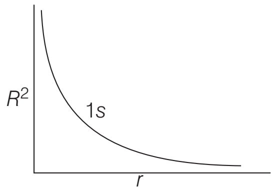
The graph initially increases and then decreases. It reaches a maximum at a distance (a_0) very close to the nucleus and then decreases. The maximum in the curve corresponds to the distance at which the probability of finding the electron in maximum (i.e. a_0). But the electron can be found at a distance at $2a_0$ also from the nucleus.

(b) The P.E value = –27.2 eV

K.E value = 13.6 eV

So, the magnitude of PE is double that of its kinetic energy on an average.

(c) For 1*s*-orbital radial probability density (R^2) against r is given as



For 1*s*-orbital, probability density decreases sharply as we move away from nucleus. Thus, the probability density of finding the electron is maximum at the nucleus.

(d) Correct statement (d) is : The total energy of the electron is minimum when it is at a distance a_0 from the nucleus.

Because at a_0 electron is at stable position and we know that if a electron acquired stability then its energy is minimum.

48. Given, frequency $\nu = \dfrac{c}{\lambda} = 3.29\times 10^{15}\text{ Hz}\left(\dfrac{1}{3^2} - \dfrac{1}{n^2}\right)$

$\lambda = 1285 \text{ nm} = 1285\times 10^{-9}\text{ m}$

$$\nu = \frac{3.0\times 10^{8}\text{ms}^{-1}}{1285\times 10^{-9}\text{ m}} = 3.29\times 10^{15}\text{ Hz}\left(\frac{1}{9} - \frac{1}{n^2}\right)$$

$$\frac{3.0\times 10^{8}\text{ms}^{-1}}{1285\times 10^{-9}\text{ m}\times 3.29\times 10^{15}\text{ Hz}} = \left(\frac{1}{9} - \frac{1}{n^2}\right)$$

$$0.0709 = 0.1111 - \frac{1}{n^2}$$

$$\frac{1}{n^2} = 0.1111 - 0.0709 = 0.0402 \approx 0.04 = \frac{1}{25}$$

$$n^2 = 25 \text{ or } n = 5$$

$\therefore$ The electron jumps from $n = 5$ to $n = 3$, i.e. the transition occurs in Paschen series and lies in infrared region.

49. Atoms corresponds to different transitions from higher energy levels to lower energy levels.

51. Radius of nth orbit of H like species,

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

$$r_1 = 1.3225 \text{ nm} = 1322.5 \text{ pm} = \frac{52.9\, n_1^2}{Z}$$

$$r_2 = 211.6 \text{ pm} = \frac{52.9\, n_2^2}{Z}$$

$$\frac{r_1}{r_2} = \frac{1322.5}{211.6} = \frac{n_1^2}{n_2^2}$$

$$\frac{n_1^2}{n_2^2} = 6.25 \text{ or } \frac{n_1}{n_2} = 2.5$$

If $n_1 = 5$, $n = 2$, so, the transition (emission transition) is from 5th orbit to 2nd orbit and it belongs to Balmer series.

$$\bar{\nu} = \frac{1}{\lambda} = 1.09677 \times 10^7 \left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right] \text{m}^{-1}$$

$$\frac{1}{\lambda} = 1.09677 \times 10^7 \left[\frac{1}{2^2} - \frac{1}{5^2}\right] \text{m}^{-1}$$

$$\frac{1}{\lambda} = 1.09677 \times 10^7 \times \frac{21}{100} = 2.303 \times 10^6 \text{ m}^{-1}$$

$$\lambda = 0.434 \times 10^{-6} \text{m} = 434 \times 10^{-9} \text{m} = 434 \text{ nm}$$

It belongs to visible region.

Note In the above Rydberg formula if $n_1 = 1, 2 \ldots$ then $n_2 = n_1 + 1, n_1 + 2 \ldots$ For Balmer series, spectral region is visible.

52. Among the given option, transiton in option (a) require largest amount of energy.

The amount of energy required $\propto \left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$

On putting the value of n_1 and n_2, the calculated energy is maximum for electron transition from $n = 1$ to $n = 2$

$$\Rightarrow \quad \left[\frac{1}{1^2} - \frac{1}{2^2}\right] = 0.75$$

53. According to Rydberg's formula,

$$\text{wave number } (\bar{\nu}) = R_H Z^2 \left[\frac{1}{n_i^2} - \frac{1}{n_f^2}\right]$$

Given, $\quad n_i = n, \; n_f = 8$

[$\because$ it is the case of emission]

$$\bar{\nu} = R_H \times (1)^2 \left[\frac{1}{n^2} - \frac{1}{8^2}\right]$$

$$\bar{\nu} = R_H \left[\frac{1}{n^2} - \frac{1}{64}\right] = \frac{R_H}{n^2} - \frac{R_H}{64}$$

On comparing with equation of straight line, $y = mx + c$, we get

Slope $= R_H$, intercept $= \frac{-R_H}{64}$.

Thus, plot of wave number $(\bar{\nu})$ against $\frac{1}{n^2}$ will be linear with slope $(+R_H)$.

54. $$\Delta E = h\nu = \frac{2\pi^2 m Z^2 e^4 k^2}{h^2} \left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$$

If electron falls from n_2 level to n_1 level.

$\therefore$ In He$^+$ for the $n_2 = 4$ to $n_1 = 2$ transition

$$v(\text{He}^+) = \text{constant } (4) \left[\frac{1}{2^2} - \frac{1}{4^2}\right] \qquad [\because Z_{\text{He}^+} = 2]$$

$$= \text{constant} \times 4 \left[\frac{3}{16}\right] = \frac{3}{4} \text{ constant}$$

$$v(\text{H}) = \text{constant } (1)^2 \left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$$

$$= \text{constant} \times \left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$$

(a) For $n_2 = 3$ and $n_1 = 1$

$$v(\text{H}) = \text{constant} \left[\frac{1}{1} - \frac{1}{9}\right]$$

$$= \frac{8}{9} \text{ constant}$$

$$\neq \frac{3}{4} \times \text{constant}$$

(b) For $n_2 = 2$ and $n_1 = 1$

$$v(\text{H}) = \text{constant} \times \left[\frac{1}{1} - \frac{1}{4}\right]$$

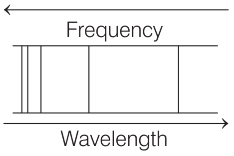
$$= \frac{3}{4} \times \text{constant} = v(\text{He}^+)$$

55. Balmer series lies in the visible region of the electromagnetic spectrum. Photons that correspond to these energies will not strongly absorb highly excited hydrogen gas. So, there is the possibility for detecting absorption at Balmer line wavelength.

Paschen, Brackett and Pfund series lies in the infrared region whereas, only Layman series lies in the ultraviolet region of the electromagnetic spectrum.

56. Statements I, II and III are correct. The explanations of these statements are as follows

I. In each series of hydrogen spectrum, lines converge at the higher frequency or lower wavelength limit.



$\therefore$ This is correct.

II. For Balmer series, $n_1 = 2$

$\therefore$ This is correct.

III. Longest wavelength represents the smallest wave number

$$\bar{\nu} = R_H \left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right). \; (n_2 > n_1)$$

When $n_1 = 2$, smallest value of $\bar{\nu}$ is for $n_2 = 3$

$\therefore$ This is a correct statement.

IV. This statement is not correct. It's corrected form is as follows: Ionisation energy of hydrogen can be calculated from Lyman series lines ($n = 1$) only by using the following formula,

$$\bar{\nu} = R_H \left[\frac{1}{(1)^2} - \frac{1}{\infty^2}\right]$$

57. As we know that, $\Delta E = \frac{hc}{\lambda}$

Hence, λ will be, $\lambda = \frac{hc}{\Delta E}$

For, λ = minimum, i.e. shortest, ΔE = maximum

For Lyman series, $n = 1$ and for $\Delta E_{\max}$ transition must be form $n_2 = \infty$ to $n_1 = 1$.

$$\text{So,} \quad \frac{1}{\lambda} = R_H Z^2 \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \qquad (\because n_1 = 1 \text{ and } n_2 = \infty)$$

$$\frac{1}{\lambda} = R_H \left(\frac{1}{1^2} - \frac{1}{\infty^2} \right) \times (1)^2$$

$$\frac{1}{\lambda} = R_H \, (1 - 0)$$

$$\Rightarrow \quad \frac{1}{\lambda} = R_H \times (1)^2 \Rightarrow \lambda_1 = \frac{1}{R_H} \qquad \text{...(i)}$$

For longest wavelength, ΔE = minimum for Balmer series, $n_2 = 3$ to $n_1 = 2$ will have ΔE minimum.

For He^+, $Z = 2$

$$\text{So,} \quad \frac{1}{\lambda_2} = R_H \times 2^2 \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

$$\frac{1}{\lambda_2} = R_H \times 4 \left(\frac{1}{4} - \frac{1}{9} \right), \frac{1}{\lambda_2} = R_H \times 4 \times \frac{5}{36}$$

$$\frac{1}{\lambda_2} = R_H \times \frac{5}{9}$$

$$\Rightarrow \quad \lambda_2 = \lambda_1 \times \frac{9}{5} \qquad \text{[From eq. (i)]}$$

59. Given that, $m = 10 \text{ g} = 10 \times 10^{-3}$ kg

$$\text{Uncertainty in speed } (\Delta \nu) = 4\% \text{ of } 90 \text{ ms}^{-1} = \frac{4 \times 90}{100} = 3.6 \text{ ms}^{-1}$$

From Heisenberg uncertainty principle,

$$\Delta x \cdot \Delta \nu = \frac{h}{4\pi m} \text{ or } \Delta x = \frac{h}{4\pi m \Delta \nu}$$

Uncertainty in position,

$$\Delta x = \frac{6.626 \times 10^{-34} \text{ kg m}^2 \text{s}^{-1}}{4 \times 3.14 \times 10 \times 10^{-3} \text{ kg} \times 3.6 \text{ ms}^{-1}}$$

$$= 1.46 \times 10^{-33} \text{ m}$$

60. Wavelength, $\lambda = \frac{h}{mv} \Rightarrow \nu = \frac{h}{\lambda m}$

Mass of neutron, $m = 1.675 \times 10^{-27}$ kg

$$\lambda = 800 \text{ pm} = 800 \times 10^{-12} \text{ m}$$

$$\nu = \frac{6.626 \times 10^{-34} \text{ kg m}^2 \text{ s}^{-1}}{1.675 \times 10^{-27} \text{ kg} \times \lambda}$$

$$\nu = \frac{6.626 \times 10^{-34} \text{ kg m}^2 \text{ s}^{-1}}{1.675 \times 10^{-27} \text{ kg} \times 800 \times 10^{-12} \text{ m}}$$

$$= 0.494 \times 10^3 \text{ ms}^{-1} = 4.94 \times 10^2 \text{ ms}^{-1}$$

61. Number of waves $= \frac{\text{Circumference}}{\text{Wavelength}}$

$$n = \frac{2\pi r}{\lambda} \Rightarrow 2\pi r = n\lambda \qquad \text{...(i)}$$

Also, we know that radius (r) of an atom is given by

$$r = \frac{a_0 n^2}{Z}$$

$$\text{Thus, Eq. (i) becomes } 2\pi a_0 \frac{n^2}{Z} = n\lambda \qquad \text{...(ii)}$$

$$\therefore \quad 2\pi a_0 \frac{n^2}{Z} = n \, (1.5 \, \pi a_0) \qquad [\text{Given, } \lambda = 1 .5 \, \pi a_0]$$

$$\frac{n}{Z} = \frac{1.5\pi a_0}{2\pi a_0} = \frac{1.5}{2} = 0.75$$

62. Given, $m = 100 \text{ g} = 0.1$ kg

$$v = 100 \text{km/h} = \frac{100 \times 1000}{60 \times 60} = \frac{1000}{36} \text{ ms}^{-1}$$

From de-Broglie equation, wavelength, $\lambda = \frac{h}{mv}$

$$\lambda = \frac{6.626 \times 10^{-34} \text{ kg m}^2 \text{ s}^{-1}}{0.1 \text{ kg} \times \frac{1000}{36} \text{ ms}^{-1}} = 238.5 \times 10^{-36} \text{ m}$$

(As the wavelength is very small so wave nature cannot be detected)

63. From de-Broglie equation, wavelength, $\lambda = \frac{h}{mv}$

For the same wavelength of different particles, i.e. electron, proton, neutron and α-particle, $m_1 v_1 = m_2 v_2$ as (h is constant). Lesser the mass of the particle, greater will be the velocity. Hence, electron will have higher velocity.

64. de-Broglie wavelength,

$$\lambda = \frac{h}{mv}$$

$$\text{or} \quad \lambda \propto \frac{1}{m} \qquad \text{If } v = \text{constant (same)}$$

Among the given molecules, oxygen has the highest mass (m). Thus, it has smallest de-Broglie wavelength.

65. We know that kinetic energy $= eV$

$$\text{or} \quad = \frac{1}{2} mv^2$$

$$\text{So,} \quad \frac{1}{2} mv^2 = eV$$

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

$$\therefore \quad v = \sqrt{\frac{2eV}{m}}$$

66. **Plan** As you can see in options, energy term is mentioned hence, we have to find out relation between $\frac{h}{\lambda}$ and energy. For this, we shall use de-Broglie wavelength and kinetic energy term in eV.

de-Broglie wavelength for an electron $(\lambda) = \frac{h}{p}$

$$\Rightarrow \quad p = \frac{h}{\lambda} \qquad \text{...(i)}$$

Kinetic energy of an electron = eV

As we know that, $\text{KE} = \dfrac{p^2}{2m}$

$$\therefore \qquad \text{eV} = \frac{p^2}{2m} \text{ or } p = \sqrt{2meV} \qquad \ldots\text{(ii)}$$

From equations (i) and (ii), we get $\dfrac{h}{\lambda} = \sqrt{2meV}$

67. $\lambda = \dfrac{h}{mv} = \dfrac{6.6 \times 10^{-34} \text{ kg m}^2 \text{ s}^{-1}}{6.6 \times 10^{-27} \text{ kg} \times 10^3 \text{ ms}^{-1}} = 1 \times 10^{-10} \text{ m}$

68. The de-Broglie wavelength associated with the charged particles as

For electron, $\lambda = \dfrac{12.27}{\sqrt{V}} \text{Å}$

For proton, $\lambda = \dfrac{0.286}{\sqrt{V}} \text{Å}$

For α-particles, $\lambda = \dfrac{0.101}{\sqrt{V}} \text{Å}$

69. $\Delta x \cdot \Delta P = \dfrac{h}{4\pi}$

$$\Delta x \cdot \Delta P = \frac{6.63 \times 10^{-34}}{4 \times 3.14 \times 10^{-5}}$$

$$\Delta x = \frac{5.27 \times 10^{-35}}{1 \times 10^{-5}}$$

$[\because \Delta P = 1 \times 10^5 \text{ kg m/s given}]$

$$= 5.27 \times 10^{-30} \text{m}$$

70. $\lambda = \dfrac{h}{\sqrt{2Em}}$

When kinetic energy of electron becomes four times, the de-Broglie wavelength will become half.

72. The arrangement of orbitals is based upon $(n+l)$ rule. According to which,lower the value of $(n+l)$, lower is the energy.

For the orbitals having similar value of $(n+l)$ lower the value of n, lower is the energy. Thus, the correct order of arrangement are

(a) $1s < 2s < 2p < 3s$

(b) $3s < 3p < 4s < 4d$

(c) $4d < 5p < 6s < 4f < 5d$

(d) $7s < 5f < 6d < 7p$

73. For g-subshell $l = 4$ and to have $l = 4$ minimum value of $n = 5$ [because the value of $l = 0$ to $(n-1)$]

74. The electronic configuration of the given atoms are as

$$\text{He} \longrightarrow 1s^2$$
$$\text{B} \longrightarrow 1s^2, 2s^2, 2p^1$$
$$\text{Be} \longrightarrow 1s^2, 2s^2$$
$$\text{Li} \longrightarrow 1s^2, 2s^1$$

Among these atoms, only B has p-subshell which is a non-spherical shell.

75. (I) is not possible as $n \neq 0$

(II) is possible ($1s$)

(III) is not possible because if $n = 1$, $l = 0$ only. Thus, $l \neq 1$

(IV) is possible ($2p$)

(V) is not possible because if $n = 3$, $l = 0, 1$ and 2. Thus, $(l \neq 3)$

(VI) is possible ($3p$)

76 Total number of orbitals associated with nth shell $= n^2$

$\therefore$ Total number of orbitals associated with 3rd shell $= (3)^2 = 9$

77. Number of angular nodes $= l$

For 4th orbital, $(n = 4)$ and $l = 2$ for d-orbital

$\therefore$ Number of angular nodes $= 2$

78. $l = 0$ means element is in 's' orbital

Angular nodes $= n - l - 1 = 2$

Radial nodes $= n - 1 = 2$

$$n = 3$$

81. For a particular value of azimuthal quantum number, given the total number of magnetic quantum number,

$m = 2l + 1$ or $2l = m - 1$

$$l = \frac{m-1}{2}$$

82. For $4d$ electron,

$n = 4, l = 2, m = -2, -1, 0, +1, +2$

$$s = +\frac{1}{2} \text{ or } -\frac{1}{2}$$

83. $+\dfrac{1}{2}$ and $-\dfrac{1}{2}$ spinning produces angular momentum equal to Z-component of angular momentum which is given as $m_s(h/2\pi)$.

84. Higher values of ψ^2 means greater probability for finding electron and a zero value of ψ^2 means the probability for finding the electron is zero (at nucleus).

85. The four lobes of $d_{x^2-y^2}$ orbital are lying along x and y axes, while the two lobes of d_{z^2} orbital are lying along z-axis, and contain a ring of negative charge surrounding the nucleus in xy plane.

$2s$ orbital has only one spherical node, where electron density is zero.

p-orbital have directional character.

Orbital $\longrightarrow$	p_z	p_x	p_y
$m \longrightarrow$	0	± 1	± 1
Nodal plane $\longrightarrow$	xy	yz	zx

86. Quantum nature of atoms are associated with following phenomena or processes

(i) Absorption spectrum

(ii) Emission spectrum

(iii) Black body radiation

(iv) Photo-electricity

Internal energy (U) of particles like atoms depends upon the thermodynamic variables (p, V, T) of the system. Thus, $U = f(p, T)$

or $\quad U = f_1(T, V)$

or $\quad U = f_2(p, V)$

So, quantum nature of atom is not associated with its internal energy.

Graph (c) is not a direct manifestation of the quantum nature of atoms.

87. Principal quantum number (n) signifies the shell or orbit number.

From the number of values of azimuthal quantum number (l), we can calculate number of subshells present in a shell as, $l = 0 \ldots. (n-1)$

So, when $n = 4$

The permissible values of l and subshells are

$$\begin{aligned} l &= 0 \rightarrow s\text{-subshell} \\ &= 1 \rightarrow p\text{-subshell} \\ &= 2 \rightarrow d\text{-subshell} \\ &= 3 \rightarrow f\text{-subshell} \end{aligned}$$

But, here values of l are restricted by the value of magnetic quantum number, $m = -2$, where, m depends on l as

$$m = -l \ldots. 0 \ldots. + l$$

So, $m = -2$ value is possible for two subshells, *viz.*, $l = 3$ (f-subshell) and $l = 2$ (d-subshell) only.

$l = 3 \Rightarrow m = -3, -2 -1, 0, +1, +2, +3$

$l = 2 \Rightarrow m = -2, -1, 0, +1, +2$

88. Hypothetical situation,

Azimuthal quantum number (l) = 0 − (n + 1)

n = Principal quantum number

For, $n = 1$ $\qquad l = 0, \quad 1, \quad 2$

$$\begin{array}{ccc} \downarrow & \downarrow & \downarrow \\ 1s & 1p & 1d \\ 1s^2 & 1p^6 & 1d^{10} \end{array}$$

Number of electrons in s-orbital = 2

Number of electrons in p-orbital = 6

Number of electrons in d-orbital = 10

$Z = 13$ (Half-filled valence sub-shell)

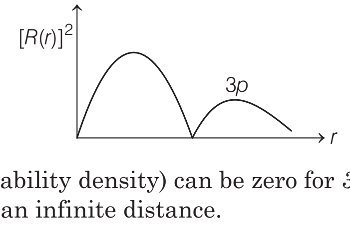
For $n = 1$, $1s^2 1p^6 1d^5$ ($Z = 13$)

Number of electrons in $1d$-orbital are 5. (It is half-filled).

Element with atomic number 9 is not first alkali metal but a halogen $1s^2 2s^2 2p^5$.

First noble gas has atomic number 2 not 8.

89.



ϕ^2 (Probability density) can be zero for $3p$-orbital other than infinite distance.

Since, $n = 3$, $l = 1$ for $3p$-orbital, the number of radial nodes = 3 − 1 − 1 = 1

90. I. Angular momentum, $mvr = \dfrac{nh}{2\pi}$

$\Rightarrow mvr \propto n \propto$ distance from the nucleus

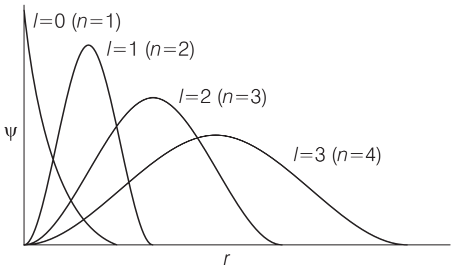
II. This statement is incorrect as size of an orbit $\propto$ Azimuthal quantum number (l) $\quad (\because n = \text{constant})$

III. This statement is incorrect as at ground state, $n = 1$, $l = 0$

$\Rightarrow$ Orbital angular momentum (wave mechanics)

$$= \sqrt{l(l+1)}\,\frac{h}{2\pi} = 0 \qquad [\because l = 0]$$

IV. The given plot is



91. Given, Atomic number of Rb, $Z = 37$

Thus, its electronic configuration is [Kr] $5s^1$.

Since the last electron or valence electron enter in $5s$ subshell.

So, the quantum numbers are

$$\begin{aligned} n &= 5, \\ l &= 0 \text{ (from } s\text{-orbital)} \\ m &= 0 \; (\therefore m = +l \text{ to } -l), \\ s &= +\frac{1}{2} \text{ or } -\frac{1}{2} \end{aligned}$$

92. (a) Z_{eff} of $2s > Z_{\text{eff}}$ of $2p$

(b) energy of $2s$-orbital < energy of $2p$-orbital

(c) Z_{eff} of $1s \neq Z_{\text{eff}}$ of $2s$

(d) For the two electrons of $2s$ orbital,

the value of m_s is $+\dfrac{1}{2}$ and $-\dfrac{1}{2}$.

93. $\text{Cr}_{24} = [\text{Ar}]\,3d^5, 4s^1$

$\text{Cr}^{3+} = [\text{Ar}]\,3d^3$

$\text{Fe}_{26} = [\text{Ar}]\,3d^6, 4s^2$

$\text{Fe}^{3+} = [\text{Ar}]\,3d^5$

$\text{Mn}_{25} = [\text{Ar}]\,3d^5, 4s^2$

$\text{Mn}^{2+} = [\text{Ar}]\,3d^5$

$\text{Co}_{27} = [\text{Ar}]\,3d^7, 4s^2$

$\text{Co}^{3+} = [\text{Ar}]\,3d^6$

$\text{Sc}_{21} = [\text{Ar}]\,3d^1, 4s^2$

$\text{Sc}^{3+} = [\text{Ar}]$

Thus, Fe^{3+} and Mn^{2+} have the same electronic configuration.

94. Option (b) is incorrect.
Correct configuration should be $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^1$ for the copper which has atomic number 29($_{29}$Cu). Due to extra stability of full filled orbital of *d*-subshell, the last electron enter into *d*-orbital instead of *s*-orbital.

96. The energy of electrons in the same orbital is the same. For $3d$ orbitals, $3d_{xy}, 3d_{yz}, 3d_{zx}, 3d_{z^2}, 3d_{x^2-y^2}$, are at the same level of energy, irrespective of their orientation. The electronic configuration $3d_{xy}^2, 3d_{yz}^2, 3d_{zx}^2, 3d_{x^2-y^2}^2, 3d_{z^2}^2, 4s^1$ has maximum exchange energy.

97. A subshell having nearly half-filled or nearly completely filled configurations tends to acquire exactly half-filled or exactly completely filled nature to have lower energy level in order to attain extra stability.

Round II

1. $\lambda = \dfrac{c}{v} = \dfrac{3.0 \times 10^8 \text{ms}^{-1}}{4.620 \times 10^{14} \text{ Hz}} = 0.6494 \times 10^{-6} \text{ m} = 649.4 \text{ nm};$

Thus, it belongs to visible region.

2. $m = -1$ is not possible for *s*-orbital ($l = 0$).

3. (a) Total electrons if $n = 4 = 2n^2$

$$= 2 \times 4^2 = 32$$

Half of the total electrons, i.e. 16 electrons have $m_s = -\dfrac{1}{2}$

(b) $n = 3, l = 0$ it is $3s$-orbital and it can have two electrons.

4. The uncertainty in the position of electron would be less than λ.

5. $_{29}\text{Cu} = 1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^1, 3d^{10}$

$\text{Cu}^+ = 1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^{10}, 4s^0$

Total number of shells occupied = 3

Number of sub-shells occupied = 6

Number of orbitals filled = 14

Number of unpaired electrons = 0

6. O^{2-} and N^{3-} both species have same number of electrons (10 electrons).

7. Heavy atoms such as gold, platinum have heavy nucleus. These heavy nucleus contains large amount of positive charge. When a beam of α-particles is shot at a thin gold foil, most of them pass through.

Some however, are deflected back or by small angles due to enormous repulsive force of heavy nucleus.

If light aluminium foil is used, the number of α-particles deflected back or those deflected by small angles will be negligible because of the lighter nucleus of aluminium.

Thus, all the particles pass through without much effect.

8. Energy of photon $= \dfrac{hc}{\lambda} \text{ J} = \dfrac{hc}{e\lambda} \text{ eV}$

$$= \frac{6.626 \times 10^{-34} \times 3 \times 10^8}{300 \times 10^{-9} \times 1.602 \times 10^{-19}} = 4.14 \text{ eV}$$

For photoelectric effect to occur, energy of incident photons must be greater than work functions of metal from the given elements only Li, Na, K and Mg have work functions less than 4.14 V.

9. $\dfrac{1}{\lambda} = Z^2 \cdot R_H \left(\dfrac{1}{n_1^2} - \dfrac{1}{n_2^2} \right)$

For He$^+$, $\dfrac{1}{\lambda} = 2^2 \cdot R_H \left[\dfrac{1}{2^2} - \dfrac{1}{4^2} \right] = 4 \times \dfrac{3}{16} = \dfrac{3}{4}$

For H, $\dfrac{1}{\lambda} = 1^2 \cdot R_H \left[\dfrac{1}{1^2} - \dfrac{1}{2^2} \right] = \dfrac{3}{4}$

Hence, for hydrogen the given transition corresponds to $n = 2$ to $n = 1$ transition,

10.

	Subshell notation	***n + l***
I. $n = 4, l = 2, m_l = -2, m_s = -\frac{1}{2}$	$4d$	$4 + 2 = 6$
II. $n = 3, l = 2, m_l = 1, m_s = +\frac{1}{2}$	$3d$	$3 + 2 = 5$
III. $n = 4, l = 1, m_l = 0, m_s = +\frac{1}{2}$	$4p$	$4 + 1 = 5$
IV. $n = 3, l = 2, m_l = -2, m_s = -\frac{1}{2}$	$3d$	$3 + 2 = 5$
V. $n = 3, l = 1, m_l = -1, m_s = +\frac{1}{2}$	$3p$	$3 + 1 = 4$
VI. $n = 4, l = 1, m_l = 0, m_s = +\frac{1}{2}$	$4p$	$4 + 1 = 5$

$$\text{V} < \text{II} = \text{IV} < \text{III} = \text{VI} < \text{I}$$
$$3p < 3d = 3d < 4p = 4p < 4d$$

(Arrangement of orbitals in order of their increasing energies.)

11. $\lambda = \dfrac{h}{mv}$, or $\lambda = \dfrac{1}{\sqrt{2mE}}$

So, $\lambda_e = \dfrac{h}{\sqrt{\dfrac{2m_p}{1800} \times 16E}}$

$$\lambda_p = \frac{h}{\sqrt{2m_p \times 4E}} = \frac{h}{\sqrt{8m_p E}}$$

$$\lambda_\alpha = \frac{h}{\sqrt{2 \times 4m_p \times 4E}} = \frac{h}{\sqrt{8m_p E}}$$

The denominator value of λ_e is very less thus, λ_e is very high as compare of λ_p and λ_α. λ_p and λ_α have same value.

Thus, correct order is $\lambda_e > \lambda_p = \lambda_\alpha$.

12. Energy of one photon, $E = \dfrac{hc}{\lambda}$

$$= \frac{6.626 \times 10^{-34} \times 3 \times 10^8}{550 \times 10^{-9} \text{ m}}$$
$$= 3.61 \times 10^{-19} \text{ J}$$

∴ Number of photons $= \dfrac{\text{energy required}}{\text{energy of one photon}}$

$$= \frac{10^{-17}}{3.61 \times 10^{-19}} = 27.67 \approx 28$$

13. In Bohr orbit,

$$\text{KE of } e^- = \frac{1}{2}\frac{Zke^2}{r_n}$$

$$\text{PE of } e^- = \frac{Zke^2}{r_n}$$

Thus, $\text{KE} = -\frac{1}{2}\,\text{PE}$

14. For $3p$-orbital, principal quantum number, $n = 3$ and azimuthal quantum number, $l = 1$

Number of angular nodes $= l = 1$

Number of radial nodes $= n - l - 1 = 3 - 1 - 1 = 1$

15. Let the number of electrons in an ion $= x$

$\therefore$ Number of neutrons, $n = x + \frac{11.1}{100}x = 1.111x$

(As the number of neutrons are 11.1% more than the number of electrons.)

In the neutral atom, number of electrons, $e^- = x - 1$

(as the ion carries – 1 charge)

Similarly, number of protons, $p = x - 1$

we know that, mass number $= n + p = 37$

or $\quad 1.111x + x - 1 = 37$

$2.111\,x = 37 + 1 = 38$

$$x = \frac{38}{2.111} = 18.0009 \approx 18$$

Number of protons = atomic number $= 18 - 1 = 17$

Therefore, the symbol of the ion is ${}^{37}_{17}\text{Cl}^-$.

16. Energy change, $\Delta E = E_f - E_i$

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

When $n_i = 5$ and $n_f = \infty$,
Energy change,

$$\Delta E = 2.18\times 10^{-18}\ \text{J}\left(\frac{1}{5^2} - \frac{1}{\infty}\right) = 0.0872\times 10^{-18}\ \text{J}$$

When $n_i = 1$ and $n_f = \infty$, energy change,

$$\Delta E' = 2.18\times 10^{-18}\ \text{J}\left(\frac{1}{1^2} - \frac{1}{\infty}\right)$$

$$\Delta E' = 2.18\times 10^{-18}\ \text{J}$$

$$\frac{\Delta E'}{\Delta E} = \frac{2.18\times 10^{-18}}{0.0872\times 10^{-18}} = 25$$

Hence, energy required to remove an electron from first orbit is 25 times than that required to remove an electron from fifth orbit.

17. Wave number, $\bar{\nu} = \frac{1}{\lambda} = R\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$

(Rydberg constant, $R = 109677\ \text{cm}^{-1}$)

$$\frac{1}{\lambda} = 109677\left(\frac{1}{2^2} - \frac{1}{4^2}\right)\ \text{cm}^{-1}$$

$$\frac{1}{\lambda} = 109677\left(\frac{3}{16}\right)\ \text{cm}^{-1}$$

$$\frac{1}{\lambda} = 20564.4\ \text{cm}^{-1}$$

$$\lambda = \frac{1}{20564.4}\ \text{cm} = 486\times 10^{-7}\ \text{cm}$$

$$= 486\times 10^{-9}\ \text{m} = 486\ \text{nm}$$

The colour corresponding to this wavelength is blue.

18. $\frac{1}{\lambda} = R\left[\frac{1}{1^2} - \frac{1}{2^2}\right] = \frac{3R}{4}$

Also, $\quad \lambda = \frac{h}{P}$

$$P = \frac{h}{\lambda} = h\times\frac{3R}{4} = \frac{3Rh}{4}$$

19. Uncertainty in velocity $= 3\times 10^4 \times \frac{0.001}{100} = 0.3$ cm/s

$$\Delta x\cdot\Delta v = \frac{h}{4\pi m} = \frac{6.6\times 10^{-27}}{4\times 3.14\times 9.1\times 10^{-28}}$$

$$\Delta x = \frac{6.6\times 10^{-27}}{4\times 3.14\times 9.1\times 10^{-28}\times 0.3} = 1.92\ \text{cm}$$

20. Energy, $E = \frac{nhc}{\lambda}$

$$\Rightarrow\ 60\times 1\ \text{Js} = \frac{n\times 6.63\times 10^{-34}\ \text{Js}\times 3\times 10^8\ \text{m}}{663\times 10^{-9}\text{m}}$$

$$\left[\because \text{Power} = \frac{\text{energy}}{\text{time}}\right]$$

$$\because\quad n = \frac{60\times 1\times 663\times 10^{-9}}{6.63\times 10^{-34}\times 3\times 10^8} = 2\times 10^{20}$$

21. $\lambda = \frac{h}{\sqrt{2eVm_e}}$

$e = 1.6\times 10^{-19}$ C, $V = 10{,}000$ V, $m_e = 9.1\times 10^{-31}$ kg

$$\lambda = \frac{6.63\times 10^{-34}}{\sqrt{2\times 1.6\times 10^{-19}\times 10{,}000\times 9.1\times 10^{-31}}} = 0.123\ \text{Å}$$

22. Energy given to I_2 molecule $= \frac{hc}{\lambda}$

$$= \frac{6.626\times 10^{-34}\times 3\times 10^8}{4500\times 10^{-10}} = 4.4\times 10^{-19}\ \text{J}$$

Energy of I_2 molecule $= 240\times 10^3$ J/mol

$$= \frac{240\times 10^3}{6.023\times 10^{23}}\ \text{J/atom} = 3.98\times 10^{-19}\ \text{J/atom}$$

$$\text{KE} = (4.4\times 10^{-19}) - (3.98\times 10^{-19}) = 0.42\times 10^{-19}\ \text{J/atom}$$

$$\text{KE of I atoms} = \frac{0.42}{2}\times 10^{-19} = 0.21\times 10^{-19}$$

23. $\lambda_A = \frac{h}{m_A v_A}$ and $\lambda_B = \frac{h}{m_B v_B}$

$$\frac{\lambda_A}{\lambda_B} = \frac{m_B v_B}{m_A v_A} \qquad \text{...(i)}$$

Given, $m_B = \frac{m_A}{4} \Rightarrow v_B = \frac{3}{4} v_A$

By putting there values in Eq. (i), we get

$$\frac{1 \times 10^{-10}}{\lambda_B} = \frac{m_A \times 3v_A}{m_A \times 4 \times v_A \times 4}$$

$$\lambda_B = \frac{16 \times 10^{-10}}{3} = 5.33 \text{ Å}$$

24. Given, $\Delta x = \Delta P$ or $\Delta x = m \cdot \Delta v$

From Heisenberg's uncertainty principle,

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

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

$$(\Delta v)^2 = \frac{h}{4\pi m^2}$$

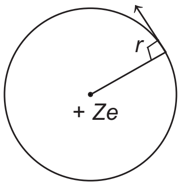
$$\Delta v = \frac{1}{2m}\sqrt{\frac{h}{\pi}}$$

$$= \frac{1}{2 \times 9.1 \times 10^{-31}}\sqrt{\frac{6.63 \times 10^{-34}}{3.14}}$$

$$= 7.98 \times 10^{12} \text{ ms}^{-1} \approx 8 \times 10^{12} \text{ ms}^{-1}$$

25. Use, $\Delta v \times \Delta x = \frac{h}{4\pi m}$ or $\Delta x = \frac{h}{4\pi m \cdot \Delta v}$

26. The frequency of revolution of an electron is given by



$$\text{Frequency} = \frac{1}{\text{Time period}} \quad \text{...(i)}$$

$$\text{Time period} = \frac{\text{Total distance covered in one revolution}}{\text{Velocity}}$$

$$= \frac{2\pi r}{v} \quad \text{...(ii)}$$

From Eq. (i) and (ii), we get

$\therefore$ Frequency $= \frac{v}{2\pi r}$

Calculate the velocity (v_2) and radius (r_2) of the electron in the second Bohr orbit in H atom

$Z = 1$ for H atom

Using $r_n = 0.529 \frac{n^2}{Z}$ Å

We get, $r_2 = 0.529 \times 10^{-10} \frac{(2)^2}{1}$ m $= 2.12 \times 10^{-10}$m

$$v_n = 2.18 \times 10^6 \, (1/n) \text{ ms}^{-1}$$

$$v^2 = 2.18 \times 10^6 (1/2) = 1.09 \times 10^6 \text{ ms}^{-1}$$

$$\therefore \text{ Frequency} = \frac{v_2}{2\pi r_2} = \frac{1.09 \times 10^6}{2(\pi)\,(2.12 \times 10^{-10})}$$

$$v = 8.18 \times 10^{14} \text{Hz}$$

Note Frequency of revolution $(f) = \frac{1}{T}$

where, $T = \frac{2\pi r}{v} \propto \frac{n^3}{Z^2}$ $\left[\because r \propto \frac{n^2}{Z} \text{ and } v \propto \frac{Z}{n}\right]$

27. 1 mol ^{14}C = 14 g $= 6.022 \times 10^{23}$ carbon atoms

Number of neutrons in 1 carbon atom

= mass number − atomic number $= 14 - 6 = 8$ neutrons

$\because 6.023 \times 10^{23}$ carbon atoms will contain $6.023 \times 10^{23} \times 8$ neutrons

$\therefore$ 14 g carbon-14 have $6.023 \times 10^{23} \times 8$ neutrons

and 7 mg or 7×10^{-3} g carbon-14 will have

$$\frac{7 \times 10^{-3} \times 6.023 \times 10^{23} \times 8}{14} \text{ neutrons}$$

$$= 24.092 \times 10^{20} \text{ neutrons}$$

$$= 2.4092 \times 10^{21} \text{ neutrons}$$

Mass of 1 neutron $= 1.675 \times 10^{-27}$ kg

Mass of 2.4092×10^{21} neutrons

$$= 2.4092 \times 10^{21} \times 1.675 \times 10^{-27} \text{ kg}$$

$$= 4.0347 \times 10^{-6} \text{ kg}$$

The value of x is 6.

28. 25 watt $= 25$ Js^{-1} (1watt $= 1$ Js^{-1})

Wavelength, $\lambda = 0.57 \mu$m

$= 0.57 \times 10^{-6}$ m (1μm $= 10^{-6}$ m)

Energy of one photon,

$$E = \frac{hc}{\lambda} = \frac{6.626 \times 10^{-34} \text{Js} \times 3.0 \times 10^8 \text{ ms}^{-1}}{0.57 \times 10^{-6} \text{ m}}$$

$$E = 34.87 \times 10^{-20} \text{ J}$$

Number of photons emitted per second

$$= \frac{\text{Total energy per second}}{\text{Energy of photon}}$$

$$= \frac{25 \text{ Js}^{-1}}{34.87 \times 10^{-20}} = 0.7169 \times 10^{20} \text{ photons per second}$$

$$= 7.169 \times 10^{19} \text{ photon per second}$$

The value of x is 19.

29. Kinetic energy $= h(\nu - \nu_0)$

$$\text{KE} = h\nu - h\nu_0$$

$$\nu_0 = \nu - \frac{\text{KE}}{h} = 2 \times 10^{15} - \frac{6.63 \times 10^{-19}}{6.63 \times 10^{-34}} = 1 \times 10^{15} \text{ s}^{-1}$$

Thus, the numerical value is 1.

30. Number of lines produced when electron from nth shell drops to ground state $= \frac{n\,(n-1)}{2}$

When $n = 6$, number of lines produced

$$= \frac{6\,(6-1)}{2} = \frac{6 \times 5}{2} = 15$$

31. Number of spherical nodes in $4p$-orbital

$$= n - l - 1 = 4 - 1 - 1 = 2$$

32. The radius of an orbit, $r_n \propto n^2$

Where, n = principal quantum number

$$\Rightarrow \qquad \frac{r_1}{r_3} = \frac{1}{3^2}$$

If $\qquad r_1 = x$ then $r_3 = 9x$

For third shell, $\quad 2\pi r_3 = 3\lambda$

$$\lambda = \frac{2\pi r_3}{3} = \frac{2\pi 9x}{3} = 6\pi x$$

33. KE = quantum energy – threshold energy

$$= \frac{6.626\times 10^{-34}\times 3\times 10^{8}}{3000\times 10^{-10}} - \frac{6.626\times 10^{-34}\times 3\times 10^{8}}{4000\times 10^{-10}}$$

$$= 6.626\times 10^{-19} - 4.9695\times 10^{-19}$$

$$= 1.6565\times 10^{-19}\ \text{J}$$

$$\text{KE} = 1.6565\times 10^{-19} = \frac{1}{2}\ mv^2$$

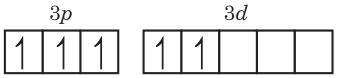
$$\therefore \quad m^2v^2 = 2\times 1.6565\times 10^{-19}\times 9.1\times 10^{-31}$$

$$mv = 5.49\times 10^{-25}$$

de-Broglie wavelength, $\lambda = \dfrac{h}{mv} = \dfrac{6.626\times 10^{-34}}{5.49\times 10^{-25}}$

$$= 1.2\times 10^{-9}\ \text{m}$$

34. Configuration in second excited state is written as



n	3	3	3	3	3
l	1	1	1	2	2
m	–1	0	+1	+2	+1

Total $n + l + m$ = 25

35. Energy of electron in the nth orbit in terms of R_H is

$$E_n = \frac{-R_H Z^2}{n^2}$$

For hydrogen atoms $Z = 1$, thus

$$E_n = -\frac{R_H}{n^2}$$

On comparing the above equation with the given equation, we get

$$n^2 = 16,\ n = 4$$

For, $n = 4 \quad l = 0(s) \qquad m = 0$

$l = 1\ (p) \qquad m = -1, 0, +1$

$l = 2(d) \qquad m = -2, -1, 0, +1, +2$

$l = 3(f) \qquad m = -3, -2, -1, 0, +1, +2, +3$

Degeneracy = total number of orbitals = 16

36. Bohr radius $(r_n) = \in_0 n^2h^2$

$$r_n = \frac{n^2h^2}{4\pi^2 me^2kZ}$$

$$\Rightarrow \qquad k = \frac{1}{4\pi \in_0}$$

$$\therefore \qquad r_n = \frac{n^2h^2\in_0}{\pi me^2Z} = n^2\frac{a_0}{Z}$$

where, m = mass of electron,
e = charge of electron,
h = Planck's constant,
k = Coulomb constant

$$r_n = \frac{n^2\times 0.53}{Z}\ \text{Å}$$

Radius of n^{th} Bohr orbit for H-atom

$= 0.53\ n^2$ Å $\qquad$ [$Z = 1$ for H-atom]

∴ Radius of 2^{nd} Bohr orbit for H-atom

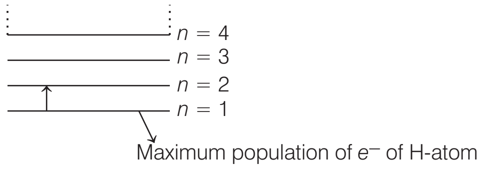
$= 0.53\times(2)^2 = 2.12$ Å

37. $\Delta E = 2.178\times 10^{-18}\left(\dfrac{1}{1^2}-\dfrac{1}{2^2}\right) = \dfrac{hc}{\lambda}$

$$2.178\times 10^{-18}\left(\frac{1}{1^2}-\frac{1}{2^2}\right) = \frac{6.62\times 10^{-34}\times 3.0\times 10^{8}}{\lambda}$$

$$\therefore \qquad \lambda \approx 1.21\times 10^{-7}\ \text{m}$$

38.



Since, at $n = 1$, the population of electrons is maximum, i.e. at ground state. So, maximum excitation will take place from $n = 1$ to $n = 2$.

Hence, $n = 2$ is the possible excited state.

Now, we have the formula for energy of H-atom

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

where, Z = atomic number

Z for H-atom = 1

$$\therefore \qquad (E_n)_H = -13.6\times\frac{1}{2^2}\ \text{eV} = -\frac{13.6}{4}\ \text{eV} = -\ 3.4\ \text{eV}$$

39. $n = 4$ and $m_l = -3$

Hence, l value must be 3.

Now, number of radial nodes = $n - l - 1 = 4 - 3 - 1 = 0$

40. For, $n = 5$

$l = (0, 1, 2, 3, 4)$

If $l = 0, m = 0$

$l = 1,\ m = \{-1, 0, +1\}$

$l = 2, m = \{-2, -1, 0, +1, +\mathbf{2}\}$

$l = 3,\ m = \{-3, -2, -1, 0, +1, +2, +\mathbf{3}\}$

$l = 4,\ m = \{-4, -3, -2, -1, 0, +1, +\mathbf{2}, +3, +4\}$

$5d, 5f$ and $5g$ subshell contain one-one orbital having $m_l = +2$