Structure of Atom

CHEMISTRY

BOARD Std. XI

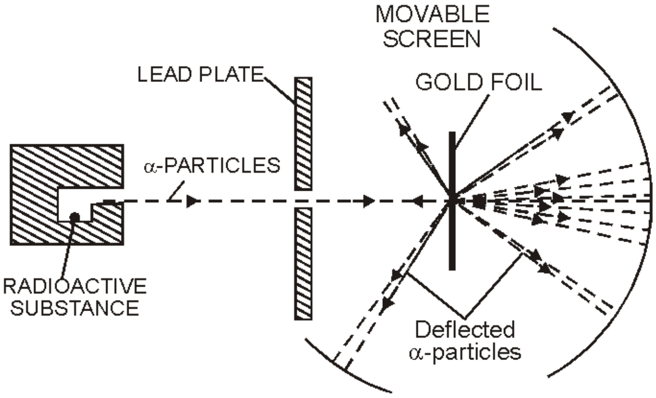
COMPOSITION OF ATOM

An atom consist of three constituents (i) electron, (ii) proton, (iii) neutron.

Particle	Symbol	Mass	Charge	Radius	Position in the atom
Electron	e, e^-, β^-, ${}_{-1}^{0}e$	9.108×10^{-28} g or, 0.0005486 amu	-1.6×10^{-19} C or -4.8024×10^{-10} esu or -1[as unit]	2.5×10^{-13} cm	In different extra nuclear orbits
Proton	p, ${}_{1}^{1}\mathrm{H}$	1.6725×10^{-24} g or, 1.00728 amu	$+1.6\times10^{-19}$ C or $+4.8024\times10^{-10}$ esu or $+1$[as unit]	1.2×10^{-13} cm	In the nucleus of an atom
Neutron	n, ${}_{0}^{1}n$	1.675×10^{-24} g or, 1.00867 amu	0		
Positron	e^+, β^+, ${}_{+1}^{0}e$	9.108×10^{-28} g or, 1.0005486 amu	$+1.6\times10^{-19}$ C or $+4.8024\times10^{-10}$ esu or $+1$[as unit]		
π -meson	π^-, π^+, π^0	0.1514 amu 0.1514 amu 0.1454 amu	-1 $+1$ 0		
Neutrino	ν	Negligible mass, less than that of an electron			

RUTHERFORD’S MODEL

Rutherford allowed a narrow beam of α–particles to fall on a very thin gold foil (thickness 0.0004 nm) The thin gold foil had a circular fluorescent zinc sulphide screen around it. Whenever α–particles struck the screen, a tiny flash of light was produced at that point. The results of scattering experiment were quite unexpected. According to Thomson model of atom, the mass of each gold atom in the foil should have been spread evenly over the entire atom, and α– particles had enough energy to pass directly through such a uniform distribution of mass. It was expected particles would slow down and change directions only by a small angles as they passed through the foil.



Schematic view of Rutherford's scattering experiment When a beam of alpha (α) particles is "shot" at a thin gold foil, most of them pass through without much effect. Some, however, are deflected

OBSERVATIONS:

- Most of the α- particles passed through gold foil with no deflection
- A small fraction of α- particles got deflected through small angles
- Very few α- particles (~1 in 20,000) did not pass through foil but suffered large deflection nearly 180°

CONCLUSIONS:

- Since most of the α-particles passed through foil with no deflection, it means most of the space in atom is empty
- Since some of the α-particles are deflected to certain angles, it means the deflection must be due to enormous repulsive force showing that the positive charge of the atom is not spread throughout the atom as Thomson had presumed. The positive charge has to be concentrated in a very small volume that repelled and deflected the positively charged α– particles.
- Calculations by Rutherford showed that the volume occupied by the nucleus is negligibly small as compared to the total volume of the atom. The radius of the atom is about 10^{-10} m, while that of nucleus is 10^{-15} m.
- Strong deflections or even bouncing back of α-particles from gold foil were due to direct collision with positively charged mass in atom

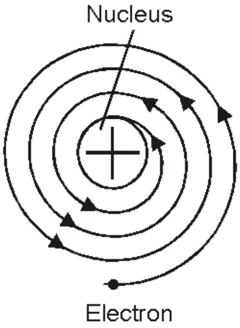
Postulates of Rutherford's Atomic Model:

Rutherford proposed the nuclear model of atom (after the discovery of protons). According to this model:

- The positive charge and most of the mass of the atom was densely concentrated in extremely small region. This very small portion of the atom was called **nucleus** by Rutherford.
- The nucleus is surrounded by electrons that move around the nucleus with a very high speed in circular paths called **orbits**. Thus, Rutherford's model of atom resembles the solar system in which the nucleus plays the role of sun and the electrons that of revolving planets.
- Electrons and the nucleus are held together by electrostatic forces of attraction.

Drawbacks of Rutherford's model of atom:

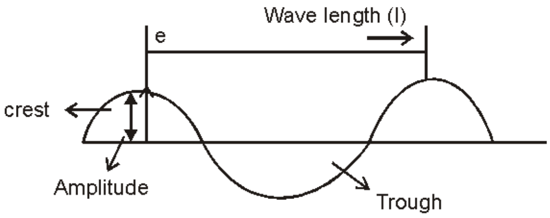
- **Position of electrons:** The exact positions of the electrons from the nucleus are not mentioned.
- **Stability of the atom:** Maxwell pointed out that Rutherford's atom should be highly unstable. According to the law of electro–dynamics, when a charged body moves under the influence of an attractive force, it loses energy continuously in the form of electromagnetic radiation.



The electron should therefore, continuously emit radiation and lose energy. As a result of this a moving electron will come closer and closer to the nucleus and after passing through a spiral path, it should ultimately fall into the nucleus.

NATURE OF ELECTROMAGNETIC RADIATION

A wave is a sort of disturbance which originates from some vibrating source and travels outward as a continuous sequence of alternating crests and troughs. Every wave has five important characteristics, namely, wavelength (λ), frequency (ν), velocity (c), wave number ($\bar{\nu}$) and amplitude (a).



Ordinary light rays, X–rays, γ–rays, etc. are called electromagnetic radiations (EMR) because similar waves can be produced by moving a charged body in a magnetic field or a magnet in an electric field. These radiations have wave characteristics and do not require any medium for their propagation.

(i) Wave length or λ :- It is the distance between succession points of equal phase of a wave.

(ii) Frequency or ν :- It is number of cycles or vibration of a wave motion in unit time.

i.e. $\nu = \dfrac{\text{Velocity}}{\text{Wave length}}$

(iii) Velocity :- It is the distance travelled by the wave in one second.

(iv) Wave Number :- It is defined as the number of waves in unit length.

i.e. $\bar{\nu} = \left(\dfrac{1}{\lambda}\right)$

(v) Amplitude :- If any quantity is varying in an oscillatory manner about an equlibrium value, the maximum departure from that equlibrium is called amplitude.

An electromagnetic spectrum includes a characteristic range of wave lengths. The characteristic range of wave lengths of electromagnetic spectrum are given below.

Name	Radiowave	microwave	far infrared wave	infrared wave	visible wave	ultra violet wave	x-rays
λ in cm	1 to 10^{2}	1 to 10^{-1}	10^{-2}	10^{-3} to 10^{-4}	10^{-4} to 10^{-5}	10^{-5} to 10^{-6}	10^{-6} and above

ATOMIC TERMS :

- **Nuclide:** Various species of atoms in general.
- **Nucleons :** Sub-atomic particles in the nucleus of an atom, i.e., protons and neutrons.
- **Mass number (A):** Sum of the number of protons and neutrons, i.e. the total number of nucleons
- **Atomic number (Z):** The number of protons in the nucleus of an atom. This, when subtracted from A, gives the number of neutrons.
- **Isotopes :** Species with same atomic number (z) but different mass number (A).
  e.g. - $_1H^1$, $_1H^2$, $_1H^3$ etc.
- **Isobars :** Species with same mass number (A) but different atomic number (z).
  e.g. - $_{88}Ra^{228}$, $_{90}Th^{228}$
- **Isotones :** Species with different atomic number as well as different mass number (A) but having same numbers of neutrons (n).
  e.g. - $_{18}Ar^{38}$, $_{19}K^{39}$
- **Isosters :** No. of atoms = same, no. of electron = same, physical properties same.
  e.g. - CO_2, N_2O
- **Isodiaphers :** neutrons – proton = same
  e.g. - $_{92}U^{235}$, $_{90}Th^{231}$

Concept Illustrator

What is the relation between $_{33}As^{77}$ and $_{34}Ge^{78}$?

Sol. $_{33}As^{77} \rightarrow$ No. of neutron = 44

$_{34}Ge^{78} \rightarrow$ No. of neutron = 44

As two elements have same number of neutrons but different number of protons so they are isotone.

PLANCK'S QUANTUM THEORY

Radiant energy is emitted or absorbed in the integral multiple of some smallest unit of packet energy, each packet of energy being called one quantum of energy. In Einstein's term, each packet of energy is photon, carrying energy equal to one quantum of radiation. There is a slight difference between Planck's concept and Einstein's theory. Planck thought that radiant energy is itself continuous but its absorption or emission takes place in the unit of quantum whereas Einstein made a step forward and through that radiation is itself discrete and it has photon constitution, *i.e.* light is streams of photons.

The energy associated with one quantum of energy is expressed as —

$$E = h\nu = h\frac{c}{\lambda} = hc\bar{\nu}$$

Concept Illustrator

Calculate the energy of a photon associated with a wave length of 4000 Å .

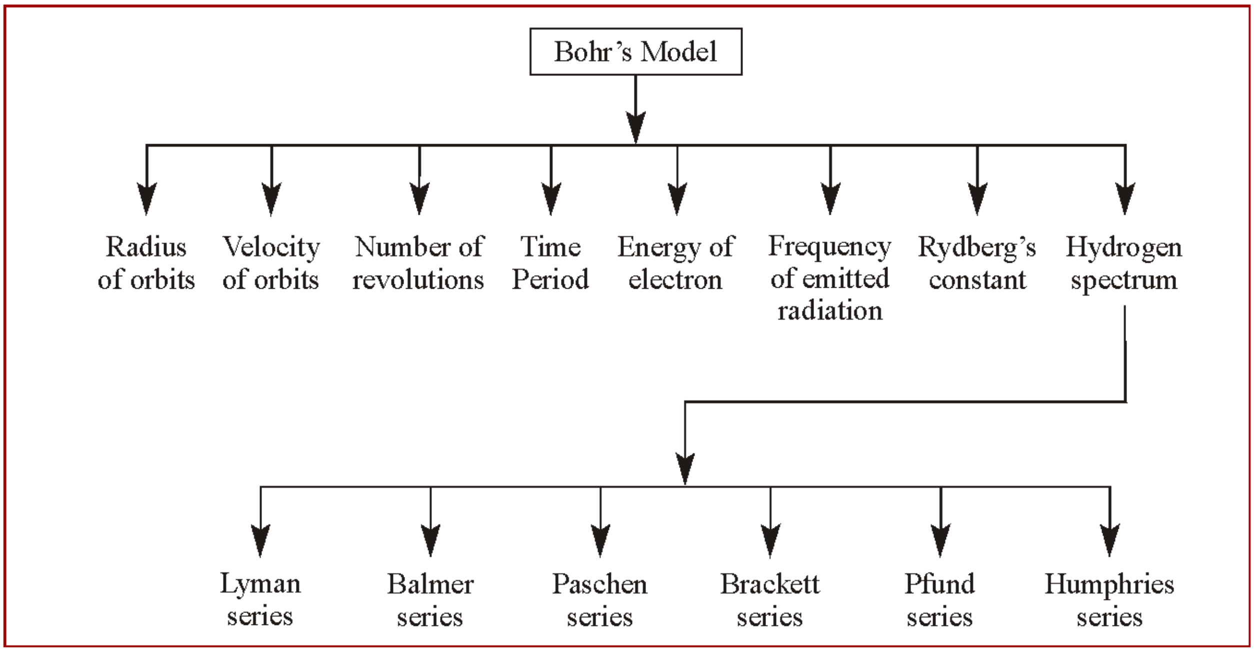
Sol. λ = 4000 Å = 4000 × 10^{-8} cm

c = 3 × 10^{10} cm/sec, h = 6.62 × 10^{-27} erg. sec.

Now energy of the photon = $\frac{hc}{\lambda} = \frac{6.62\times10^{-27}\times3\times10^{10}}{4\times10^{-5}} = 4.96\times10^{-12}$ ergs.

BOHR'S MODEL

Neils Bohr applied the quantum theory to develop a model for hydrogen atom and a hydrogen-like electronic species (e.g., He^+).



- **Relation between P. E., K. E. & T. E. :**

$$\boxed{\text{T.E.} = \frac{\text{P.E.}}{2} = -\text{K.E.}}$$

(a) $\text{T. E.} = -13.6 \times \frac{Z^2}{n^2}$ eV / atom

(b) $\text{T. E.} = -21.8 \times 10^{-19} \times \frac{Z^2}{n^2}$ J / atom

(c) $\text{T. E.} = -21.8 \times 10^{-12} \times \frac{Z^2}{n^2}$ erg / atom

(d) $\text{T. E.} = -313.6 \times \frac{Z^2}{n^2}$ Kcal / mole

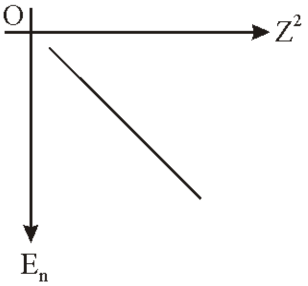
Note

The important points are aid in your memory

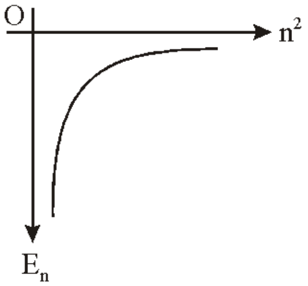
- Since, m, e, h and ε_0 are constant

$$\therefore \quad E_n \propto -\left(\frac{Z^2}{n^2}\right)$$

Hence,



(a)
For different H-like species



(b)
For different orbit of a given species

It is clear from the graphs that the value of n increases, 'E_n' also increase and Z increases, E_n decreases.

- Why is the energy of an electron negative?
  The energy released due to attraction electrostatic force is very effective than that of kinetic energy due to centrifugal. Hence energy of an electron decreases on approaching the electron towards the nucleus, i.e., the energy of the electron becomes negative as the electron moves away from the nucleus.
- For different hydrogen like species to a given orbit (say, species are A and B)
  $$\frac{E_A}{E_B} = \frac{{Z_A}^2}{{Z_B}^2}$$
- For different orbits of a given H or Hydrogen like atom,
  $$\frac{E_1}{E_2} = \frac{{n_2}^2}{{n_1}^2}$$
- For different orbits of different species,
  $$\frac{E_1}{E_2} = \frac{{Z_A}^2}{{Z_B}^2} \times \frac{{n_2}^2}{{n_1}^2}$$
- In the case of isotopes of hydrogen (H, D, T) (when the mass of the nucleus is considered) $E_H > E_D > E_T$ (or a particular orbit)
- Total energy of an revolving electron in the infinityth orbit is zero.
- The energy be in eV : then the gradiation of 'E_n' and $\frac{Z^2}{n^2}$ will be – 13.6.
- Energy of an electron in n^{th} orbit does not vary in 'log'.
- Although the energy of electron increases with increases in the value of n (orbit)
  $E_1 < E_2 < E_3 <$ ..... etc.
  Yet the difference of energy between successive orbits decreases. Thus
  $E_2 - E_1 > E_3 - E_2 > E_4 - E_3 >$ .... etc.

❖ Kinetic Energy of an electron in n^{th} orbit

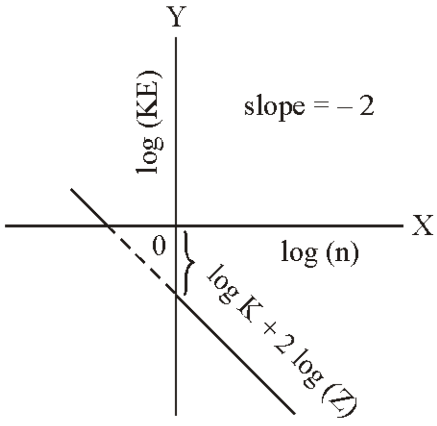
- Kinetic energy $= \frac{1}{2} m {V_n}^2 = \left(\frac{me^4}{8h^2{\varepsilon_0}^2}\right)\frac{Z^2}{n^2} = 2.16 \times 10^{-18} \frac{Z^2}{n^2}$ J / atom
- $$\text{K.E.} \propto \frac{Z^2}{n^2} = 13 \times 10^5 \frac{Z^2}{n^2} \ \text{J / mol}$$

  $\text{K.E.} \propto Z^2$ (where n is constant)

  $\text{K.E.} \propto \frac{1}{n^2}$ (where Z is constant)

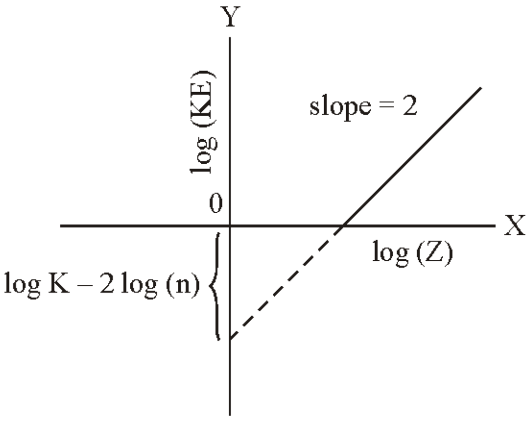
  Hence for two species of a particular orbit (Say, A and B)
  $$\frac{(\text{K.E.})_A}{(\text{K.E.})_B} = \frac{{Z_A}^2}{{Z_B}^2}$$
  And for two orbits of a particular atom
  $$\frac{(\text{K.E.})_1}{(\text{K.E.})_2} = \frac{{n_2}^2}{{n_1}^2}$$

- $\frac{(\text{K.E.})_1}{(\text{K.E.})_2} = \frac{Z_1^2}{Z_2^2} \times \frac{n_2^2}{n_1^2}$ [For different orbits of different species]
- The positive sign of 'K.E.' shows that 'n' increases, 'K.E.' decreases and 'Z' increases 'K.E.' increases. If $n = \infty$, K.E. = 0, hence velocity of the electron in infinityth orbit is zero.
- In the case of the isotopes of hydrogen
  $(\text{K.E.})_H < (\text{K.E.})_D < (\text{K.E.})_T$ (if mass of the nucleus is considered)



(a)

For greatest value of Z, the line intercepts on positive Y-axis.



(b)

For greatest value of n, the line does not intercept on positive Y-axis.

where $K = \left(\frac{me^4}{8h^2\varepsilon_0^2}\right) = 2.16 \times 10^{-18}$ J/atom

- At the ionisation energy the value of 'K.E.' will be zero.

❖ Potential Energy of an electron in nth orbit

- $\text{P.E.} = \frac{-1}{4\pi\varepsilon_0} \times \frac{Ze^2}{r_n} = -\left(\frac{e^4 m}{4h^2\varepsilon_0^2}\right)\frac{Z^2}{n^2}$

  $= -4.32 \times 10^{-18}\frac{Z^2}{n^2}$ J/atom $= -26.019 \times 10^5 \frac{Z^2}{n^2}$ J/atom

- 'P.E.' has negative sign due to the action of attractive force towards the nucleus.
- More the value of 'P.E.' in negative, the atom will be more in stable form. This is why an electron return in ground state from excited state.
- If 'n' increase 'P.E.' increases and 'n' decreases 'P.E.' decreases. Similarly 'Z' increases 'P.E.' decreases and vice-versa.
- The absolute value of 'P.E.' is greater than 'K.E.'. Hence, – P.E./2 = K.E. 'P.E.' is just opposite to the double of K.E. Hence, the gradiation between K.E. and P.E. will be '– 2'. Which is the straight line passes through the origin (according to y = mx + c)
- At $n = \infty$, P.E. = 0, hence the atom will be very unstable in such case.
- For a given orbit the graph between P.E. and Z varies in parabola form.

Concept Illustrator

An electron in an excited hydrogen atom acquired an energy of 12.1 eV. To what energy level did it jump? How many spectral lines may be emitted in the course of the transition to lower energy levels? Calculate the corresponding wavelength.

Sol. We have $E_n = -2.18 \times 10^{-18} \dfrac{Z^2}{n^2}$

Here $n = 1,\ s = ?$

$$\therefore\ 12.1 \times 1.6 \times 10^{-19} = 2.18 \times 10^{-18} \times 1^2 \left(\frac{1}{1^2} - \frac{1}{s^2} \right)$$

or, $s = 3$

Three lines may be emitted

$s = 3$ to $n = 1$

$s = 3$ to $n = 2$

$s = 2$ to $n = 1$

For $3 \to 1,\ \bar{v} = 1.097 \times 10^7 \times \left(1 - \frac{1}{9}\right) = \frac{8}{9} \times 1.097 \times 10^7$

or $\lambda = \dfrac{1}{\bar{v}} = \dfrac{9}{8 \times 1.097 \times 10^7} \text{m} = 1025\,\text{Å}$

For $3 \to 2$, $\bar{v} = 1.097 \times 10^7 \left(\frac{1}{4} - \frac{1}{9} \right) = \frac{5}{36} \times 1.097 \times 10^7$ or $\lambda = \dfrac{36}{5 \times 1.097 \times 10^7} = 6563\ \text{Å}$

For $2 \to 1,\ v = 1.097 \times 10^7 \left(1 - \frac{1}{4}\right) = \frac{3}{4} \times 1.097 \times 10^7$ or $\lambda' = \dfrac{4}{3 \times 1.097 \times 10^7} \text{m} = 1215\ \text{Å}$

☐ DERIVATION OF RELATION FOR VELOCITY OF AN ELECTRON IN ORBIT

Substituting the value r in equation (iv)

$$v = \frac{nh}{2\pi m} \times \frac{4\pi^2 zme^2}{n^2h^2} \quad (k = 1)$$

$$v = \frac{2\pi ze^2}{nh}$$ Hence, $v \propto \dfrac{1}{n}$

Note

If the velocity of the electron is v_1 in the orbit with prinicipal quantum number n_1 and if the velocity is v_2 in another orbit with principal quantum number n_2 in the same atom then $\dfrac{v_1}{v_2} = \dfrac{n_2}{n_1}$

Regarding velocity it is worthnothing that –

☐ $V_n = 2.18 \times 10^6 \times \dfrac{Z}{n}\ \text{m/s}$

i.e., $V_n \propto \dfrac{Z}{n}$

or, $V_n \propto Z$ (where n is constant)

$$V_n \propto \frac{1}{n} \text{ (where Z is constant)}$$

It is clear that for a given species.

$V_1 > V_2 > V_3 >$ .... (where 1, 2, 3, ... indicates to orbit number)

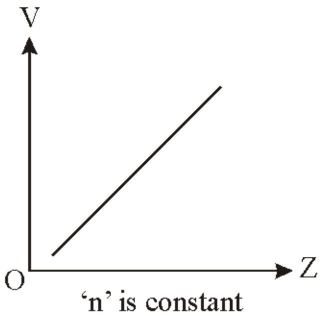
For different species and a given orbit (H, He^+, Li^{2+}, Be^{3+}, ... etc.)

$V_H > V_{He} > V_{Li} > V_{Be} >$ .... Because the kinetic energy is directly proportional to the attractive force.

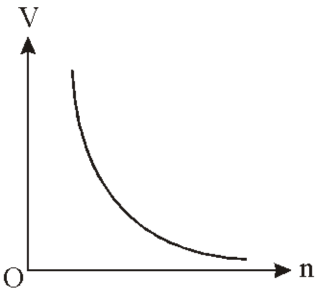
- In the case of two different orbits of two different species (say 1 and 2)

$$\frac{V_1 n_1}{V_2 n_2} = \frac{Z_1}{Z_2}$$

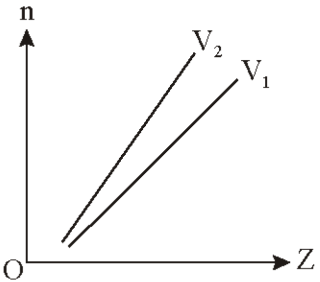
- Graphical view of velocity with respect to 'n' and 'Z'.



'n' is constant
(a)



'Z' is constant
(b)



$V_1 > V_2$
(c)

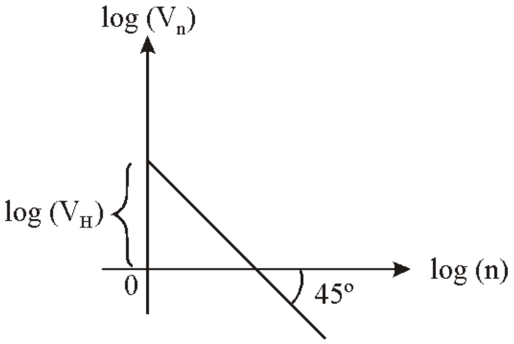
Since in figure (a) 'V' is increasing function with respect to Z, and in figure (b) 'V' is decreasing function with respect to 'n'.

It is clear from figure (a) that –

$V_1 - V_2 > V_2 - V_3 > V_3 - V_4 >$ ......

- For hydrogen atom Z = 1, n = 1; thus V_H is called Bohr's velocity which,

$V_H = 2.18 \times 10^6$ m/s.



$$\because \quad \log(V_n) = \log(V_H) + \log(Z) - \log(n)$$

For H atom, Z = 1

$$\therefore \quad \log(V_n) = \log(V_H) + (-1)\log(n) \qquad [\because \ Y = mx + c]$$

Concept Illustrator

Find the ratio of velocities of a hydrogen electron, rotated in 1st and 2nd orbit.

Sol. The velocity of electron rotated in n^{th} orbit is $V = \frac{2\pi e^2}{nh}$

velocity in first orbit $V_1 = \frac{2\pi e^2}{1 \times h}$

velocity in second orbit $V_2 = \frac{2\pi e^2}{2h}$ $\therefore V_1 : V_2 = 1 : 2$

☐ Number of revolutions made by an electron moving in n^{th} orbit :

$$\text{Number of revolutions} = \frac{V_n}{2\pi r_n}$$

On putting the values of V_n and r_n as $\text{N.O.R.} = \left(65.71 \times 10^{14}\right)\frac{Z^2}{n^3}\ \sec^{-1}$

In the case of number of revolutions (N.O.R.)

- $\text{N.O.R.} \propto \frac{Z^2}{n^3}$

  or, $\text{N.O.R.} \propto Z^2$ (where n is constant)

  $\text{N.O.R.} \propto \frac{1}{n^3}$ (where Z is constant)

- For two different orbits of an atom,

  $$\frac{(\text{N.O.R.})_1}{(\text{N.O.R.})_2} = \frac{n_2{}^3}{n_1{}^3}$$

- For an orbit of different species (Say A and B)

  $$\frac{(\text{N.O.R.})_A}{(\text{N.O.R.})_B} = \frac{Z_A{}^2}{Z_B{}^2}$$

- For two different orbits of two different species

  $$\frac{(\text{N.O.R.})_1}{(\text{N.O.R.})_2} = \frac{Z_1{}^2}{Z_2{}^2} \times \frac{n_2{}^3}{n_1{}^3}$$

- In the case of isotopes, atomic mass increases, the number of revolutions also increases, e.g., the number of revolutions is a increasing function with respect to atomic mass of isotopes. (but only in that case, when the mass of the nucleus is considered).
- In the case of H-spectrum, supplied energy increases, number of revolutions decreases, hence at the ionisation energy, the number of revolutions will be zero.

Concept Illustrator

Calculate the frequency of revolution of an electron in the first orbit of an aluminium atom.

Given that mass of electron $= 9 \times 10^{-31}\text{kg},\ e = 1.6 \times 10^{-19}\,\text{C}$**, radius of the orbit** $= 0.2 \times 10^{-11}\,\text{m}$ **.**

Sol. Aluminium atom is $^{27}_{13}Al$. Hence there are 13 protons in the nucleus of aluminium atom.

$$\text{Centripetal force} = \frac{1}{4\pi\varepsilon_0 r^2} = m\omega^2 r$$

$$\text{or, } \frac{13e^2}{4\pi\varepsilon_0 r^2} = m\omega^2 r$$

$$\text{or, } \omega^2 = \frac{1}{4\pi\varepsilon_0} \times \frac{13e^2}{mr^3} = 9\times10^9 \times \frac{13\left(1.6\times10^{-19}\right)^2}{9\times10^{-31}\times9\left(0.2\times10h-11\right)^2}$$

$$= \frac{9\times13\times2.56}{9\times(0.2)^3}\times10^{35} = 416\times10^{36} \Rightarrow \omega = 20.4\times10^{18}$$

$$\text{and } v = \frac{\omega}{2\pi} = \frac{20.4}{2\pi}\times10^{18} = 3.25\times10^{18}\,s^{-1}$$

❑ DERIVATION OF RELATION FOR THE TIME PERIOD OF AN ELECTRON IN ORBIT

$v = 2\pi r N$ (N = revolution frequency)

$$N = \frac{v}{2\pi r} = \frac{2\pi^2 KZe^2 . 4\pi^2 mKZe^2}{nh.2\pi.n^2h^2}$$

$$\boxed{N = \frac{4\pi^3 . K^2 mZ^2 e^4}{n^3 h^3}}$$

$$\text{Time period } (T_n) = \frac{1}{\text{Revolution frequency}} = \boxed{\frac{n^3h^3}{4\pi^3 . K^2 mZ^2 e^4}}$$

so , $T_n \propto \frac{n^3}{z^2}$

The important points regarding the time period given as below –

◎ $T \propto \frac{n^3}{Z^2}$

$\Rightarrow$ $T \propto n^3$ (where Z is constant)

$T \propto \frac{1}{Z^2}$ (where n is constant)

e.g., The plots of 'T' against 'n' gives positive gradiation and 'T' against 'Z' gives negative gradiation.

◎ For different orbits of an atom,

$$\frac{T_1}{T_2} = \frac{{n_1}^3}{{n_2}^3}$$

◎ For a given orbit of two different species (say A and B)

$$\frac{T_A}{T_B} = \frac{{Z_B}^2}{{Z_A}^2}$$

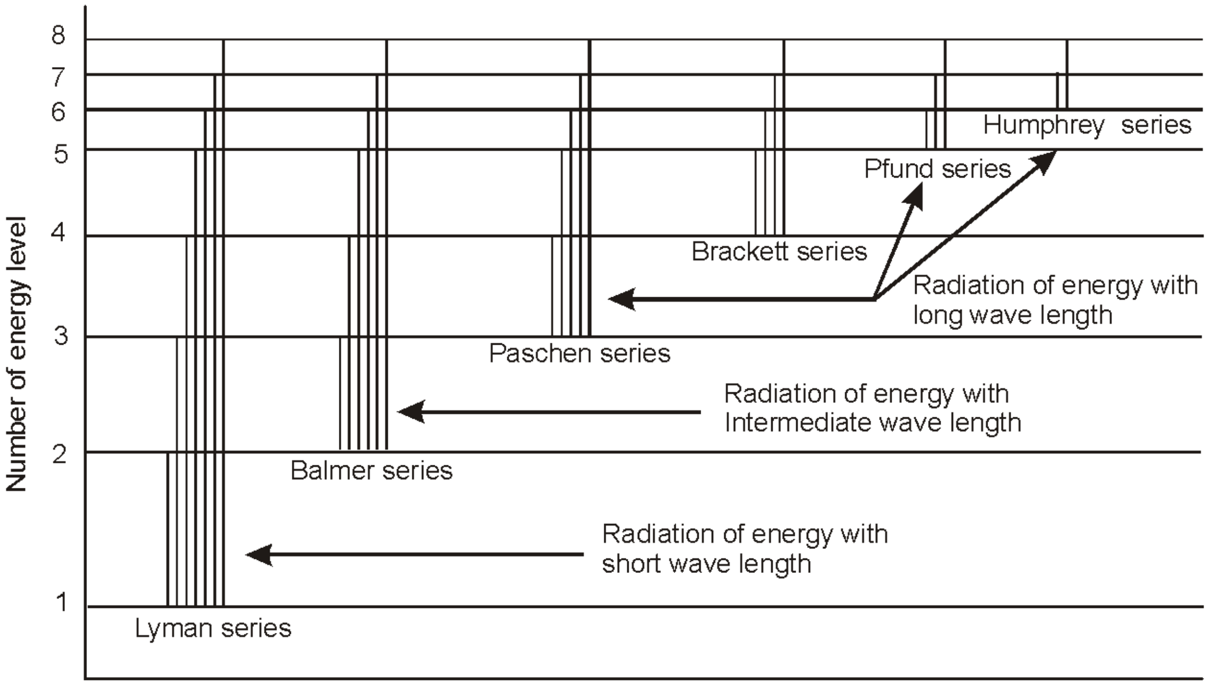
◎ For two different orbits of two different species,

$$\frac{T_1}{T_2} = \frac{n_1^3}{n_2^3} \times \frac{Z_2^2}{Z_1^2}$$

➲ LIMITATIONS OF BOHR'S MODEL :

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

- It does not explain the spectra of atoms having more than one electron.
- Bohr's atomic model failed to account for the effect of magnetic field (Zeeman effect) or electric field (Stark effect) on the spectra of an atoms or ions. It was observed that when the source of a spectrum is placed in a strong magnetic or electric field, each spectral line further splits into a number of lines. This observation could not be explained on the basis of Bohr's model.
- It could not explain the ability of atoms to form molecules by chemical bonds.
- de Broglie suggested that electrons like light have dual character. It has particle and wave character. Bohr treated the electron only as a particle
- Another objection to Bohr's theory came from Heisenberg's Uncertainty Principle. According to this principle "It is impossible to determine simultaneously the exact position and momentum of a small moving particle like an electron". The postulate of Bohr, that electrons revolve in well defined orbits around the nucleus with well defined velocities is thus not tenable.



Hydrogen atomic spectra

■ Lyman Series

(a) It is a first series of spectral series of H.

(b) It was found out in ultraviolet region in 1898 by ***Lyman***.

(c) It's value of $n_1 = 1$ and $n_2 = 2, 3, 4....$ where 'n_1' is ground state and 'n_2' is called excited state of electron present in a H - atom.

(d) If the electron goes to $n_1 = 1$
to $n_2 = 2$ — First Lyman series
If the electron goes to $n_1 = 1$
to $n_2 = 3$ — Second Lyman series
If the electron goes to $n_1 = 1$
to $n_2 = 4$ — Third Lyman series ----- so on.

(e) $\frac{1}{\lambda} = R_H\left[\frac{1}{1^2} - \frac{1}{n_2^{\ 2}}\right]$ where $n_2 > 1$ always.

(f) The wavelength of marginal line = $\frac{n_1^{\ 2}}{R_H}$ for all series. So, for Lyman series = $\frac{1}{R_H}$

■ Balmer series :

(a) It is the second series of H-spectral series.

(b) It was found out in 1892 in visible region by **Balmer**.

(c) Balmer series was found out before all series. Because it was found to be in visible region.

(d) It's value of $n_1 = 2$ and $n_2 = 3, 4, 5$ .... where n_1 is ground state and n_2 is excited state.

(e) If the electron goes to $n_1 = 2$
to $n_2 = 3$ — First Balmer series
If the electron goes to $n_1 = 2$
to $n_2 = 4$ — Second Balmer series
If the electron goes to $n_1 = 2$
to $n_2 = 5$ — Third Balmer series .... so on

(f) The wavelength of marginal line of Balmer series = $\frac{n_1^{\ 2}}{R_H} = \frac{2^2}{R_H} = \frac{4}{R_H}$

(g) $\frac{1}{\lambda} = R_H\left(\frac{1}{2^2} - \frac{1}{n_2^{\ 2}}\right)$ where $n_2 > 2$ always

■ Paschen series :

(a) It is the third series of H - spectrum.

(b) It was found out in infra-red region by ***Paschen***.

(c) It's value of $n_1 = 3$ and $n_2 = 4, 5, 6$ .... where n_1 is ground state and n_2 is excited state.

(d) If the electron goes to $n_1 = 3$
to $n_2 = 4$ — First Paschen series
If the electron goes to $n_1 = 3$
to $n_2 = 5$ — Second Paschen series
If the electron goes to $n_1 = 3$
to $n_2 = 6$ — Third Paschen series ------ so on.

(e) The wavelength of marginal line of Paschen series = $\frac{n_1^2}{R_H} = \frac{3^2}{R_H} = \frac{9}{R_H}$.

(f) $\frac{1}{\lambda} = R_H\left[\frac{1}{3^2} - \frac{1}{n_2^2}\right]$ where $n_2 > 3$ always.

- **Brackett series :**

(a) It is fourth series of H - spectrum.

(b) It was found out in fra infra-red region by **Brackett**.

(c) It's value of $n_1 = 4$ and $n_2 = 5, 6, 7$ .... where n_1 is ground state and n_2 is excited state.

(d) If the electron goes to $n_1 = 4$
to $n_2 = 5$ — First brackett series
If the electron goes to $n_1 = 4$
to $n_2 = 6$ — Second brackett series
If the electron goes to $n_1 = 4$
to $n_2 = 7$ — Third brackett series ------ so on.

(e) The wavelength of marginal line of brackett series = $\frac{n_1^2}{R_H} = \frac{4^2}{R_H} = \frac{16}{R_H}$

(f) $\frac{1}{\lambda} = R_H\left[\frac{1}{4^2} - \frac{1}{n_2^2}\right]$, where $n_2 > 4$ always.

- **Pfund series :**

(a) It is fifth series of H - spectrum.

(b) It was found out in fra infra-red region by Pfund.

(c) It's value of $n_1 = 5$ and $n_2 = 6, 7, 8$ .... where n_1 is ground state and n_2 is excited state.

(d) If the electron goes to $n_1 = 5$
to $n_2 = 6$ — first Pfund series
If the electron goes to $n_1 = 5$
to $n_2 = 7$ — second Pfund series
If the electron goes to $n_1 = 5$
to $n_2 = 8$ — third Pfund series -----so on.

(e) The wavelength of marginal line of Pfund series = $\frac{n_1^2}{R_H} = \frac{5^2}{R_H} = \frac{25}{R_H}$

(f) $\frac{1}{\lambda} = R_H\left[\frac{1}{5^2} - \frac{1}{n_2^2}\right]$ where $n_2 > 5$ always.

- **Humphrey series :**

(a) It is the sixth series of H - spectrum.

(b) It was found out in fra infra-red region by ***Humphrey***.

(c) It's value of $n_1 = 6$ and $n_2 = 7, 8, 9$ --------- where n_1 is ground state of electron and n_2 is excited state.

(d) If the electron goes to $n_1 = 6$
to $n_2 = 7$ — first Humphrey series
If the electron goes to $n_1 = 6$
to $n_2 = 8$ — second Humphrey series
If the electron goes to $n_1 = 6$
to $n_2 = 9$ — third Humphrey series ... so on.

(e) The wavelength of marginal line of Humphrey series = $\frac{n_1^2}{R_H} = \frac{6^2}{R_H} = \frac{36}{R_H}$

(f) $\frac{1}{\lambda} = R_H\left[\frac{1}{6^2} - \frac{1}{n_2^2}\right]$ where $n_2 > 6$.

Note

- The order of λ and $\bar{\nu}$ for the spectrum lines :

  $\bar{\lambda}_1 > \bar{\lambda}_2 > \bar{\lambda}_3$ ......

  $\nu_1 < \nu_2 < \nu_3$ ......
- Energy of the spectral lines :
  $E_1 < E_2 < E_3$ .....
- The intensity of spectral lines :
  $I_1 > I_2 > I_3$ .... (where I = Intensity, I_1 = intensity of first line)
- The intensity of spectral lines in the H-like species.

  $I_H > I_{He^{++}} > I_{Li^+}$ .....
- In any spectral series, the total number of spectral lines.

  $\sum n_2 - n_1$ (where electron jumps from n_2 to n_1)

  or, $\frac{(n_2 - n_1)(n_2 - n_1 + 1)}{2}$
- Electron jumps from $n_2 = 5$ to $n_1 = 2$

  Thus total spectral lines will be $\sum(5-2) = \sum 3 = 1 + 2 + 3 = 6$
- The isotopes of an element has different spectrum of wavelength.

Concept Illustrator

Calculate the wave number for the shortest wavelength transition in the Balmer series of atomic hydrogen.

Sol. Shortest wave length in balmer series means, $n_1 = 2$, $n_2 = \infty$

Substitute the values in the following relation

$$\bar{\nu} = \frac{1}{\lambda} = R_H \times z^2\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right] = 109677 \times 1^2\left[\frac{1}{4} - 0\right] = \frac{109677}{4} = 27419.25\ \text{cm}^{-1}$$

What are resonance potential, excitation potential, ionisation potential and critical potential?

- **Resonance Potential :** The minimum potential to accelerate a bombarding electron to its higher state.
- **Excitation Potential :** The values of potentials necessary to cause excitation of higher states are called excitation potentials.
- **Ionisation Potential :** The potential needed to accelerate the bombarding electron so as to completely detach an electron from the atom is called ionisation potential.
- **Critical Potential :** The resonance, excitation and ionisations potential are collectively called critical potentials.

Concept Illustrator

The energy required to remove an electron from $n=1$ to $n=\infty$ orbit is called the ionisation potential or ionisation energy for the hydrogen atom.

Sol. Ionisation potential for hydrogen atom $=\frac{1}{2}\frac{Z^2e^4m}{(4\pi\varepsilon_0)^2\hbar^2}\left[\frac{1}{1}-\frac{1}{\infty}\right]$

$$=\frac{1}{2}\times\frac{1^2\times\left(1.6\times10^{-19}\right)^4\times9\times10^{-31}\times\left(9\times10^9\right)^2}{\left(1.054\times10^{-34}\right)^2}\text{J}$$

$$=2150\times10^{-21}\,\text{J}=\frac{2150\times10^{-21}}{1.6\times10^{-19}}eV=13.4\text{ eV}$$

Note

Velocity of electron is independent of mass, therefore it is unaffected by the motion of nucleus.

PHOTOELECTRIC EFFECT

☐ INTRODUCTION :

When light of sufficiently high frequency is incident on a metal surface electrons are ejected from the metal. This phenomenon is called the photoelectric effect. The electrons ejected from the metal are called photoelectrons.

☐ SOME DEFINITIONS :

❖ **Work Function (φ) :**

The minimum energy required by an electron to free itself from the surface of the metal is called work function of the metal. It is a property of the metal and is different for different metals.

❖ **Threshold Energy :**

The minimum energy of incident light for which photoelectric effect is possible is called threshold energy. Threshold energy and work function of a metal are equal in magnitude.

Thus, if $h\nu_0$ is the threshold energy and ϕ is work function of the material, then $\boxed{h\nu_0=\phi}$

❖ **Threshold Frequency (ν_0) :**

The minimum frequency of photons of light for which photoelectric effect is possible is called threshold frequency.

It is frequency of photons of threshold energy.

Thus, $h\nu_0=\phi$

$\Rightarrow \boxed{\nu_0=\phi/h}$

If frequency of incident light, ν is less than threshold frequency then no photoelectric effect takes place.

i.e., $\nu<\nu_0$ $\Rightarrow$ no photoelectric effect.

❖ **Threshold Wavelength (λ_0) :**

The maximum wavelength of photons of incident light for which photoelectric effect is possible is called the threshold wavelength of the metal.

Threshold energy = work function

$$\Rightarrow \boxed{\lambda_0=\frac{hc}{\phi}} \quad \Rightarrow \lambda_0=\frac{12420\,(\text{eV}-\text{Å})}{\phi(\text{in eV})} \quad \Rightarrow \eta\nu_0=\phi \;\Rightarrow\; \frac{hc}{\lambda_0}=\phi$$

☐ EINSTEIN’S THEORY OF PHOTOELECTRIC EFFECT :

Photon is an energy packet, i.e., quantum of light energy with no charge and zero rest mass which carries energy E (= $h\nu$) and momentum p (= E /c).

When an electron absorbs a photon with energy $h\nu$ which is greater than threshold energy then it may come out with a

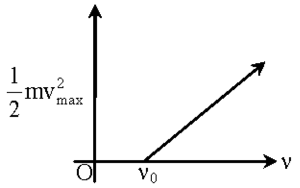
$$KE = h\nu - \phi \;;\quad \phi = \text{work function.}$$

While coming out it may loose some part of its KE in collisions with other atoms or electrons so $(h\nu - \phi)$ is the maximum KE with which it may come out.

$$K_{min} = \text{zero}; \quad \boxed{K_{max} = h\nu - \phi}$$

The above equation is called Einstein’s equation for photoelectric - effect.

If v_{max} is the speed of most energetic photoelectron ejected from the metal, then



Plot of maximum kinetic energy versus frequency of incident light

$\frac{1}{2}mv^2_{max} = K_{max} = h\nu - \phi$? and

$\phi = h\nu_0$, where ν_0 = threshold frequency

$$\therefore \quad \frac{1}{2}mv^2_{max} = h(\nu - \nu_0)$$

Note The range of kinetic energy of photoelectrons ejected is $0 \le K \le K_{max}$

i.e., $0 \le K \le (h\nu - \phi)$

❖ Stopping Potential (V_s) :

It is the minimum negative potential with respect to the cathode which is just sufficient to stop the most energetic photoelectrons.

As an electron when accelerated by V volt acquires energy, eV ; the maximum kinetic energy of photoelectrons in terms of stopping potential will therefore be ,

$$K_{max} = eV_s$$

❖ Dependence of Photoelectric current on various factors :

Photoelectric current

Photoelectric current, i = ne

Where n = the number of photoelectrons collected per sec by the collector and e is the charge of an electron.

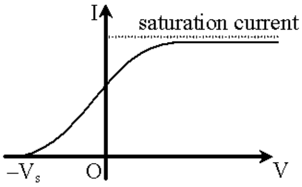
The photoelectric current depends on the following factors.

- Intensity of incident light
- Potential difference between the plate and the collector
- Frequency of the incident light.

❖ Effect of the intensity of incident light on photoelectric current

The photoelectric current is proportional to the intensity of the light as shown in adjacent figure.

❖ Effect of Potential difference on photoelectric current



Current versus potential difference (V) curve

The photoelectric current I increases with the potential difference V.

❖ Effect of frequency on photoelectric current

Higher the frequency higher the value of stopping potential .

The maximum kinetic energy of the electrons depends on the light sources and the plate material, but not on the intensity of the source.

Concept Illustrator

The work function of a photoelectric material is 3.3 eV. Find out its threshold frequency.

Sol. Threshold frequency $\nu_0 = \dfrac{\text{Work function}}{h} = \dfrac{3.3 \times 1.6 \times 10^{-19}\,\text{J}}{6.6 \times 10^{-34}\,\text{JS}} = 8 \times 10^{-14}\,\text{S}^{-1}$

☐ de BROGLIE'S THEORY

Inorder to rectified the Bohr's theory de Broglie's wave partical duality is very much important.

Light has dual property –

i) wave property ii) particle property

The wave property can be expressed by the Plank's equation

$$E = h\nu \qquad \text{... (i)}$$

The particle property can be expressed by the Einstein equation –

$$E = mc^2 \qquad \text{... (ii)}$$

From (i) and (ii) we get

$$h\nu = mc^2 \qquad \text{or, } \nu = \frac{mc^2}{h} \qquad \text{or, } \frac{c}{\lambda} = \frac{mc^2}{h}$$

$$\text{or, } \frac{1}{\lambda} = \frac{mc}{h} \qquad \text{or, } \lambda = \frac{h}{p} \quad \text{[Where p = momentum]}$$

According to de Broglie like light all moving matter which associated with both wave property as well as particle property. According to him

$$\lambda_{\text{light}} = \frac{h}{mc}, \qquad \lambda_{\text{matter}} = \frac{h}{mv}$$

So, the de Broglie's equation is $\lambda_{\text{matter}} = \dfrac{h}{mv}$

Note

The waves associated with material particles or objects in motion are called **matter waves** or **de Broglie waves.**

■ de Broglie's equation and K.E.

Let K.E. of the particle of mass 'm' is E.

$E = \frac{1}{2}mv^2$ $\qquad$ $2Em = m^2v^2$

$\sqrt{2Em} = mv = P$ $\qquad$ $\lambda = \frac{h}{P} = \frac{h}{\sqrt{2Em}}$

Number of waves in an orbital

$n = \frac{2\pi r}{\lambda} = \frac{2\pi r \times mv}{h}$ $\qquad$ $n = \frac{mvr \times 2\pi}{h}$

mvr = angular momentum = $\frac{nh}{2\pi}$ (according to Bohr Model) where n = 1, 2, 3, ...

Thus number of waves in an orbital = $\frac{nh}{2\pi} \times \frac{2\pi}{h} = n$

$\therefore$ Number of waves in an orbital = n.

Note

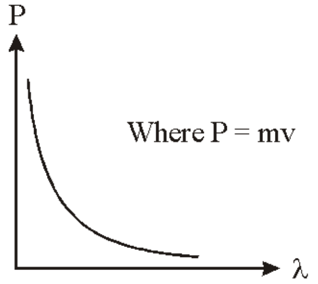
If ω be angular velocity of the electron then –

$mr\omega = \frac{h}{\lambda}$ $\qquad$ or, $\omega = \frac{h}{\lambda \times (mr)}$

Always keep in your mind that :

$mv(p) \propto 1/\lambda$ $\qquad$ or, $v \propto 1/\lambda$

Hence,



In the case of Dual equation :

- The particle at rest has infinity wavelength $(\because \ \lambda = h/mv, \ \text{If} \ v \to 0, \ \lambda \to \infty)$
- The nucleus of an atom does not acquire infinity wavelength because nucleus does not at rest.
- de-Broglie's equation was verified by Davisson and Germer.
- Velocity of an electron $\neq$ velocity of light i.e., $v \neq c$

  If v = c, then from equation, $m_v = \frac{m_e}{\sqrt{1 - \frac{v^2}{c^2}}}$, $mv \to 0$, which it is impossible.

- $\lambda \propto \frac{n}{Z}$ $\quad (\because \ \lambda \propto 1/v \ \text{and} \ v \propto Z/n)$

  Hence, wave length of an electron for definite orbit.

  $\lambda_H > \lambda_{He} > \lambda_{Li} > .....,$ and for different orbits of n atom, $\lambda_1 < \lambda_2 < \lambda_3$ ...... viz in infinity orbit, $\lambda = \infty$.

Concept Illustrator

Calculate the wave length associated with an electron moving with a velocity of 10^8 cm per second.

Sol. According to de Broglie relationship $\lambda = \frac{h}{mv}$

$$\therefore \lambda = \frac{6.62\times10^{-34}}{9.1\times10^{-31}\times10^{6}} = \frac{6.62\times10^{-9}}{9.1} m = 7.27 \times 10^{-10} = 7.27 \text{ Å}$$

☐ HEISENBERG UNCERTAINTY PRINCIPLE

According to Heisenberg uncertainty principle for a moving particle it is never possible to determine both the position and momentum simultaneously acurately.

This is given in the form of an equation $\Delta x \times \Delta p \geq \frac{h}{4\pi}$

Where Δx is the uncertainty in the position of an electron and Δp is the uncertainty in its momentum measured simultaneously. This equation can also be written as $\Delta x \times m\Delta v \geq \frac{h}{4\pi}$

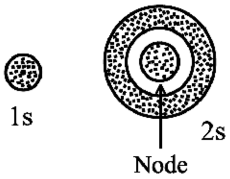
Concept Illustrator

Calculate the uncertainity in the velocity of a bullet weighing 10 gm, whose position is known with ± 0.01 mm.?

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

$$\Delta v = \frac{h}{4\pi m\Delta x} \quad \therefore \Delta v = \frac{6.62\times10^{-34}}{4\times3.142\times10^{-2}\times10^{-5}} = 0.527 \times 10^{-27} \text{ m/s}$$

NODES AND NODAL POINTS



The point where there is zero probability of finding an electron is called nodal point or node. No. of radial or spherical nodes = $n - \ell - 1$

No. of angular nodes = ℓ

Total no. of nodes = $n - 1$

No. of nodal planes = No. of angular nodes = ℓ

Concept Illustrator

Calculate the radial node number of 3s, 3p and 3d.

Sol. Radial node number = $n - \ell - 1$

Radial node number of 3s = 3 – 0 – 1 = 2

Radial node number of 3p = 3 – 1 – 1 = 1

Radial node number of 3d = 3 – 2 – 1 = 0

VARIOUS QUANTUM NUMBERS AND THEIR SIGNIFICANCE

The numbers used for completely characterizing each electron of atom are known as quantum numbers. Four such quantum numbers are found to be necessary for describing an electron

A. Principal Quantum Number (*n*)

Origin : In Bohr's model, it was introduced from the hypothesis, *i.e.*, $mur = n\left(\frac{h}{2\pi}\right)$, while in the wave mechanics, it gets automatically originated in having the well-behaved radial wave functions $R(r)$ from the solution of the Schrodinger wave equation.

It may have any non zero positive integral value up to infinity, *i.e.*, $n = 1, 2, 3 \cdots\cdots\infty$

Information provided by the quantum number (*n*)

(i) In Bohr's model and in Schrodinger's non-relativistic wave mechanical model, the energy of the electron in a hydrogen like system is absolutely governed by the principal quantum number as follows :

$$E_n = \frac{2\pi^2 m Z^2 e^4}{n^2 h^2}$$, (*m* = mass of the electron) (in CGS system)

$$= -\frac{2\pi^2 \mu Z^2 e^4}{n^2 h^2}$$, (more correct representation, where μ = reduced mass)

Therefore, $E_1 < E_2 < E_4 \cdots\cdots$, and $(E_\infty - E_1)$ gives the measure of ionisation energy for the hydrogen-like systems in ground state. Thus with the increase of *n*, the energy of the electron increases.

The shells or energy levels are designated by the capital letters, *K, L, M*, ···· according to the values of *n* as follows :

$K(n=1), L(n=2), \ M(n=3), \ N(n=4)\cdots\cdots$

(ii) The Bohr's model, the position of the electron measured from the nucleus is governed by the quantum number, *n* as follows (in CGS system) :

$$r_n = \frac{n^2 h^2}{4\pi^2 m e^2 Z}; \quad \text{or} \quad r_n \propto n^2$$

In the wave mechanical model, the most probable region for the existence of the electron cloud is governed by both *n* and azimuthal quantum number, *l* (*cf*, radial distribution function). But it is worth mentioning that in the wave mechanical model also, the distance of the most probable region from the nucleus is majorly governed by the principal quantum number and the effect of the azimuthal quantum number is comparatively small. Thus the conclusion drawn either from the Bohr's model or from the wave mechanical model is roughly the same.

(iii) The principal quantum number determines the total number of electrons which can be accommodated in a particular shell. This maximum capacity is given by $2n^2$ as given below :

Shell	K	L	M	N
Max. Capacity :	2×1^2	2×2^2	2×3^3	2×4^2

This $2n^2$ relationship results from the consideration of Pauli exclusion principle.

B. Azimuthal Quantum Number (*l*)

Origin : In the Sommerfeld's atomic model, the azimuthal quantum number (*k*) gets originated from the hypothesis introduced in the concept of elliptical locus for the moving electron. But in the wave mechanical model it comes to our picture to make functions, $\Theta(\theta)$ (a part of the spherical harmonic in the total wave function) acceptable.

The wave mechanical azimuthal quantum number (*l*) and the Sommerfeld's azimuthal quantum number (*k*) are related $: l = k - 1$. The quantum number *l* can have values, $0, \ 1, \ 2, \cdots (n-1)$. It is also called the angular momentum quantum number as it gives the measure of angular momentum of the electron. It is also called orbital or subsidiary quantum number.

Information provided by the quantum number (*l*)

(i) In the Sommerfeld' model, the azimuthal quantum number determines the shape, *i.e.*, the ellipticity of the orbit under consideration. In the wave mechanical model, the spherical harmonic *i.e.*, the angular part of the complete wave function, determines the shape of the corresponding orbital. This spherical harmonic is dependent on both the azimuthal quantum number, *l* and the magnetic quantum number, *m* Thus, in both the models, the azimuthal quantum number determines the shape of the orbit or orbital. The *s*-orbital is spherically symmetrical, the *p*-orbitals are dumb-bell shaped and the *d*-orbitals are four lobed in general.

(ii) The types of the orbitals are designated by the values of the azimuthal quantum number as follows :

l :	0	1	2	3	4	5
Type of the orbital :	*s*	*p*	*d*	*f*	*g*	*h*

The names of the first four orbitals, *i.e., s, p, d* and *f* (the first letters of the spectroscopic terms, sharp, principal, diffuse and fundamental respectively), are coined from the spectroscopy. The corresponding spectral lines developed for the electron transition from the higher levels to these orbitals (*i.e., s, p, d* and *f*) are called sharp, principal, diffuse and fundamental respectively. The names of the remaining orbitals follow alphabetically.

Thus, the number of orbitals for a particular shell is given as follow :

$$\begin{array}{llll} K-shell & L-shell & M-shell & N-shell \\ (n=1) & (n=2) & (n=3) & (n=4) \\ \downarrow & \downarrow & \downarrow & \downarrow \\ \hline 1s & 2s,\ 2p & 3s,\ 3p,3d & 4s,\ 4p,\ 4d,\ 4f \end{array}$$

(iii) In the radial wave function, the number of radial nodes of the orbitals is given by $(n-l-1)$. In the angular wave function, the number of nodal surface is given by *l*.

(iv) From the radial distribution probability in the wave mechanics, and from the ellipticity of the orbits in Sommerfeld's model, the penetrating power of the orbitals or orbits is given in the sequence, $s > p > d > f$ for a particular principal quantum number.

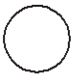
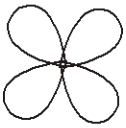
(v) The orbital angular momentum p_t is quantised as follows :

$$\vec{l} = p_l = l\left(\frac{h}{2\pi}\right), \text{ (in classical mechanics) } = \sqrt{l(l+1)}\left(\frac{h}{2\pi}\right), \text{ (in wave mechanics)}$$

(vi) In spectral transition, the selection rule governed by *l* is given by $\Delta l = \pm 1.$ Δl values also controls the intensity rule.

(vii) In both Dirac's relativistic wave mechanical model and Sommerfeld's relativistic classical model, the energy is found to depend slightly on *l*.

(viii) Shapes of orbital.

ℓ value	Subshell	Shape of orbitals	
$\ell = 0$	s	Spherical	
$\ell = 1$	p	Dumb-bell	
$\ell = 2$	d	Double dumb-bell	
$\ell = 3$	f	Complicated	

From ℓ = 4 onward, the subshells are denoted by letters in alphabetical orders, *e.g.* ℓ = 4, g subshell, ℓ = 5, h sub-shell and so on.

C. Magnetic Quantum Number, $m(\equiv m_1 \text{ in vector Model})$

Origin: To have the acceptable solutions of the function, $\Phi(\phi)$, a part of the spherical harmonic of the complete wave function, the magnetic quantum number *m* comes to the picture. In the vector model, it appeared to explain the Zeeman effect and Stark effect. In the vector model, we have designated this by m_l. In the vector model, the quantum number, m_l appears due to the quantised orientation of the orbital momentum vector with respect to the direction of the external magnetic field.

The magnetic quantum number, *m* can have values as : $m = \pm l,\ \pm(l+1),\ \pm(l-2)$

Therefore, for a particular value of *l* it can have $(2l+1)$ values.

- **Information provided by the quantum number, *m* or m_l**

(i) From the permitted values of *m* the following results appear :

	s-orbital	p-orbital	d-orbital	f-orbital
m :	$(l=0)$	$(l=1)$	$(l=2)$	$(l=3)$
	0	$0,\ \pm1$	$0,\ \pm1,\ \pm2$	$0,\ \pm1,\ \pm2,\ \pm3$
	(one orbital)	(a set of three orbitals)	(a set of five orbitals)	(a set of seven orbitals)

(ii) The wave functions developed from the permitted values of *m* are not always real. The real wave functions such as $(p_x,\ p_y,\ p_z)$ or $d_{xy},\ d_{yz},\ d_{xz},\ d_{x^2-y^2},\ d_z^2$ do not have one to one correspondence with the *m* values except when $m=0$. For example $m=0,\ (l=1,\ n=2,\ 3.....)$ leads to p_z and $m=0,\ (l=2,\ n=3,\ 4,...)$ leads to d_z^2 while the orbitals like $p_x,\ p_y,\ d_{xy},\ d_{yz},\ d_{xz},\ d_{x^2-y^2}$ are the linear combinations of the wave functions described by the nonzero values of *m*. For example, p_x and p_y are obtained from the linear combination of the wave functions developed from $m=\pm1,\ (l=1,\ n=2,\ 3,\ 4......)$. Similarly $m=\pm2,\ (l=2, n=3, 4, 5....)$ produces $d_{x^2-y^2}$ and d_{xy} through the linear combinations. Thus the real orbitals (except, $m=0$) are obtained through the linear combinations of the imaginary wave functions (*i.e,* spherical harmonics) produced from the nonzero values of m.

(iii) The spherical harmonic, *i.e.*, angular part of the complete wave function, is given by $: Y_{l,m} = \Theta_{\lambda,\ \mu}(\theta)\times\Phi_m(\phi)$ which determines the shape of the orbitals. Thus, *l* and *m* jointly determine the angular wave function, *i.e.*, the shape of the orbitals.

(iv) In the absence of any external magnetic field, the orbitals generated for a particular value of *l* due to the different *m* values (*e.g.* the three *p*-orbitals determined by $m=0,\ \pm1$ or the five *d*-orbitals determined by $m=0,\ \pm1,\ \pm2$ or the seven *f*-orbitals determined by $m=0,\ \pm1,\ \pm2,\ \pm3$) are degenerate. But in the presence of any external magnetic or electric field, the degeneracy is removed. This splitting by an external magnetic field can explain the Zeeman effect and similarly, the Stark effect is also explainable due to the splitting of the orbitals (having different *m* values for a particular value of *l* in the presence of an external electric field.

D. Spin Quantum Number (*s*)

Origin: In Dirac's relativistic wave mechanical model, the spin quantum number appears to make the solutions acceptable. But it has got no existence in the nonrelativistic Schrodinger's wave equation. In the vector model, the concept of a spinning electron was introduced by Uhlenbeck and Goudsmit. It is having the nonintegral value, $\frac{1}{2}$. It actually measures the angular momentum of the electron due to its spinning motion. In a magnetic field, it has got only two quantised orientations giving rise to the magnetic spin quantum number (m_s) which is given by $\pm s, \quad i.e., \pm\frac{1}{2}$.

- **Information provided by the spin quantum numbers :**

(i) It is extremely important to explain the observation in the experiment of Stern and Gerlach. Due to the two possible orientations of the spinning angular momentum vector in the presence of an external magnetic field, the beam of doublet $\left(S=\frac{1}{2}\right)$ atoms such as hydrogen, silver or copper etc. containing one unpaired electron undergoes bifurcation. The singlet systems $(S=0)$ containing paired electrons for which the resultant spin quantum number becomes zero, do not undergo any splitting in the presence of an external magnetic field. According to the Pauli exclusion principle, the two paired electrons are having opposite spins.

(ii) The spin angular momentum (p_s) developed due to the spinning motion of the electron around its own axis is given by,

$$\vec{s} = p_s = s\left(\frac{h}{2\pi}\right), \qquad \text{(in classical mechanics)}$$

$$= \sqrt{s(s+1)}\left(\frac{h}{2\pi}\right) \qquad \text{(in wave mechanics)}$$

(iii) During the electron transition between the states, the selection rule, $\Delta S = 0$ (where S stands for the resultant spin quantum number) is maintained.

(iv) It determines spin only value of the magnetic moment of any atom, molecule or ion using the equation.

$$\mu_s = \sqrt{n(n+2)}\,B.M$$

❖ **Relationship between the various quantum number**

Principal quantum number (n)	Azimuthal quantum number (ℓ)	Magnetic quantum number (m)	Spin quantum number (s)	Number of orbitals in a sub shell
1	one → 0	one (0)	$\pm\frac{1}{2}$	1 → 1s
2	Two → 0 → 1	one (0) Three (+1, 0, −1)	$\pm\frac{1}{2}$ $\pm\frac{1}{2}, \pm\frac{1}{2}, \pm\frac{1}{2}$	1 → 2s 3 → $2p_x$, $2p_y$, $2p_z$
3	Three → 0 → 1 → 2	one (0) Three (+1, 0, −1) Five (+2, +1, 0, −1, −2)	$\pm\frac{1}{2}$ $\pm\frac{1}{2}, \pm\frac{1}{2}, \pm\frac{1}{2}$ $\pm\frac{1}{2}, \pm\frac{1}{2}, \pm\frac{1}{2}, \pm\frac{1}{2}, \pm\frac{1}{2}$	1 → 3s 3 → $3p_x$, $3p_y$, $3p_z$ 5 → $3d_{xy}$, $3d_{yz}$, $3d_{xz}$, $3d_{x^2-y^2}$, $3d_{z^2}$

Concept Illustrator

Write the four quantum number values for the unpaired electron, present in ground state of 'Cu' atom.

Sol. The electronic configuration of 'Cu' atom in ground state is

$$_{29}Cu \rightarrow 1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,3d^{10}\,4s^1.$$

The unpaired electron is in the '4s' orbital for which n = 4, ℓ = 0, m = 0 and s = $+\frac{1}{2}$ or $-\frac{1}{2}$

SHAPE OF ATOMIC ORBITALS

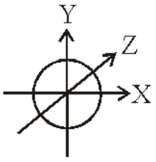
An orbital is the region of space around the nucleus within which the probability of finding an electron of given energy is maximum (90 – 95%). The shape of this region (electron cloud) gives the shape of the orbital. It is basically determined by the Azimuthal quantum number ℓ, while the orientation of orbital depends on the magnetic quantum number (m). Let us now see the shapes of orbitals in the various subshells.

(i) Shape of 's' orbital :

(a) For 's' subshell $\ell = 0$ & $m = 0$ so 's' orbital have only one unidirectional orientation i.e. the probability of finding the electron is same in all directions. The shape of s orbital is sperical

(b) The size and energy of 's' orbital with increasing 'n' will be 1s < 2s < 3s < 4s.

(c) It does not consist any directional property.

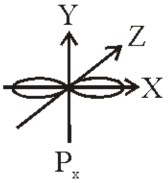


(ii) Shape of p-orbitals :

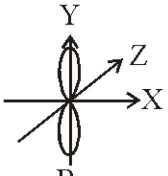
(a) For 'p' subshell $\ell = 1$ & $m = +1, 0, -1$ means there are three 'p' orbitals, which is symbolised as p_x, p_y, p_z.

(b) Shape of 'p' orbital is dumbbell in which the two lobes on opposite side separated by the nodal plane.

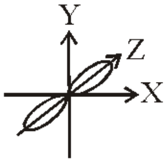
(c) p-orbital has directional properties.



P_x



P_y



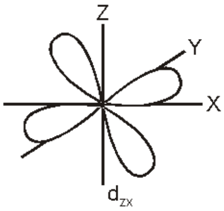
P_z

(iii) d-orbitals :

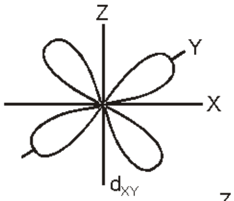
(a) For the 'd' subshell $\ell = 2$ then the values of 'm' are –2, –1, 0, +1, +2. It shows that the 'd' orbitals has five orbitals as d_{xy}, d_{yz}, d_{zx}, d_{x2-y2}, d_{z2} .

(b) The 'd' orbital is bidumb-belled.

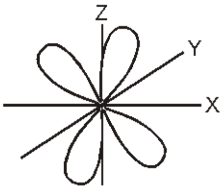
(c) It has directional properties.



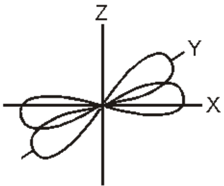
d_{zx}



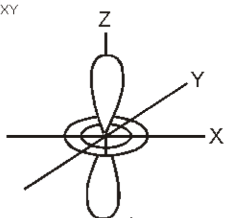
d_{XY}



d_{YZ}



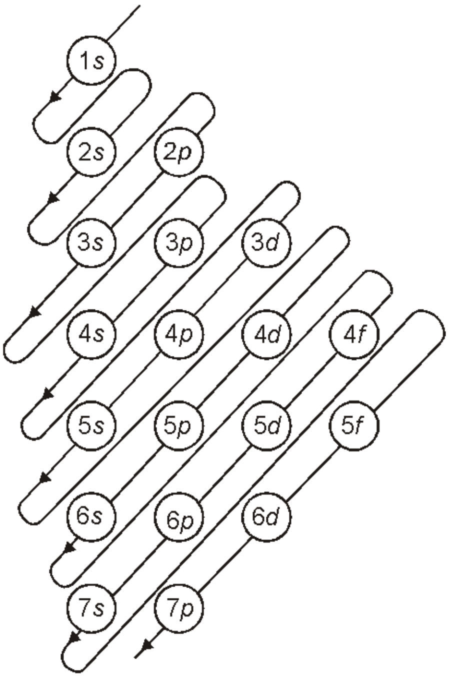
$d_{X^2-Y^2}$



d_{Z^2}

DISTRIBUTION OF ELECTRONS

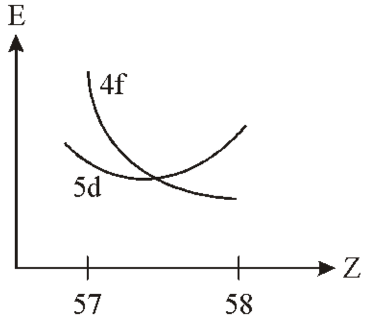
(a) **Aufbau Principle :** The word '*aufbau*' in German means 'building up', The building up of orbitals means the filling up of orbitals with electrons. The principle states**: In the ground state of the atoms, the orbitals are filled in order of their increasing energies**. In other words, electrons first occupy the lowest energy orbital available to them and enter into higher energy orbitals only after the lower energy orbitals are filled. The order in which the energies of the orbitals increase and hence the order in which the orbitals are filled as follows : 1*s*, 2*s*, 2*p*, 3*s*, 3*p*, 4*s*, 3*d*, 4*p*, 5*s*, 4*d*, 5*p*, 4*f*, 5*d*, 6*p*, 7*s*...



❖ **Deviation of Aufbau Principle :**

Electronic configuration of La_{57} should be [Xe] $6s^2\ 5d^0\ 4f^1$ (according to Aufbau principle) but actual electronic configuration is [Xe] $6s^2\ 5d^1\ 4f^0$. Similarly, for Ac_{89} according to Aufbau [Rn] $7s^2\ 6d^0\ 5f^4$ but acutal electronic configuration is [Xe] $7s^2\ 6d^1\ 5f^0$.

Explanation : Upon an increase in the charge of the nucleus the electrostatic attraction to it of an electron in given energy sublevel becomes stronger, and the energy of the electron diminishes. The energy of the electrons in the different sublevels changes differently because the charge of the nucleus screened to a different extent with respect to these electrons. In particularly the energy of 4f electrons diminishes with a growth in the charge of the nucleus more sharply than the energy of the 5d electrons.



Dependence of the energy of the 4f and 5d electrons on the nuclear charge

- $(n+l)$ **Rule :** From the above discussion, it appears that both the wave mechanics and classical mechanics can predict easily the order of energy of the sublevels originated from a particular principal quantum number. But it becomes extremely difficult to predict the sequence of energy of different sublevels (*i.e.* orbitals) developed from different principal quantum numbers. In this connection, the empirical $(n+l)$ rule is of much practical importance at least for the lighter elements. It is also applicable for the orbitals of the same principal quantum number. It is formulated as :

  (i) The energy of the orbitals increases with the increase of $(n+l)$ values. It is illustrated in the following cases :
  Energy : $1s<2s<3s<4s<5s;\ 4s<3d<4d<4f$
  $(n+l)$: $1<2<3<4<5;\ 4<5<6<7$

  (ii) For the same values of $(n+l)$ for a number of orbitals, the energy increases with the increase of *n*, It is illustrated as follows :
  Energy : 3d < 4p < 5s; 4f < 5d < 6p
  (*n*+*l*) 5 5 5 7 7 7
  n : 3 < 4 < 5 4 < 5 < 6

  Thus taking into the consideration of the $(n+l)$ rule, the following energy sequence can be formulated.
  $1s<2s<2p<3s<3p<4s<3d<4p<5s<4d<5p<6s<4f<5d<6p<7s<5f<6d<7p<8s$

- **Some exceptions to $(n+l)$ rule :**

  (i) $Ba(Z=56)$ is having electronic configuration $[Xe]6s^2$ where $[Xe]$ represents the electronic configuration of $Xe(Z=54)$ having the arrangement 2, 8, 18, 18, 8. Now for $La(Z=57)$, the 57th electron should go in $4f$ and it should be represented as : $[Xe]4f^1\ 6s^2$. But actually, it is having $[Xe]\ 4f^0\ 5d^1\ 6s^2$. Here $4f$ and 5d are having the same $(n+l)$ values, hence it should be $4f<5d$ in energy according to the $(n+l)$ rule. Thus, here it is violated. But it is interesting to note that for $Ce(Z=58)$, it is difficult to predict whether the configuration is $[Xe]\,4f^2\ 5d^0\ 6s^2$ or $[Xe]\ 4f^1\ 5d^1\ 6s^2$, as the energy difference between $4f$ and $5d$ in the range $Z=57-58$ is very small, and no general rule can be formulated

  (ii) For actinium, the same things as in the case of lanthanum occurs, $Ra(Z=88)$ is having the configuration $[Rn]7s^2$ where $Rn(Z=86)$ is having the arrangement 2, 8, 18, 32, 18, 8. For $Ac(Z=89)$, the expected configuration is $[Rn]\,5f^1\ 6d^0\ 7s^2$ but it is actually $[Rn]\,5f^0\ 6d^1\ 7s^2$. Here, again it is proposed that in this range no significant energy difference exists between $5f$ and $6d$.

(b) Pauli's exclusion principle : The number of electrons to be filled in various orbitals is restricted by the exclusion principle, given by the Austrian scientist Wolfgang Pauli (1926). According to this principle: **No two electrons in an atom can have the same set of four quantum numbers** Pauli Exclusion Principle can also be stated as : **"Only two electrons may exist in the same orbital and these electrons must have opposite spin."** This means that the two electrons can have the same value of three quantum numbers *n*, *ℓ* and *m*, but must have the opposite spin quantum number (s).

Note

(i) With the help of this principle, the maximum number of electrons that can be accommodated in an orbital, sub shell and main shell can be calculated.

(ii) An orbital is represented by a box [☐], which called a quantum unit.

(iii) If four quantum numbers of last electron of any atom are given, it can easily identify the atom with the help of this principle.

(c) **Hund's rule : It states pairing of electrons in the orbitals belonging to the same subshell (*p*, *d* or *f*) does not take place until each orbital belonging to that subshell has got one electron each i.e., it is singly occupied**.

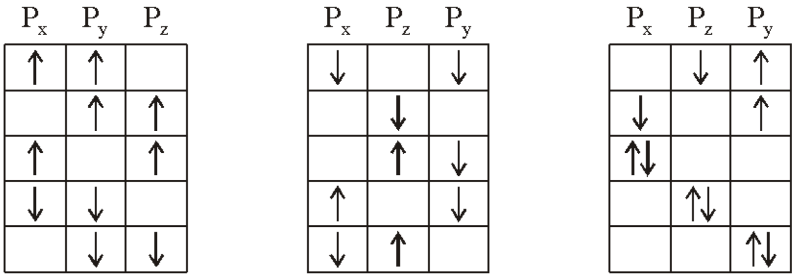
This is due to the fact that electrons being identical in charge, repel each other when present in the same orbital. This repulsion can, however, be minimised if two electrons move as far apart as possible by occupying different degenerate orbital. All the electrons in a degenerate set of orbitals will have same spin.

Note

Hund's Rule is not valid in excited state of the atom

❖ **Difference between Electronic Configuration and Electronic Arrangement of a given atom or ion :**

In order to know the difference between these two conditions, let us consider the C_6 the valence shell electronic configuration of this ion is $2p^2$. This configuration does not tell us about the method in which the two electrons of C are distributed, in a set of three degenerate 2p orbitals. It has been shown through permutations and combinations, that there are as many as 15 different ways in which the two electrons in the three 2p orbitals are distributed. In other words, we say that the electronic configuration, namely $2p^2$ can have 15 different arrangements.



Electronic arrangements for p^2 configuration

❖ **In the case of electronic arrangement :**

- The stable electronic arrangement is called electronic configuration.
- The stable electronic arrangement has lower potential energy and greater stability.
- Greater is the number of unpaired electrons with parallel spins, greater would be the stability of electronic arrangement i.e.,

Unstable

Stable

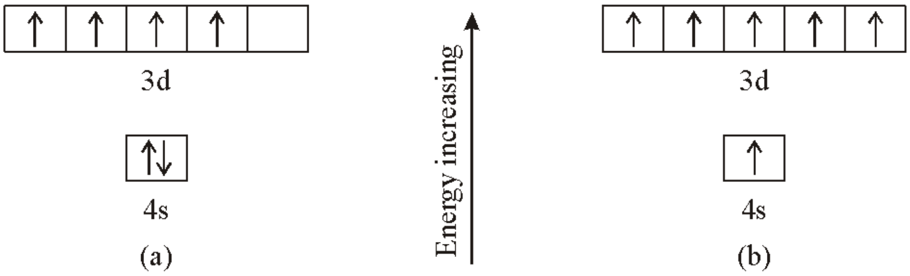
- 

(a) (b) (c)

Stability a < b < c

- When two electrons are made up in the same orbital with opposite spins energy is required. This energy is called 'pairing energy' or 'destablizing energy'. Pairing energy has positive sign hence greater pairing energy refers to lower stability of the electronic arrangement.

- The energy required to promote an electron from lower energy orbital to a higher energy orbital is called promotional energy and it has positive sign. Promotional energy increases, the stability decreases, i.e.,



The arrangement (a) is unstable, because pairing energy (p) > promotional energy (ρE).

Due to the arrangement of (b) is stable due to the symmetrical structure

☐ EXTRA STABILITY OF HALF FILLED AND COMPLETELY FILLED ORBITALS

The half-filled or full-filled orbitals are much stabler compared to the nearest half-filled or full-filled orbitals respectively. This enhanced stability for the half-filled and full-filled orbitals can be nicely explained by considering the exchange energy (E_{ex}), a quantum mechanical phenomenon, along with the Coulombic energy.

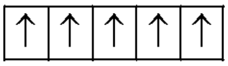
To understand the physical meaning of the exchange energy, we have to consider the following aspects. In the absence of any external field (electric or magnetic), the electrons in an atom with the parallel spins having the same *n*, *l* are indistinguishable. Thus the electrons can exchange their places, more correctly the wave functions associated with the individual electrons are exchangeable. Due to this exchange phenomenon among the indistinguishable electrons, the electrons of the system are getting a larger volume to travel. Now, according to the principle of the model, particle in a box the system is getting stabilised, as the electrons are now getting a larger dimension (a consequence of extended delocalisation) of the box in which they can travel. This extended delocalisation increases with the increases of number of such indistinguishable electrons. Very often, the exchange energy is measured by the number of sets (N) of two electrons which are indistinguish able, *i.e. n, l* are identical which can be arranged from the electrons with parallel spins, Thus, *N* is given by (for *x* number of electrons with parallel spins) :

$$N = {}^{x}C_2 = \frac{x!}{2!(x-2)!} = \frac{x(x-1)}{2};\quad \text{and } E_{ex} \propto \frac{x(x-1)}{2}$$

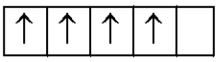
Now, let us consider the cases (figure) $d^4\,(x=4)$, $d^5\,(x=5)$ and $d^6\,(x=5)$, (there the sixth electron is antiparallel with respect to the others). The exchange energies are :

$$E_{ex}\left(d^4\right) \propto {}^4C_2 < E_{ex}\left(d^5\right) \propto {}^5C_2 = E_{ex}\left(d^6\right) \propto \left({}^5C_2 + {}^1C_2\right)$$

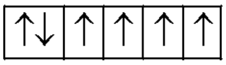
Thus the exchange energy for the d^4 system is lower compared to those of the d^5 and d^6 systems. Though the d^5 and d^6 systems are having the same exchange energy, in d^6, due to the pairing of one



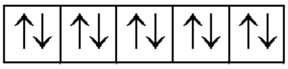
I, (d^5)



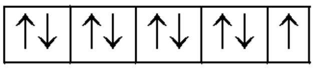
II, (d^4)



III, (d^6)



IV, (d^{10})

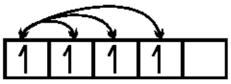


V, (d^9)

Arrangements of electrons in d^4, d^5, d^6, d^9 and d^{10} systems.

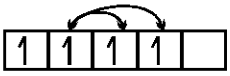
electron, it suffers from the electron-electron Coulombic repulsive force. This is why the half-filled d^5 - system is stabler compared to the other arrangements nearest to the half-filled one. This is why for chromium the ground state configuration is $3d^5 \ \ 4s^1$ instead of $3d^4 \ \ 4s^2$, In moving the $4s$ electron to $3d$ level, the disfavour is overcome by exchange energy.
Let us count the number of exchange that are possible in d^4 and d^5 configuration among electrons with parallel spins :

d^4 (1)



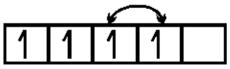
3 exchanges by 1st e^-

(2)



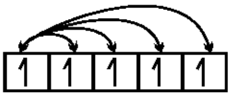
2 Exhanges by 2nd e^-

(3)



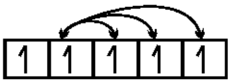
only 1 exchange by 3rd e^-
Total number of possible exchanges = 3 + 2 + 1 = 6

d^5 (1)



4 exchanges by 1st e^-

(2)

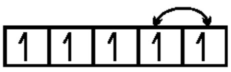


3 exchanges by 2nd e^-

(3)

2 exchanges by 3rd e^-

(4)



1 exchange by 4th e^-
Total number of possible exchanges = 4 + 3 + 2 + 1 = 10

Now, let us consider the cases $d^9\left(x_{+\frac{1}{2}}=5,\ x_{\frac{-1}{2}}=4\right)$, $d^{10}\left(x_{+\frac{1}{2}}=x_{\frac{-1}{2}}=5\right)$, where the lower right hand suffix of x indicates the magnetic spin quantum number of the group of the indistinguishable electrons, $e.g.\ x_{+\frac{1}{2}}$ indicates the electrons with $m_s=+\frac{1}{2}$. The exchange energies are :

$$E_{ex}\left(d^9\right) \propto \left({}^5C_2+{}^4C_2\right) < E_{ex}\left(d^{10}\right) \propto \left({}^5C_2+{}^5C_2\right)$$

In d^{10} system, the exchange energy is higher than that of d^9 system, but it suffers from an addition electron-electron repulsion due to the pairing of the tenth electron. The exchange energy probably overcomes the disfavour created due to the additional pairing. However, some anomalies to the preference of half-filled and full-filled shells are known. These are :

$Cr\left(3d^5\ 4s^1\right),\ W\left(5d^4\ \ 6s^2\right);\ Ni\left(3d^8 4s^2\right),\ Pd\left(4d^{10}\ \ 5s^0\right),\ Pt\left(5d^9 6s^1\right)$

Table : Illustration of the enhanced stability for just half-filled and full-filled orbitals compared to the nearest ones :

Element	Expected Configuration	Actual configuration
$Cr(Z=24)$ si	$[Ar]3d^4 4s^2$	$[Ar]3d^5\ 4s^1$
$Mo(Z=42)$	$[Kr]4d^4\ 5s^2$	$[Kr]4d^5\ \ 5s^1$
$Gd(Z=64)^a$	$[Xe]4f^8\ 5d^0\ 6s^2$	$[Xe]4f^7\ \ 5d^1\ \ 6s^2$
$Cm(Z=96)^a$	$[Rn]\ 5f^8\ 6d^0\ 7s^2$	$[Rn]5f^7\ \ 6d^1\ \ 7s^2$
$Cu(Z=29)$	$[Ar]3d^9\ \ 4s^2$	$[Ar]3d^{10}\ 4s^1$
$Pd(Z=46)$	$[Kr]4d^8\ 5s^2$	$[Kr]4d^{10}\ \ 5s^0$
$Ag(Z=47)$	$[Kr]4d^9\ 5s^2$	$[Kr]4d^{10}\ 5s^1$
$Au(Z=79)$	$[Xe]4f^{14}\ 5d^9\ 6s^2$	$[Xe]\ 4f^{14}\ 5d^{10}\ 6s^1$
$Nb(Z=41)^*$	$[Kr]4d^3\ \ 5s^2$	$[Kr]4d^4\ \ 5s^1$
$Ru(Z=44)^*$	$[Kr]4d^6\ 5s^2$	$[Kr]4d^7\ \ 5s^1$
$Rh(Z=45)^*$	$[Kr]4d^7\ 5s^2$	$[Kr]4d^8\ 5s^1$
$Pt(Z=78)^*$	$[Xe]4f^{14}\ \ 5d^8\ \ 6s^2$	$[Xe]\ 4f^{14}\ 5d^9\ \ 6s^1$

* One of the two electrons from ns^2 moves to $(n-1)d$ level to make the *ns* level half-filled. It indicates that the half-filled ns^1 is stabler than ns^2.

- **Electronic configuration and Hund's rule, *i.e.* the rule of maximum spin multiplicity :**

It states that when the electrons enter into some degenerate sublevels *i.e.* of the same energy, as they are having same (*n* and *l*), the electrons will try to avoid pairing and try to remain unpaired so long as possible with parallel spins to generate the maximum spin multiplicity $\left(2s+1,\ S=\Sigma si\right)$. It is believed that pairing or arrangements with antiparallel spins will reduce the exchange energy. Besides this, in pairing the electrons to overcome the electron-electron repulsion, pairing energy is also to be spent. Thus pairing leads to the loss of exchange energy and increase of repulsive energy while for the arrangements with unpaired antiparallel spins, only the exchange energy is lost but no repulsive energy is introduced. This is why for a number of degenerate energy levels, maximum spin multiplicity (*i.e.*, maximum number of unpaired electrons with parallel spins) is always favoured.

Example For nitrogen, the 3*p* electrons are to be placed in p_x, p_y and p_z. Here a number of possibilities considering the Pauli exclusion principle are shown in figure. In II and III arrangements, *S* is ½ while it is $\frac{3}{2}$ in I; hence I is only acceptable. Here it is noteworthy that the III contains three unpaired electrons, but because of the antiparallel fashion, it is getting rejected.

The arrangement is very often represented as, $p_x^1\, p_y^1\, p_z^1$.

That the unpaired antiparallel arrangement reduces the exchange energy is illustrated by considering the d^5 configuration.

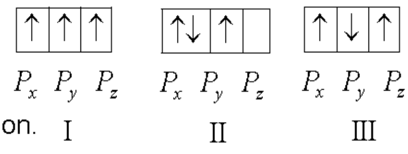
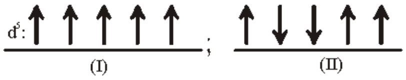


Illustration of Hund's rule of spin multiplicity in p³ configuration



Let us consider the above two possibilities. The exchange energies in the two cases are given by :

$$E_{ex} \propto {}^5C_2,\ (\text{case - I});\ \text{and}\ E_{ex}(\text{II}) \propto \left({}^3C_2 + {}^2C_2\right),\ (\text{case-II})$$

Thus, $E_{ex}(\text{I}) > E_{ex}(\text{II})$ and the arrangement I is favoured.

Based on this principle, the electronic configuration of the following elements are shown :

$C: 1s^2\ 2s^2\ 2p^1\ 2p^1\ 2p^0;\ N: 1s^2\ 2s^2\ 2p^1\ 2p^1\ 2p^1;\ 1s^2\ 2s^2\ 2p^2\ 2p^1\ 2p^1$

$F: 1s^2\ 2s^2\ 2p^2\ 2p^2\ 2p^1$

(Here, the three *p*-orbitals, *i.e.*, p_x, p_y and p_z, are energetically degenerate in the absence of any external field.)

Half-filled and completely filled sub-shells have extra stability due to the following reasons.

Tips & Trick

- The radius of nucleus is of the order of 1.5 × 10^{-11} cm to 6.5 × 10^{-13} cm.
- Red coloured light has largest wavelength, least frequency and lowest energy in visible light.
- For an element z, e and m are constants $v \propto \sqrt{\frac{1}{r}}$
- Number of revolution made per second in nth orbit $= \frac{\text{Velocity of electron in nth orbit}}{\text{Circumfrence of the nth orbit}} = \frac{V_n}{2\pi r_n}$
- If E_H and E_x are the energies associated with nth shell of hydrogen and hydrogen like specice (unielectron species) with atomic number z, $E_x = z^2 E_H$
- $E_n \propto \frac{1}{n^2}$
- Although the energy of electron increases with increase in the value of n, yet $E_2 - E_1 > E_3 - E_2 > E_4 - E_3 > E_5 - E_4$ etc.
- The number of spectral lines in the spectrum when the electron comes from nth level to the ground level will be $\frac{n(n-1)}{2}$
- Number of subshells in a main energy level is equal to n.
- Number of orbitals in a main energy level is equal to n^2.
- Number of orbitals in a subshell is equal to $(2\ell + 1)$.
- Maximum number of electrons in a subshell is equal to $2(2\ell + 1)$.
- Maximum number of electrons in a main shell is equal to $2n^2$.
- Orbital angular momentum = $\sqrt{\ell(\ell+1)}\frac{h}{2\pi}$
- Magnetic momentum $(\mu) = \sqrt{n(n+2)}$; where n = unpaired electrons

Questions and Answers

Very Short Answer Type Question

1. The frequency of the strong yellow line in the spectrum of sodium is $5.09 \times 1o^{14}s^{-1}$. Calculate the wavelength of the light in nanometer.

Ans.: $v = 5.09 \times 10^{14}\ s^{-1}$, $c = 3 \times 10^{8}\ ms^{-1}$, $\lambda = ?$

$$\lambda = \frac{c}{v} = \frac{3 \times 10^{8} ms^{-1}}{5.09 \times 10^{14} s^{-1}}$$

$$= 5.89 \times 10^{-7} m = 5.89 \times 10^{-7} \times 10^{9} nm$$

2. An atomic orbital has $n = 3$, what are the possible values of l ?

Ans.: n = 3; l = 0, 1, 2

3. Calculate the number of protons, neutrons and electrons in $^{80}_{35}Br$.

Ans.: No. of protons = 35, No. of electrons = 35, No. of neutrons = 45

4. What is shape of (*i*) s-orbital, (ii) *p*-orbital ?

Ans.: (i) Spherical (ii) Dumb-bell.

5. Define an (*i*) Isotope, *(ii)* Isobar and (i/7) Isotone.

Ans.: (i) **Isotopes** are those atoms which have different mass number but same atomic number, e.g., $^{11}_{5}B$ and $^{10}_{5}B$; $^{35}_{17}Cl$ and $^{37}_{17}Cl$; $^{1}_{1}H$, $^{2}_{1}H$ and $^{3}_{1}H$ are isotopes.

(ii) **Isobars**. Those atoms which have same mass number (A) but different atomic number(Z).

e.g., $^{40}_{20}Ca$ and $^{40}_{18}Ar$; $^{14}_{16}C$ and $^{14}_{7}N$

(iii) **Isotones**. They have same number of neutrons, e.g., $^{14}_{6}C$ and $^{16}_{8}O$, both have 8 neutrons.

6. Which of the following has equal number of neutrons and protons ?

(*i*) hydrogen, (*ii*) deuterium,

(*iii*) fluorine, (*iv*) chlorine.

Ans.: (ii) $^{2}_{1}H$ has equal number of neutrons and protons, i.e., No. of neutrons = No. of protons = 1

7. What is meant by isoelectronic species ? Give one example.

Ans.: Isoelectronic species have same number of electrons, e.g., Na^{+}, Ar, Mg^{2+}, F^{-}.

8. What is value of Bohr's radius for the first orbit?

Ans.: $r_1 = 0.529$ Å $= 0.529 \times 10^{-10}$ m

$= 5.29 \times 10^{-11}$ m

9. Why do many elements have fractional atomic masses ?

Ans.: It is because they have isotopes.

10. The ionisation energy of H-atom (in the ground state) is *x* kJ. Find the energy required for an electron to jump from 2nd to 3rd energy level.

Ans.: $E_2 = -\frac{x}{2^2} = -\frac{x}{4}$; $E_3 = -\frac{x}{3^2} = -\frac{x}{9}$;

$$E_3 - E_2 = -\frac{x}{9} + \frac{x}{4} = \frac{5}{36}x.$$

11. Which quantum number determines

(i) energy of electron

(ii) orientation of orbital?

Ans.: (i) Principal quantum number (n)

(ii) Magnetic quantum number (m).

12. State Hund's rule of maximum multiplicity. Illustrate it with an example.

Ans.: It states 'in p, d and f-orbitals, electrons are first singly filled and then pairing of electrons takes place'.

$N(7): 1s^2 2s^2 2p_x^2 2p_y^1$ (Incorrect)

$N(7): 1s^2 2s^2 2p_x^1 2p_y^1 2p_z^1$ (Correct)

13. Out of X-rays, infra-red, visible rays and microwaves, which has largest frequency?

Ans.: X-rays have largest frequency.

14. What is meant by (i) Stark effect, *(ii)* Zeeman effect ?

Ans.: (i) The splitting of spectral lines in electric field is called Stark effect.

(ii) The splitting of spectral lines in magnetic field is called Zeemen effect.

15. Define line spectrum or atomic spectrum.

Ans.: The spectrum of elements consisting of discrete sharp lines having different wavelength separated by dark bands is called atomic spectrum. It is a characteristic of an element.

16. Why is energy of electron-ve ?

Ans.: When electron is at infinite distance from nucleus, its energy is zero. When it is brought near to the nucleus, energy becomes less than zero, i.e., –ve due to force of attraction between nucleus and electron.

17. What is *(i)* emission spectrum, *(ii)* absorption spectrum ?

Ans.: (i) **Emission spectrum.** It is obtained when radiations emitted by the excited substance are analysed. It consists of bright coloured lines separated by dark bands. It is obtained at high temperature.

(ii) **Absorption spectrum.** It is obtained when the white light is passed through substance in gaseous state or in solution and transmitted light forms dark lines separated by bright bands. It is obtained at room temperature.

18. Why is 4*s* orbital filled before 3*d* orbital ?

Ans.: 4s-orbital has $(n + l) = 4 + 0 = 4$. which is lower than of 3d, i.e., $3 + 2 = 5$.

19. Why is energy of Is electron lower than 2s electron?

Ans.: Is electron is closer to nucleus than 2s, therefore, has more force of attraction.

20. What is meant by quantization of energy ?

Ans.: Quantization of energy means the energy of energy levels can have some specific values of energy and not all the values.

21. Define (*i*) frequency, *(ii)* wavelength.

Ans.: (i) Frequency is defined as number of waves passing through a point per unit time.

(ii) Wavelength is distance between centre of two adjacent crests or troughs.

22. How is wavelength related to (*i*) frequency, (*ii*) wave number, (iii) energy ?

Ans.: (i) $\boxed{\lambda = \frac{c}{\nu}}$ (ii) $\boxed{\lambda = \frac{1}{\nu}}$ (iii) $E = \frac{hc}{\lambda}$,

i.e., $\boxed{\lambda = \frac{hc}{E}}$

23. Define an orbital. What does angular quantum number tell about an orbital ?

Ans.: An orbital is a region or space where there is maximum probability of finding electron. Angular eqantum number tells about the shape of an orbital.

24. How many electrons will be present in '*g*' orbital and why ?

Ans.: 'g' orbital has $l = 4$, $m = -4, -3, -2, -1, 0, +2, +4$, i.e., it has 9 orbitals which can have $9 \times 2 = 18$ electrons.

25. How many spherical node surface are there in (*i*) 3*s* sub-shell, (*ii*) 3*p* sub-shell ?

Ans.: Number of spherical nodes in an orbital is equal to $n - l - 1$.

(i) 3*s* orbital has $3 - 0 - 1 = 2$

(ii) 3*p* sub-shell has $3 - 1 - 1 = 1$

26. How many unpaired electrons are there in Ni^{2+} ion ? Atomic number of Ni(28).

Ans.: Ni(28) has electronic configuration $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^8$

Ni^{2+} ion has electronic configuration $1s^2 2s^2 2p^6 3s^2 3p^6 4s^0 3d^8$

The number of unpaired electrons are

2.

↑↓	↑↓	↑↓	↑	↑

3d

27. How does change in velocity of a moving particle alter the wavelength of the particle ?

Ans.: 'λ' (wavelength) decreases with increase in velocity of moving particle, i.e., $\boxed{\lambda = \frac{h}{mV}}$

28. State physical significance of Ψ^2.

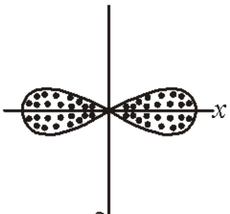
Ans.: ψ^2 represents probability of finding electron.

29. Which quantum number will express the difference in the two electrons in K-shell

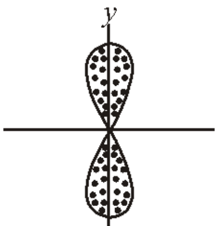
Ans.: Spin quantum number.

30. Draw the shape of orbital with $n = 3$, $l = 1$.

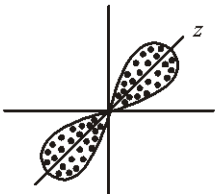
Ans.: $n = 3$, $l = 1$ is 3p orbital. Its shape is dumb-bell.



$3p_x$



$3p_y$



$3p_z$

31. Which quantum number determines the shape and orientation of the orbitals ?

Ans.: Azimuthal quantum number determines the shape and magnetic quantum number determines the magnetic orientation of orbitals.

32. Write electronic configuration of Cu^{2+} ion. (At. No. of Cu = 29).

Ans.: $Cu^{2+}(29)$: $1s^2$, $2s^2\ 2p^6$, $3s^2$, $3p^6$, $3d^6$, $3d^9$ because electrons are first removed from 4s orbital and then from 3d orbital.

33. State Pauli Exclusion Principle.

Ans.: It states 'No two electrons in an atom can have all the four quantum numbers same. They will differ at least in spin quantum number.

34. Write the mathematical expression by which the energies of various stationary states in the hydrogen atom can be calculated.

Ans.: $E_n = -\frac{1312\ \text{kJ mol}^{-1}}{n^2}$

35. Write all the four quantum numbers of the electron in the outermost shell of rubidium (At. No. = 37) atom.

Ans.: $n = 5$, $l = 0$, $m = 0$, $s = +\frac{1}{2}$ (either $+\frac{1}{2}$ or $-\frac{1}{2}$); Rb(37) : $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^1$

36. What is the possible value of angular momentum quantum number (*l*) for the unpaired electron in the atom of an element whose atomic number is 17 ?

Ans.: l = 1 for unpaired electron of Cl(17) : $1s^2 2s^2 2p^6 3s^2 3p^2{}_x 3p^2{}_y 3p^1{}_z$

37. Name two phenomena that indicate the dual nature of electrons.

Ans.: (i) Photoelectric effect

(ii) Diffraction.

38. Write the number of unpaired electron(s) present in atom of an element with an atomic number 21.

Ans.: The electronic confitguration of element with atomic number 21 is $(Ar)4s^2 3d^1$. There is one unpaired electron.

39. Which quantum number determines the orientation of atomic orbital ?

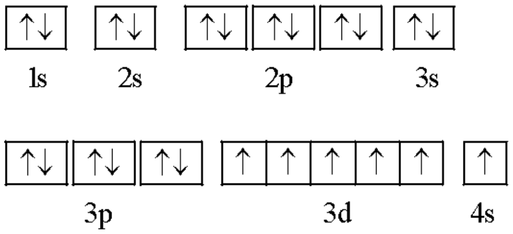
Ans.: Magnetic quantum number determines magnetic orientation of atomic orbital.

40. What values of magnetic quantum number 'm' are permitted for an electron having angular quantum number value l = 2 ?

Ans.: When l = 2, m = –2, –1, 0, +1, +2.

41. One unpaired electron in atom contributes a magnetic moment of 1.1 BM. Calculate the magnetic moment of chromium (At. No. 24).

Ans.: Cr(24)



There are 6 unpaired electrons

$\therefore$ $\mu = 1.1 \times 6 = 6.6$ B.M. (Bohr's magneton)

42. Write the ground state electronic configuration of Molybdenum (Z = 42).

Ans.: Mo(42) : $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^1 4d^5$

43. Write down the value of n, l and m for electron present in $3p_z$

Ans.: n = 3, l = 1, m = 0

44. Write electronic configuration of Cu^{2+} ion (Cu = 29).

Ans.: Cu^{2+}(29) : $1s^2 2s^2 2p^6 3s^2 3p^6 4s^0 3d^{9*********}$

Short Answer Type Question

1. Define the terms (*i*) atomic number and (ii) mass number.

Ans.: (i) Atomic number is equal to number of protons. It is also equal to number of electrons in neutral atom.

(ii) Mass number is equal to sum of number of neutrons and protons.

2. What is electromagnetic spectrum?

Ans.: The spectrum of all types of electromagnetic rediations incouding visible rays in the increasing order of their wavelengths and decreasing order of their frequencies and energies is called electromagnetic spectrum.

3. Write a short note on Planck's quantum theory.

Ans.: **Planck's quantum theory.** (i) Energy is absorbed or radiated not continuously but discontinuously in form of small packets called photons.

(ii) The energy of each proton is directly proportional to its frequency.

$E \propto v \Rightarrow E = hv$ where 'h' is Planck's constant $= 6.63 \times 10^{-34}$ J s.

4. How is spectrum of hydrogen obtained?

Ans.: It is obtained by passing electric discharge through the hydrogen gas taken in a discharge tube at a low pressure. The emitted light is analysed with the help of spectroscope.

5. Give Rydberg formula for the calculation of wave number of various spectral lines of the spectrum. What is the value of Rydberg constant?

Ans.: $\bar{V} = R\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$ where $\bar{V}$ is wave number, R is Rydberg constant = 109677 cm^{-1}, n_1 and n_2 are energy levels, e.g., for Lyman series $n_1 = 1$ and $n_2 = 2, 3, 4, 5,$ ....

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

Ans.: $E = h\nu = 6.626 \times 10^{-34}\ Js \times 5 \times 10^{14} s^{-1} = 33.130 \times 10^{-20} J$

7. What will be the wavelength of a ball of mass 0.1 kg moving with a velocity of 10 ms^{-1}?

Ans.: $\lambda = \frac{h}{mv} = \frac{6.62 \times 10^{-34} kgm^2 s^{-1}}{0.1 kg \times 10 ms^{-1}} = 6.620 \times 10^{-34} m$

8. What is the number of photons of light with a wavelength of 4000 pm that provide 1 J of energy.

Ans.: $E = \frac{hc}{\lambda} = \frac{6.62 \times 10^{-34} \times 3 \times 10^8}{4000 \times 10^{-12} m}$

$$= \frac{19.86}{4} \times 10^{-17} = 4.965 \times 10^{-17} J$$

$$\text{Number of photons } = \frac{1 J}{4.965 \times 10^{-17} J}$$

$$= \frac{10}{4.965} \times 10^{16} = 2.014 \times 10^{16} \text{photons}$$

9. Calculate and compare the energies of two radiations one with a wavelength of 800 nm and other with wavelength of 400 nm.

Ans.: $E_1 = h\frac{c}{\lambda}$

$$E_1 = \frac{6.626 \times 10^{-34} \times 3 \times 10^8}{800 \times 10^{-9} m} = 2.48 \times 10^{-19} J$$

$$E_2 = \frac{6.626 \times 10^{-34} \times 3 \times 10^8}{400 \times 10^{-9} m} = 4.97 \times 10^{-19} J$$

$$\frac{E_1}{E_2} = \frac{1}{2} \text{ or } E_2 = 2E_1$$

10. State (n + l) rule. Illustrate with the help of example. Give the sequence of filling orbitals using (n + l) rule.

Ans.: (i) **(n + 1) rule** : It states orbitals having lowest value of (n + 1) will be filled first. If two orbitals have same value of (n + 1), then the one which has lower value of n will be filled first, e.g., for 4s orbital, $n + l = 4 + 0 = 4$, for 3d. $n + l = 3 + 2 = 5$ ∴ 4s orbital is filled before 3d orbital.

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

11. The quantized energy of an electron in hydrogen atom for the nth level is given by

$E_n = \frac{1.312}{n^2} \times 10^6 Jmol^{-1}$. Calculate the energy required to remove the electron completely from an excited hydrogen atom when its quantized level, n = 3. ($N_A = 6.02 \times 10^{23}$ mol^{-1})

Ans.: $\Delta E = \frac{-1.312 \times 10^6}{6.02 \times 10^{23}}\left(\frac{1}{n_2^2} - \frac{1}{n_1^2}\right)$

$$= -2.18 \times 10^{-18}\left(\frac{1}{\infty} - \frac{1}{9}\right) = 2.18 \times 10^{-18} J \times \frac{1}{9}$$

$$= 2.42 \times 10^{-19} J$$

12. Calculate the wavelength of an electron that has been accelerated in a particle accelerator through a potential difference of 100 million volts. (1 eV = 1.6×10^{-19} J, $m_e = 9.1 \times 10^{-31}$ kg, $h = 6.6 \times 10^{-34}$ Js, $e = 3.0 \times 10^8$ ms^{-1})

$$\lambda = 1.24 \times 10^{-14} m$$

Ans.: K.E. of the electron

= 100 MeV = 100 × 10^6 eV = 10^8 eV

= 10^8 eV × 1.6 × 10^{-19} J/eV = 1.6 × 10^{-11} J

$$\lambda = \frac{hc}{K.E.} = \frac{6.6 \times 10^{-34} Js \times 3 \times 10^8 ms^{-1}}{1.6 \times 10^{-11} J}$$

13. Write the de Broglie equation and establish a relation between wavelength of a moving subatomic particle and its kinetic energy.

Ans.: $\lambda = \frac{h}{mc}$; $K.E. = \frac{1}{2}$

$$mc^2 \Rightarrow c^2 = \frac{2 \times K.E.}{m} \Rightarrow c = \sqrt{\frac{2 \times K.E}{m}}$$

$$\lambda = \frac{h}{m\sqrt{\frac{2 \times K.E.}{m}}} = \frac{h}{\sqrt{2 \times K.E. \times m}}$$

14. Two particles *A* and *B* are in motion. The momentum of particle 'B' is half of 'A'. If the wavelength associated with the particle 'A' is 5×10^{-8} m, calculate the wavelength associated with the particle 'B'

Ans.: Momentum (p) of B is $\frac{1}{2}$ of A, $\lambda_A = \frac{h}{p}$

$$\Rightarrow h = p \times 5 \times 10^{-8}\ m$$

$$p = \frac{h}{5 \times 10^{-8} m}, \lambda_B = \frac{h}{\frac{1}{2}p} \Rightarrow \lambda_B = \frac{h \times 5 \times 10^{-8} m}{\frac{1}{2}h}$$

$$= 10 \times 10^{-8} = 10^{-7}\ m$$

15. Calculate the uncertainty in the position on an electron if the uncertainty in velocity is

$5.7 \times 10^5\ ms^{-1}$.

($h = 6.6 \times 10^{-34}$ Js and mass of electron

$= 9.1 \times 10^{-31}$ kg)

Ans.: $\Delta x \times \Delta V = \frac{h}{4m\pi} \Rightarrow \Delta x = \frac{h}{4m\pi \times \Delta V}$

$$= \frac{6.6 \times 10^{-34} kg\ m^2 s^{-1} \times 7}{22 \times 4 \times 9.1 \times 10^{-31} kg \times 5.7 \times 10^5 ms^{-1}};$$

$$\Delta x = 1.012 \times 10^{-10}\ m$$

16. Calculate the kinetic energy of a moving electron which has a wavelength of 4.8 pm.

(Mass of electron = 9.11×10^{-31} kg,

$h = 6.63 \times 10^{-34}$ Js)

Ans.: λ = 4.8 pm = 4.8×10^{-12} m, m = 9.11×10^{-31} kg,

$h = 6.63 \times 10^{-34}$ Js.

$$\lambda = \frac{h}{mc} \Rightarrow c = \frac{h}{m\lambda} = \frac{6.63 \times 10^{-34} kgm^2 s^{-1}}{9.11 \times 10^{-31} kg \times 4.8 \times 10^{-12} m}$$

$$c = 1.156 \times 10^8\ ms^{-1}$$

$$K.E. = \frac{1}{2}mc^2 = \frac{1}{2} \times 9.11 \times 10^{-31} \times (1.516 \times 10^8)^2\ J$$

$$= 10.46 \times 10^{-15}\ J = 1.046 \times 10^{14}\ J$$

17. Calculate the de Broglie wavelength of an electron travelling with a speed equal to 10% of the speed of light.

Ans.: $c = 3 \times 10^8\ ms^{-1} \times \frac{10}{100} = 3 \times 10^7\ ms^{-1}$

($\therefore$ velocity of light is $3 \times 10^8\ ms^{-1}$)

$$\lambda = \frac{h}{mc} = \frac{6.62 \times 10^{-34} kg\ m^2 s^{-1}}{9.1 \times 10^{-31} kg \times 3 \times 10^7 mg^{-1}}$$

$$= \frac{66.2}{27.3} \times 10^{-35+31-7}$$

$$= 2.44 \times 10^{-11}\ m \times 10^{12} = 24.4\ pm$$

18. What do you understand by quantum numbers? What is significance of spin quantum number?

Ans.: Quantum numbers are numbers which characterise an electron, i.e., they differentiates one electron from another. Spin quantum number determines spin of electron.

19. How many photons of light having wavelength of 1200Å are necessary to provide 1kJ of energy?

($h = 6.6 \times 10^{-34}$ Js)

Ans.: $\lambda = 1200 \text{Å} = 1200 \times 10^{-10}$ m

$$E = \frac{hc}{\lambda} = \frac{6.6 \times 10^{-34} \times 3 \times 10^{8}}{1200 \times 10^{-10} \text{m}}$$

$$= \frac{19.8}{1200} \times 10^{-16} = \frac{19.8}{12} \times 10^{-18} = 1.65 \times 10^{-18} \text{J}$$

Number of photons

$$= \frac{\text{Total energy}}{\text{Energy of photon}} = \frac{1 \text{kJ}}{1.65 \times 10^{-18} \text{J}}$$

$$= \frac{1000 \text{J}}{1.65 \times 10^{-18} \text{J}} = 6.0 \times 10^{20}$$

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

Ans.: $\Delta x . \Delta V = \frac{h}{4 m \pi}$

$$\Rightarrow \Delta V = \frac{6.626 \times 10^{-34} \times 7}{4 \times 9.1 \times 10^{-31} \times 22 \times 0.1 \times 10^{-10} \text{m}} ;$$

$$\Delta V = \frac{46.382 \times 10^{-34}}{8.008 \times 10^{-40}} = 5.79 \times 10^{6} \text{ms}^{-1}$$

21. Calculate the wavelength of 1000 kg rocket moving with a velocity of 300 km per hour

($h = 6.626 \times 10^{-34}$Js)

Ans.: $\lambda = \frac{h}{mV}$

m = 1000 kg V = 300 km per hour

$$V = \frac{300 \times 10^{3} \text{m}}{60 \times 60 \text{s}}$$

$$\lambda = \frac{6.626 \times 10^{-34} \text{kg m}^{2} \text{s}^{-1} \times 60 \times 60 \text{s}}{1000 \text{kg} \times 300 \times 10^{3} \text{m}}$$

$[1 \text{J} = 1 \text{kg m}^{2} \text{s}^{-2}]$

$$= \frac{6.626 \times 6 \times 6 \times 10^{-32} \text{kg m}^{2}}{3 \times 10^{8} \text{kg m}}$$

$\lambda = 7.95 \times 10^{-39}$ m

22. Calculate the uncertainty in position of dust particle with mass equal to 1 mg if the uncertainty in velocity is 5.5×10^{-20} ms^{-1}.

($h = 6.626 \times 10^{-34}$ Js)

Ans.: m = 1 mg = 10^{-6} kg

$\Delta V = 5.5 \times 10^{-20}$ ms^{-1}

$$\Delta x = \frac{h}{4 m \pi \Delta V} = \frac{6.626 \times 10^{-34} \text{kg m}^{2} \text{s}^{-1}}{4 \times 10^{-6} \text{kg} \times 3.14 \times 5.5 \times 10^{-20} \text{ms}^{-1}}$$

$$\Delta x = \frac{6.626}{12.56 \times 5.5} \times 10^{-8} \text{m}$$

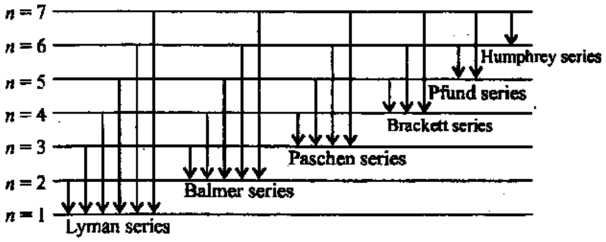
$$\Delta x = \frac{6.626}{69.08} \times 10^{-8} \text{m}$$

$\Delta x = 0.0959 \times 10^{-8}$ m $= 9.59 \times 10^{-10}$ m

Long Answer Type Question

1. Explain spectrum of hydrogen on the basis of Bohr's model of atom.

Ans.: **Hydrogen spectrum.** When energy is supplied to electrons they get excited to higher energy levels. When they come back to lower energy levels, they emit energy of particular wavelength. If we observe these radiated energy with the help of spectrometer, we get series of lines as shown in diagram in hydrogen spectrum.



2. Give six differences between orbit and orbital.

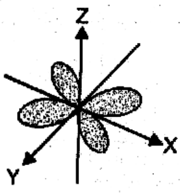
Ans.:

Orbit	Orbital
(i) It is assumed path of electron in which electron was supposed to revolve.	(i) It is region or space where there is maximum probability of finding electron.
(ii) It is two dimensional	(ii) It is three dimensional
(iii) It can have maximum electrons = $2n^2$.	(iii) It has maximum 2 electrons.
(iv) Energy of orbit increases with increase in distance from nucleus.	(iv) Energy of an orbital is given by (n + l)
(v) Orbits are circular or disc-shaped.	(v) s-orbital are spherical, p-orbitals are dumb-bell shaped, d-orbitals are double dumb-bell shaped, f-orbitals are quadruple dumb-bell shaped.
(vi) It is against uncertainty principle and assumes electron as particle only.	(vi) It is in accordance with dual nature of electron and uncertainty principle.

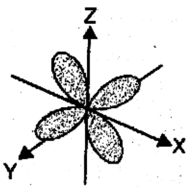
3. Give shapes of *d* orbitals.

Ans.:

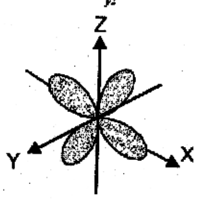
d_{xy}



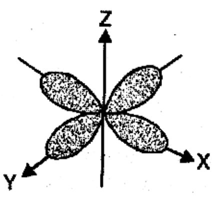
d_{xz}



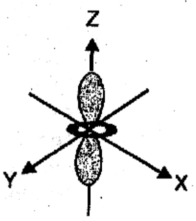
d_{yz}



$d_{x^2-y^2}$



d_{z^2}



4. When electromagnetic radiation of wavelength 300 nm falls on the surface of sodium, electrons are emitted with a kinetic energy of $1.68 \times 10^5 \text{J mol}^{-1}$. What is the minimum energy needed to remove an electron from sodium? What is the maximum wavelength that will cause a photoelectron to be emitted?

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

$$h\nu = \frac{hc}{\lambda} = \frac{6.62 \times 10^{-34}\,\text{Js} \times 3.0 \times 10^{8}\,\text{ms}^{-1}}{300 \times 10^{-9}\,\text{m}}$$

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

The energy of 1 mol 0.1 of photons

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

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

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

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

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

The minimum energy for one electron

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

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

This corresponds to the wavelength calculated as follows.

$$\lambda = \frac{hc}{E} = \frac{6.626 \times 10^{-34}\,\text{Js} \times 3.0 \times 10^{8}\,\text{ms}^{-1}}{3.84 \times 10^{-19}\,\text{J}}$$

= 517 nm (This corresponds to green light).

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

Ans.: $E = \dfrac{hc}{\lambda}$

$$E = \frac{6.626\times10^{-34}\,\text{Js}\times3\times10^{8}\,\text{ms}^{-1}}{242\times10^{-9}\,\text{m}}\times6.023\times10^{23}$$

$= 494\ \text{kJ mol}^{-1}$

6. What is the wavelength of light emitted when the electron in a hydrogen atom undergoes transition from an energy level with $n = 2$ to an energy level with $n = 2$?

Ans.: $$\bar{\nu} = \frac{1}{\lambda} = 109677\left(\frac{1}{n_1^2}-\frac{1}{n_2^2}\right)$$

$$= 109677\left(\frac{1}{2^2}-\frac{1}{4^2}\right) = 109677\times\left(\frac{1}{4}-\frac{1}{16}\right)$$

$$= 109677\times\frac{3}{16}$$

$$= \frac{329031}{16}$$

$$\bar{\nu} = \frac{3.29\times10^{5}\,\text{cm}^{-1}}{16}$$

$$\lambda = \frac{16}{3.29\times10^{5}\,\text{cm}^{-1}} = 4.86\times10^{-5}\,\text{cm}\times10^{7} = 486\ \text{nm}$$

7. How much energy is required to ionise a H atom if the electron occupies n = 5 orbit? Compare your answer with the ionization enthalpy of H atom (energy required to remove the electron from n = 1 orbit)

Ans.: $$\Delta E = -1312\ \text{kJ mol}^{-1}\left(\frac{1}{n_2^2}-\frac{1}{n_1^2}\right)$$

$$= -1312\ \text{kJmol}^{-1}\left(\frac{1}{\infty}-\frac{1}{5^2}\right)$$

$$= \frac{1312\times10^{3}\,\text{J/atom}}{25\times6.023\times10^{23}\,\text{atom}^{-1}}$$

$= 8.72\times10^{-20}\ \text{J}$

For ionisation from 1st energy level,

$n_1 = 1,\ n_2 = \infty$

$$\Delta E' = \frac{-1312\times10^{3}}{6.023\times10^{23}}\left(\frac{1}{\infty}-\frac{1}{1^2}\right) = 2.18\times10^{-18}\,\text{J}$$

$$\text{Ratio}\ \frac{\Delta E'}{\Delta E} = \frac{2.18\times10^{-18}\,\text{J}}{8.72\times10^{-20}\,\text{J}} = 25$$

Thus the energy required to remove an electron from 1st energy level is 25 times than required to remove electron from 5th energy level.

8. What is the maximum number of emission lines when the excited electron of a H atom in $n = 6$ drops to the ground state?

Ans.: Number of spectral lines

$$= \frac{n(n-1)}{2} = \frac{6(6-1)}{2} = \frac{30}{2} = 15$$

9. Which of the following are isoelectronic species, *i.e.*, those having the same number of electrons?

Na^+, K^+, Mg^{2+}, Ca^{2+}, S^{2-}, Ar.

Ans.: $Na^+(11 - 1 = 10)$, $Mg^{2+}\ (12 - 2 = 10)$ have same number of electrons

$K^+(19 - 1 = 18)$, $Ca^{2+}(20 - 2 = 18)$, $S^{2-}(16 + 2 = 18)$, Ar(18) are isoelectronic, i.e., they have same number of valence electrons.

10. (a) What is the lowest value of n that allows 'g' orbitals to exist?

(b) An electron is in one of the 3d orbitals. Give the possible values of n, l and m for this electron.

(c) An atom of an element contains 29 electrons and 35 neutrons. Deduce (i) the number of protons and (ii) the electronic configuration of the element.

Ans.: (a) n = 5 which allows 'g' orbital to exist.

(b) $n = 3$, $l = 2$, $m_l = -2, -1, 0, +1, +2$ (any one value)

(c) Number of protons = 29

Electronic configuration

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

11. Show that the circumference of the Bohr orbit for the hydrogen atom is an integral multiple of the de Broglie wavelength associated with the electron revolving around orbit.

Ans.: r_n for H = $r_1 \times n^2 = r_1 \times 1^2 = r_1$

$$\text{Circumference} = 2\pi r \quad mVr = \frac{nh}{2\pi}$$

$$V = \frac{nh}{2m\pi r}$$

$$\lambda = \frac{h}{mV} = \frac{h}{\frac{m \times nh}{2m\pi r}}$$

$$\lambda = \frac{2\pi r}{n}$$

$$\frac{\text{Circumference}}{\lambda} = \frac{2\pi r}{2\pi r / n} = n$$

It shows circumference of the Bohr orbit for the hydrogen atom is an integral multiple of de-Broglie wavelength associated with electron revolving in that orbit.

12. Calculate the energy required for the process

$$He^{+}(g) \longrightarrow He^{2+}(g) + e^{-}$$

The ionization energy for the H atom in the ground state is 2.18×10^{-18} J atom^{-1}.

Ans.: $He^{+}(g) \rightarrow He^{2+} + e^{-}$

$$E_n = \frac{2.18 \times 10^{-18} J \times Z^2}{n^2}$$

$$= \frac{2.18 \times 10^{-18} \times 2^2}{1^2} = \frac{2.18 \times 4 \times 10^{-18}}{1}$$

$= 8.72 \times 10^{-18}$ J

13. (a) The mass of an electron is 9.1×10^{-28} g. If its K.E. is 3.0×10^{-25} J, calculate its wavelength in Angstrom.

(b) What is photoelectric effect?

Ans.: (a) m = 9.1×10^{-28} g = 9.1×10^{-31} kg

K.E. = 3.0×10^{-25} J

$$\frac{1}{2}mV^2 = 3.0 \times 10^{-25} J$$

$$\lambda = \frac{h}{\sqrt{2m \times K.E.}} = \frac{6.6 \times 10^{-34} Js}{\sqrt{2 \times 3 \times 10^{-25} \times 9.1 \times 10^{-31}}}$$

$$\lambda = \frac{6.6 \times 10^{-34}}{\sqrt{54.6 \times 10^{-56}}} = \frac{6.6 \times 10^{-34}}{7.39 \times 10^{-28}} = 9 \times 10^{-7} m$$

$\lambda = 9 \times 10^{-7} \times 10^{10}$ Å $= 9 \times 10^{3}$ Å = 9000 Å.

(b) When a beam of light having frequency more than threshold frequency is made to fall on metals like alkali metals, electrons are ejected. These electrons are called photo electrons and this phenomenon is called photo electric effect.

14. What is meant by the statement that 'an electron has dual nature'?

Calculate the wavelength associated with a moving electron having a kinetic energy of 1.1375×10^{-25} J [$m_e = 9.1 \times 10^{-31}$ kg;

$h = 6.6 \times 10^{-34}$ J s]

Ans.: An electron has both particles as well as wave like nature, i.e., it has dual nature.

K.E. = 1.1375×10^{-25} J

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

$$\frac{1}{2}mV^2 = 1.1375 \times 10^{-25} J$$

$$\frac{1}{2} \times 9.1 \times 10^{-31} kg \times V^2 = 1.1375 \times 10^{-25} J$$

$$V^2 = \frac{1.1375 \times 10^{-25} J \times 2}{9.1 \times 10^{-31} kg}$$

$$V^2 = \frac{2.2750}{9.1} \times 10^{+6}$$

$$V^2 = \frac{227.5}{9.1} \times 10^{4}$$

$V^2 = 25 \times 10^{4}$

$$V = 5 \times 10^2\ \text{ms}^{-1}$$

$$\lambda = \frac{h}{mV} = \frac{6.60 \times 10^{-34}}{9.1 \times 10^{-31} \times 5 \times 10^2} = \frac{6.6 \times 10^{-5}}{45.5}$$

$$\lambda = \frac{66 \times 10^{-6}}{45.5} = 1.450 \times 10^{-6}\,\text{m}$$

15. Explain how an electron can be considered to have a particle as well as a wave nature. Using Planck's equation, E = *hv* and Einstein's equation $E = mc^2$, deduce de Broglie relation for a photon.

Ans.: Each photoelectron causes one scintillation on Zinc sulphide screen which proves particle nature of electrons. A beam of electrons when falls on aluminium foil, the diffraction pattern obtained is similar to that of X-rays. Since X-rays are associated with wave like behaviour, therefore, electrons are also also associated with wave like behaviour.

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

$$E = mc^2$$

$$\frac{hc}{\lambda} = mc^2$$

$\boxed{\lambda = \frac{h}{mc}}$ is de Broglie relation for photon.

16. The energy of electron in hydrogen atom for n^{th} energy level is given by

$$E_n = -\frac{13.12}{n^2} \times 10^5\,\text{J mol}^{-1}$$

Calculate,

(i) First excitation energy of the electron in the hydrogen atom.

(ii) Ionisation energy of the hydrogen atom.

$[N_A = 6.02 \times 10^{23}\ \text{mol}^{-1}]$

Ans.: (i) $\Delta E = -13.12 \times 10^5\,\text{J}\left(\frac{1}{n_2^2} - \frac{1}{n_1^2}\right)$

$$= -13.12 \times 10^5 \left(\frac{1}{2^2} - \frac{1}{1^2}\right)$$

$$= -13.12 \times 10^5 \times -\frac{3}{4}$$

$$\Rightarrow \frac{+13.12 \times 10^5 \times 3}{4} = \frac{39.36}{4} \times 10^5\,\text{J}$$

$$= \frac{9.84 \times 10^5\,\text{J mol}^{-1}}{6.023 \times 10^{23}} = 1.633 \times 10^{-18}\,\text{J/electron}$$

(ii) Ionization energy = + 13.12 × 10^5 J mol^{-1} = 1312 kJ mol^{-1}.

17. The electron energy of hydrogen atom in the ground state works out to be -2.18×10^{-18} J per atom. Calculate what will happen to the position of the electron in this atom if an energy of 1.938×10^{-18} J is supplied to the each hydrogen atom.

Ans.: $\Delta E = -2.18 \times 10^{-18}\,\text{J atom}^{-1}\left(\frac{1}{n_2^2} - \frac{1}{n_1^2}\right)$

$$1.938 \times 10^{-18}\,\text{J} = -2.18 \times 10^{-18}\,\text{J}\left(\frac{1}{n_2^2} - \frac{1}{1^2}\right)$$

$$1.938 \times 10^{-18}\,\text{J} = \frac{-2.18 \times 10^{-18}\,\text{J}}{n_2^2} + 2.18 \times 10^{-18}\,\text{J}$$

$$\Rightarrow \frac{2.18 \times 10^{-18}\,\text{J}}{n_2^2} = 0.242 \times 10^{-18}\,\text{J}$$

$$\Rightarrow n_2^2 = \frac{2.18 \times 10^{-18}\,\text{J}}{0.242 \times 10^{-18}\,\text{J}} = 9 \Rightarrow n_2 = 3$$

The electron will get excited to third energy level.

18. Calculate the wavelength associated with a beam of electrons accelerated by an electric field to a velocity of $10^7\ \text{ms}^{-1}$. (Given Mass of electron 9.11×10^{-31} kg, $h = 6.63 \times 10^{-34}$ kg m^2s^{-1})

Ans.: $\lambda = \frac{h}{mV} = \frac{6.63\times10^{-34}kgm^2s^{-1}}{9.11\times10^{-31}kg\times10^7ms^{-1}}$

$$= \frac{66.3}{9.11}\times10^{-35+31-7} = 7.277\times10^{-11}m$$

19. Establish a relation between wavelength of a moving particle and its kinetic energy. The wavelength of a moving particle of mass

1.0×10^{-6} kg is 3.312×10^{-29} m. Calculate its kinetic energy. ($h = 6.625 \times 10^{-34}$ Js)

Ans.: $\lambda = \frac{h}{mc}, K.E. = \frac{1}{2}mc^2 \Rightarrow mc^2$

$$= 2\times K.E., c^2 = \frac{2\times K.E.}{m}, c = \sqrt{\frac{2\times K.E}{m}}$$

$\lambda = \frac{h}{m\sqrt{\frac{2\times K.E.}{m}}} = \frac{h}{\sqrt{2m\times K.E.}}$ where K.E. is kinetic energy.

$$3.312\times10^{-29}m = \frac{6.625\times10^{-34}}{\sqrt{2\times10^{-6}\times K.E.}}$$

$$\sqrt{2\times10^{-6}\times K.E.} = 2\times10^{-5}$$

Squaring both sides

$2 \times 10^{-6} \times K.E. = 4 \times 10^{-10}; K.E. = 2 \times 10^{-4}J$

20. The uncertainty in the position and velocity of a particle are 10^{-2} m and 5.27×10^{-24} ms^{-1} respectively. Calculate the mass of the particle ($h = 6.62 \times 10^{-34}$ kg m^{2}s^{-1})

Ans.: $\Delta x\times\Delta V = \frac{h}{4m\pi} \Rightarrow m = \frac{h}{\Delta x\times\Delta V\times4\times\pi}$

$$= \frac{6.625\times10^{-34}\times7}{10^{-2}\times5.27\times10^{-24}\times4\times22} = 1\times10^{-9}kg.$$

21. How many neutrons and protons are there in the following nuclei?

${}^{13}_{6}C, {}^{16}_{8}O, {}^{24}_{12}Mg, {}^{56}_{26}Fe, {}^{88}_{38}Sr$

Ans.:

	No. of protons	No. of neutrons
${}^{13}_{6}C$	6	$13-6=7$
${}^{16}_{8}O$	8	$16-8=8$
${}^{24}_{12}Mg$	12	$24-12=12$
${}^{56}_{26}Fe$	26	$56-26=30$
${}^{88}_{38}Sr$	38	$88-38=50$

22. Calculate the wavelength, frequency and wavenumber of a light wave whose period is 2.0×10^{-10} s.

Ans.: $v = \frac{1}{period} = \frac{1}{2\times10^{-10}s} = 0.5\times10^{10}s^{-1} = 5\times10^9s^{-1}$

$$v = \frac{c}{\lambda} \Rightarrow \lambda = \frac{c}{v} = \frac{3\times10^8}{5\times10^9}$$

$$= 0.6\times10^{-1} = 0.06\,m = 6\times10^{-2}m$$

$$\bar{v} = \frac{1}{\lambda} = \frac{1}{0.06} = \frac{100}{6} = \frac{50}{3} = 16.66\,m^{-1}$$

23. The diameter of zinc atom is 2.6 Å. Calculate (*a*) radius of zinc atom in pm and (*b*) number of atoms present in a length of 1.6 cm if the zinc atoms are arranged side by side lengthwise.

Ans.: (a) diameter of zinc = 2.6 Å

radius of zinc atom $= \frac{2.6}{2} = 1.3Å$

$= 1.3 \times 10^{-10}$ m

1 pm $= 10^{-12}$ m

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

$$1.3\times10^{-10}m = \frac{1}{10^{-12}}\times1.3\times10^{-10}pm$$

$$= 1.3\times10^2pm = 130\ pm.$$

(b) Number of atoms of $Zn = \frac{\text{Length}}{\text{Diameter in cm.}}$

$$= \frac{1.6\ cm}{2.6\times10^{-8}cm} = \frac{1.6\times10^8}{2.6} = \frac{16\times10^7}{2.6}$$

$$= 6.154\times10^7\ \text{atoms}$$

24. In Millikan's experiment, static electric charge on the oil drops has been obtained by shining X-rays. If the static electric charge on the oil drop is -1.282×10^{-18} C, calculate the number of electrons present on it.

Ans.: $\text{Number of electrons} = \dfrac{\text{Magnitude of total charge}}{\text{Charge on 1 electron}}$

$$= \frac{1.282 \times 10^{-18}\,\text{C}}{1.602 \times 10^{-19}\,\text{C}} = \frac{12.82}{1.602} = 8.00 \text{ electrons}$$

25. Symbols $^{79}_{35}\text{Br}$ and ^{79}Br can be written, whereas symbols $^{35}_{79}\text{Br}$ and ^{35}Br are not acceptable. Answer briefly.

Ans.: It is because atomic number of an element of fixed. However, mass number is not fixed as it depends upon the isotope taken. Hence it is essential to mention mass number at the top and atomic number at the bottom.

26. 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.

Ans.: Let the number of electrons be 'x'

Number of protons = x – 1

[∵ ion has one unit – ve charge]

$$\text{Number of neutrons} = x + \frac{11.1}{100}x$$

Mass number = Number of protons + Number of neutrons

$$37 = x - 1 + x + \frac{11.1}{100}x$$

$3700 = 200x - 100 + 11.1\,x$

$211.1x = 3800$

$$x = \frac{3800}{211.1} = 18$$

Number of electrons = 18

Number of protons = 17

Atomic number = 17

The symbol of the ion is Cl^-

27. Arrange the following type of radiations in increasing order of frequency :

(a) radiation from microwave oven

(b) amber light from traffic signal

(c) radiation from FM radio

(d) cosmic rays from outer space and

(e) X-rays.

Ans.: Radiation from FM radio < Microwave < Amber light from traffic signal < X-rays < Cosmic rays

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

Ans.: $\text{Frequency} = \dfrac{\text{Number of photons}}{\text{Time}}$

$$= \frac{2.5 \times 10^{15}}{2 \times 10^{-9}\,\text{s}} = 1.25 \times 10^{24}\,\text{s}^{-1}$$

$E = h\nu = 6.626 \times 10^{-34}\,\text{Js} \times 1.25 \times 10^{24}\,\text{s}^{-1}$

$E = 8.2825 \times 10^{-10}$ J.

29. The longest wavelength doublet absorption transition is observed at 589 and 589.6 nm. Calculate the frequency of each transition and energy difference between two excited states.

Ans.: $\nu_1 = \dfrac{c}{\lambda_1} = \dfrac{3 \times 10^{8}\,\text{ms}^{-1}}{589 \times 10^{-9}\,\text{m}} = \dfrac{3000 \times 10^{5+9}}{589}$

$= 5.093 \times 10^{14}$ Hz or s^{-1}

$$\nu_2 = \frac{c}{\lambda_2} = \frac{3 \times 10^{8}}{589.6 \times 10^{-9}\,\text{m}} = \frac{3000 \times 10^{14}}{589.6}$$

$= 5.088 \times 10^{14}$ Hz or s^{-1}

$\Delta E = h(\nu_1 - \nu_2)$

$= h\,(5.093 - 5.088) \times 10^{14} = 6.626 \times 10^{-34} \times 0.005 \times 10^{14} = 3.313 \times 10^{-22}$ J

30. Following results are observed when sodium metal is irradiated with different wavelengths.

Calculate (a) threshold wavelength and (b) Planck's constant.

λ (nm)	500	450	400
$V \times 10^5$ (ms^{-1})	2.55	4.35	5.20x

Ans.: For any metal

(a) K.E. = hv – Work Function

$$\frac{1}{2}mV^2 = hv - \frac{hc}{\lambda_0} \quad \text{where, } v \rightarrow \text{Frequency,}$$

$\lambda_0 \rightarrow$ Threshold wavelength, c → Velocity of light

$$\frac{1}{2}m(2.55\times10^5)^2 = \frac{hc}{10^{-9}}\left(\frac{1}{500} - \frac{1}{\lambda_0}\right) \quad \text{...(i)}$$

$$\frac{1}{2}m(4.35\times10^5)^2 = \frac{hc}{10^{-9}}\left(\frac{1}{450} - \frac{1}{\lambda_0}\right) \quad \text{...(ii)}$$

$$\frac{1}{2}m(5.20\times10^5)^2 = \frac{hc}{10^{-9}}\left(\frac{1}{400} - \frac{1}{\lambda_0}\right) \quad \text{... (iii)}$$

Dividing (ii) by (i) we get

$$\frac{\lambda_0 - 450}{450\lambda_0} \times \frac{500\lambda_0}{\lambda_0 - 500} = \left(\frac{4.35}{2.55}\right)^2$$

$$\frac{\lambda_0 - 450}{\lambda_0 - 500} \times \frac{450}{500}\left(\frac{4.35}{2.55}\right)^2$$

$$= \frac{\lambda_0 - 450}{\lambda_0 - 500} = \frac{450}{500}\left(\frac{4.35}{2.55}\right)^2 = 2.619$$

$$\Rightarrow \lambda_0 - 450 = 2.619\lambda_0 - 1309.5$$

$$\Rightarrow 1.619\lambda_0 = 859.5 \Rightarrow \lambda_0 = 531 \text{ nm.}$$

31. Emission transitions in the Paschen series end at orbit *n* = 3 and start from orbit *n* and can be represented as v = 3.29×10^{15} (Hz)

$$\left[\frac{1}{3^2} - \frac{1}{n^2}\right]$$

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

Ans.: $v = \frac{c}{\lambda}, \lambda = \frac{c}{v}, \lambda = 1285 \text{ nm};$

$v = 3.29 \times 10^{15}\text{s}^{-1}$

$$\bar{v} = R\left[\frac{1}{3^2} - \frac{1}{n^2}\right] \quad R \rightarrow \text{Rydberg's Constant}$$

$$\frac{1}{\lambda} = 1.097\times10^7 \text{m}^{-1}\left[\frac{1}{9} - \frac{1}{n^2}\right]$$

$$\frac{1}{1285\times10^{-9}} = 1.097\times10^7\left[\frac{1}{9} - \frac{1}{n^2}\right]$$

$$\frac{1}{9} - \frac{1}{n^2} = \frac{1}{1285\times10^{-9}\times1.097\times10^7}$$

$$\frac{1}{n^2} = \frac{1}{9} = \frac{100}{1285\times1.097} = \frac{1}{9} - \frac{100}{1409.645}$$

$$\cong \frac{1}{9} - 0.07093 \approx 0.1111 - 0.07093$$

$$\frac{1}{n^2} \approx 0.04018$$

$$n^2 \approx \frac{1}{0.04018} \approx 25$$

n = 5, infrared region.

32. 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 characteristic velocity associated with the neutron.

Ans.: $\lambda = 800 \text{ pm} = 800 \times 10^{-12} \text{ m} = 8 \times 10^{-10} \text{ m}$

$$\lambda = \frac{h}{mV} \Rightarrow V = \frac{h}{m\lambda} = \frac{6.626\times10^{-34}\text{Js}}{1.675\times10^{-27}\text{kg}\times800\times10^{-12}}$$

$$V = \frac{66.26}{13.400}\times10^{-35+27+10} = 4.94\times10^2 \text{ ms}^{-1}$$

33. The velocity associated with a proton moving in a potential difference of 1000 V is 4.37 × 10^5 ms^{-1}. If the hockey ball of mass 0.1 kg is moving with this velocity, calculate the wavelength associated with this velocity.

Ans.: $\lambda = \frac{h}{mV} = \frac{6.626\times10^{-34}\,Js}{0.1kg\times4.37\times10^{5}ms^{-1}}$

$$= \frac{6.626}{4.37}\times10^{-34+1-5} = 1.516\times10^{-38}m.$$

34. If the position of the electron is measured within an accuracy of ±0.002 nm, calculate the uncertainty in the momentum of the electron. Suppose the momentum of the electron is $\frac{h}{4}\pi m\times0.05\,nm$, is there any problem in defining this value

Ans.: $\Delta x = 0.002\times10^{-9}$ m;

$$\Delta x\times\Delta p = \frac{h}{4\pi}$$

$$\Delta p = \frac{h}{4\pi\times\Delta x} = \frac{6.626\times10^{-34}}{4\times3.142\times2\times10^{-12}m}$$

$$= \frac{6.626}{25.136}\times10^{-34+12}$$

$$= \frac{66.26}{25.136}\times10^{-23}kg\ ms^{-1}$$

$$= 2.636\times10^{-23}kg\ ms^{-1}$$

35. Among the following pairs of orbitals which orbital will experience the larger effective nuclear charge?

(i) 2*s* and 3*s*   (ii) 4*d* and 4*f*

(iii) 3*d* and 3*p*

Ans.: (i) 2s (ii) 4d (iii) 3p

36. A photon of wavelength 4 × 10^{-7} m strikes on metal surface, the work function of the metal being 2.13 eV. Calculate

(a) the energy of the photon (eV)

(b) the kinetic energy of the emission and

(c) the velocity of the photoelectron.

1eV = 1.602 × 10^{-19} J, mass of $e^- = 9.1\times10^{-31}$kg)

Ans.: (a) λ = 4 × 10^{-7} m ϕ = 2.13 eV

$$E = \frac{hc}{\lambda} = \frac{6.626\times10^{-34}\times3\times10^{8}}{4\times10^{-7}} = \frac{19.878}{4}\times10^{-34+8+7}$$

$$E = 4.96\times10^{-19}J = \frac{4.96\times10^{-19}J}{1.602\times10^{-19}} = 3.096\ eV$$

(b) $h(v - v_0)$ = K.E.

(K.E. = 0.966 eV = 0.966 × 1.602 × 10^{-19} J

= 1.55 × 10^{-19} J

(c) $\frac{1}{2}mV^2 = 1.55\times10^{-19}J$

$$\Rightarrow V^2 = \frac{2\times1.55\times10^{-19}J}{9.1\times10^{-31}}$$

$$= \frac{3.1\times10^{-3}}{9.1} = 0.3406\times10^{-3}$$

$V^2 = 3.406\times10^{-4} \Rightarrow V = 1.85\times10^{-2}\ ms^{-1}$

37. (a) Establish relationship between wavelength (λ) and momentum (*p*) of material particle.

Ans.: (a) $E = mc^2;\ E = \frac{hc}{\lambda}$

$$mc^2 = \frac{hc}{\lambda};\ \lambda = \frac{h}{mc};\ \boxed{\lambda = \frac{h}{p}}$$

(b) Hund's Rule of maximum multiplicity.

(c) K. E. = $h(v - v_0)$

$= 6.626 \times 10^{-34}$ Js $\times 3.0 \times 10^{14} s^{-1} = 19.878 \times 10^{-20}$ J $= 1.9878 \times 10^{-19}$ J

38. (a) Explain Aufbau principle with the help of example

(b) What is Pauli exclusion principle?

Ans.: (a) Electrons are filled in the orbitals in increasing order of their energies, i.e., orbitals with lowest energy is filled first, highest energy is filled last.

(b) **Pauli Exclusion Principle**. In an atom no two electrons can have all the four quantum numbers same.

39. (a) When energy of electron is to be taken to zero?

(b) Which of the following orbitals are not possible? Give reasons

3*s*, 1*p*, 4*f*, 2*d*

Ans.: (a) When electron is at infinite distance from the nucleus, its energy is taken as zero.

(b) 1p is not possible because when n = 1, *l* = 0 only and cannot be equal to 1.

2d is not possible because when n = 2, *l* = 0 and 1 and it cannot be equal to 2.

40. (a) Write the electronic configuration of Cu^+ ion (Z = 29)

(b) Compare the energies of the two radiations with wavelngth 6000 Å and 4000 Å.

2*s*, 2*d*, 4*f*, 5*p*.

Ans.: (a) $Cu^+(29) : 1s^2 2s^2 2p^6 3s^2 3p^6 4s^0 3d^{10}$

(b) $E_1 = \frac{hc}{\lambda_1}, E_2 = \frac{hc}{\lambda_2}$

$$\frac{E_1}{E_2} = \frac{hc}{\lambda_1} \times \frac{\lambda_2}{hc}$$

$$\frac{E_1}{E_2} = \frac{4000}{6000} = \frac{2}{3}$$

(c) 2d is not possible because when n = 2 then *l* cannot be equal to 2.