BRUSH UP YOUR CONCEPTS

Class XI

This specially designed column will help you to brush up your concepts by practicing questions. You can mail us your queries and doubts related to this topic at editor@mtg.in. The queries will be entertained by the author.*

STRUCTURE OF ATOM

In continuation to the last article :

de Broglie's work (1924)

de Broglie suggested that all moving particles have wave character also, though it has no significance for macro particles.

Wave character of electrons is proved by diffraction (Davisson and Germer) while particle nature by scintillation on ZnS coated glass tube (opposite to cathode) in cathode ray tube.

$$\lambda_{\text{matter-wave}} = \frac{h}{\text{mass}(m) \times \text{velocity}(v)} = \frac{h}{\text{momentum}(p)}$$

$$\lambda_{\text{matter-wave}} = \frac{h}{\sqrt{2m \times \frac{1}{2}mv^2}} = \frac{h}{\sqrt{2m \cdot KE}}$$

KE is in joules. If q coulombs is the charge of a particle and potential V in volts, (1 CV = 1 J)

$$\lambda_{\text{matter-wave}} = \frac{h}{\sqrt{2m \cdot qV}}$$

$$\lambda_{\text{electronic motion}} = \frac{h}{\sqrt{2m \cdot eV}} \quad (\text{Here, } e = 1.6 \times 10^{-19} \text{ C})$$

Heisenberg's work (1927)

Heisenberg gave the idea that determination of exact position (wave property) and exact momentum (particle property) of a microscopic object is not possible.

$$(\Delta x)(m\Delta v) = \Delta x \cdot \Delta p \geq \frac{h}{4\pi}$$

Δx is uncertainty (error) in measurement of position, Δv is uncertainty in measuring velocity and Δp is uncertainty in measuring momentum.

This principle had been one of the basis of failures of Bohr's view of definite circular paths for electrons in motion around nucleus.

Wave mechanical model of atom

As in Newton's classical mechanics, the pivotal equation is, Force (F) = mass (m) × acceleration (a), in wave mechanical model of atom the pivotal equation is Schrodinger wave equation :

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

or $\quad \widehat{H}\psi = E\psi$

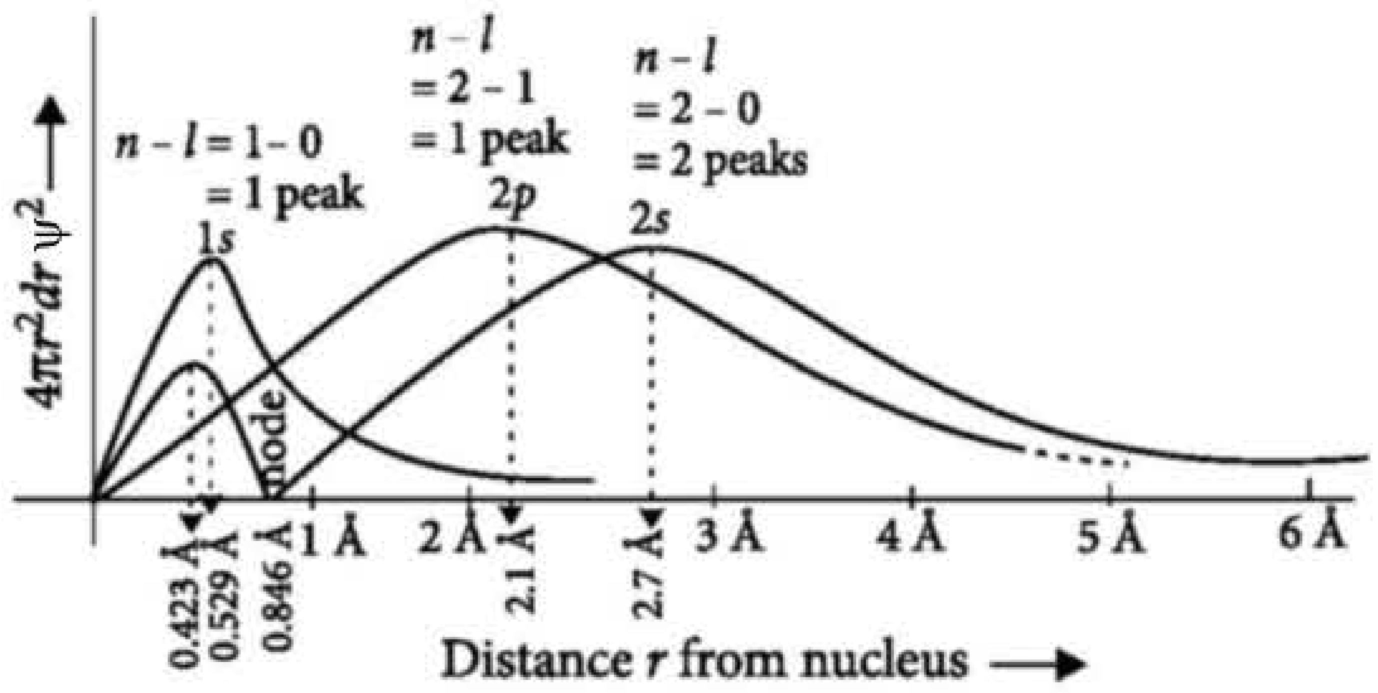
The solution of this equation is arrived at, for some definite values of ψ to get some definite sets of principal quantum number 'n', azimuthal quantum number 'l' and magnetic quantum number 'm', which are further used mathematically to know different details related to an electron in an atom. One more quantum number spin quantum number 's' is also used for the purpose of spin of electron. ψ, itself, has no significance except that it represents amplitude of electronic wave motion and now it is used to represent an orbital.

An orbital is the space around a nucleus where there is maximum probability of finding an electron.

The ψ^2, radial probability density value, which is always positive, is used to decide the number of nodes in an orbital.

Radial probability density function $4\pi r^2 \cdot dr \cdot \psi^2$ when plotted against distance from the nucleus r, gives the most probable radius of an orbital; for 1s it is 0.529 Å, for 2s it is 2.743 Å and for 2p it is 2.1 Å.

*By **R.C. Grover**, having 45+ years of experience in teaching chemistry.



- **Very important for 1s, 2s and 2p orbitals:**
  (a) Size of orbitals : $1s < 2p < 2s$
  (b) Energy of orbitals : $1s < 2s < 2p$

Principal quantum number, n (*Niels Bohr*)

- It represents orbits or energy states or shells as 1, 2, 3, ...; also designated as K, L, M, ...
- Higher the n value, farther is the electron from nucleus, *i.e.*, $r_1 < r_2 < r_3 <$ ......
- Energy of electron in n^{th} shell

$$= -1312\frac{Z^2}{n^2}\text{ kJ mol}^{-1} = -1.312\times10^6\frac{Z^2}{n^2}\text{ J mol}^{-1}$$

$$= -2.18\times10^{-18}\frac{Z^2}{n^2}\text{ J atom}^{-1} = -13.6\frac{Z^2}{n^2}\text{ eV atom}^{-1}$$

  (a) $E_1 < E_2 < E_3 <$ .....
  (b) $(E_2 - E_1) > (E_3 - E_2) >$ ......
- n^{th} shell has n subshells, n^2 orbitals and a maximum of $2n^2$ electrons.
- Angular momentum, $mvr = n\frac{h}{2\pi}$
- Spin (only) magnetic moment = $\sqrt{x(x+2)}$ B.M. Here, x is number of unpaired electrons.

$$1\text{ B.M.} = \frac{eh}{4\pi m_e} = 9.273\times10^{-14}\text{ J}$$

Azimuthal or secondary or subsidiary quantum number, l (*Sommerfeld*)

- It represents subshells.
- For n^{th} shell, l has n-values (l = 0, 1, 2, ..., (n – 1)) *i.e.* n subshells.
  1^{st} shell has only one subshell s with $l = 0$.
  2^{nd} shell has two subshells s and p with $l = 0$ and $l = 1$.
- Shapes : s has spherically symmetrical shape.
  p has dumb-bell shape.
  d has clover leaf shape with d_{z^2} having baby soother or doughnut shape.
- Any subshell has $(2l + 1)$ orbitals and a maximum of $2(2l + 1)$ electrons. s-subshell ($l = 0$) has only one orbital with its capacity of 2 electrons. p-subshell (l – 1) has three orbitals (p_x, p_y and p_z), two electrons in each (maximum) and total maximum capacity of six electrons, etc.
- Orbital angular momentum of an electron in a subshell = $\sqrt{l(l+1)}\cdot\frac{h}{2\pi}$ B.M.

Magnetic quantum number m or m_l (*Lande*)

- For any value of l, m has $(2l + 1)$ values, *i.e.*, orbitals $-l, -(l-1), ..., 0, ..., (l-1), l$
- For $l = 0$, *i.e.*, s-subshell, there is only one orbital, s-orbital with $m = 0$.
  For $l = 1$, *i.e.*, p-subshell, there are three orbitals, if p_x or p_y has $l = -1$, then p_y or p_x has $l = +1$ and p_z has $l = 0$, etc.

Spin quantum number s (*Uhlenbeck and Goudsmit*)

- It is used to represent the spin of electron, if clockwise, then +1/2 value and if anticlockwise, then –1/2 value.
- Spin angular momentum of electron

$$= \sqrt{s(s+1)}\cdot\frac{h}{2\pi}$$

- For x unpaired electrons, spin angular momentum is

$$\sqrt{\frac{x}{2}\left(\frac{x}{2}+1\right)}\cdot\frac{h}{2\pi}\text{ B.M.}$$

National Talent Search Examination

The Schedule of NTSE-2018-19

Stage	Area	Tentative Dates
Stage-I (State)	Last Date for Submission of Application Form	To be notified by the respective State/UT. May vary from state to state.
	Examination in Mizoram, Meghalaya, Nagaland and Andaman and Nicobar Islands	03th November, 2018 (Saturday)
	Examination in All other States and Union Territories	04th November, 2018 (Sunday)
	West Bengal	18th November, 2018 (Sunday)
Stage-II (National)	Examination in All States and Union Territories	12th May, 2019 (Sunday)

Nodes

These are hypothetical points around a nucleus where there is no density of electrons. These may form radial (spherical) and angular (non-spherical) surfaces.

An orbital may have $(n - l - 1)$ radial/spherical and l angular/non-spherical and total $n - 1$ nodes.

$1s$, $2p$, $3d$ and $4f$ do not have any radial/spherical nodes.

d_{z^2} has no nodes.

Writing electronic configuration

- **Aufbau principle :** In the ground state of an atom, all shells/subshells/orbitals are considered empty and electrons are fed to them one at a time according to increasing energies of subshells/orbitals, keeping in view Pauli's exclusion principle and Hund's rule. The sequence of subshells/orbitals in increasing energies obtained from Bohr-Bury's '$n + l$' rule.
- **'$n + l$' rule or Bohr-Bury's rule :** In the same atom, energies of two electrons/orbitals/subshells are compared by using '$n + l$' rule. Higher the '$n + l$' value, higher is the energy. If the two cases have the same value of '$n + l$' then higher the n value, higher is the energy.

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

  Note : H-atom is exception to this rule. Energies of all subshells/orbitals depend only on 'n' value.

  $1s < 2s = 2p < 3s = 3p = 3d < ....$
- **Pauli's exclusion principle :** No two electrons in an atom can have the same set of four quantum numbers.

  Corollary : An orbital can have at the most two electrons with opposite spins.
- **Hund's rule of maximum multiplicity :** Pairing of electrons in degenerate orbitals of p, d and f subshell starts only when they first gain one electron each with parallel spin. The new electron has opposite spin.
- It is very important to note that after atomic number 20, the electronic configurations are not written in accordance with the Aufbau principle. We follow certain more facts.
  - (a) Melting point, magnetic moment, ionisation energy, etc. are given due weightage.
  - (b) All subshells of a shell are written together.
  - (c) Half filled and completely filled orbitals of a subshell give extra stability etc.

Following elements have specially different setting of electronic configurations :

Cr(Z = 24), Cu(Z = 29), Mo(Z = 42), Ag(Z = 47), Au(Z = 79), Nb (Z = 41), Ru(Z = 44), Rh(Z = 45), Pd(Z = 46), Pt(Z = 78), La(Z = 57), Ac(Z = 89) and some inner transition elements.

MULTIPLE CHOICE QUESTIONS

1. The period number of an element in periodic table is decided by ______ quantum number of the valence shell of electronic configuration.
(a) principal (b) azimuthal
(c) magnetic (d) spin

2. The shape of a subshell/orbital in an atom is decided by ______ quantum number.
(a) principal (b) azimuthal
(c) magnetic (d) spin

3. The orientation of an orbital is decided by ______ quantum number.
(a) principal (b) azimuthal
(c) magnetic (d) spin

4. Two electrons present in the same orbital in an atom can be distinguished by ______ quantum number.
(a) principal (b) azimuthal
(c) magnetic (d) spin

5. Which of the following set of quantum numbers is not allowed in an atom?

	n	l	m	s		n	l	m	s
(i)	2	3	1	$+\frac{1}{2}$	(ii)	3	2	3	$-\frac{1}{2}$
(iii)	2	1	3	$+\frac{1}{2}$	(iv)	4	0	1	$+\frac{1}{2}$

(a) (ii) only (b) (iii) only
(c) (iv) only (d) All of these

6. Which of electron, proton and alpha particle will have highest kinetic energy if their de Broglie wavelengths are the same?
(a) Electron (b) Proton
(c) Alpha-particle (d) All have equal K.E.

7. Which of the following is correct for the uncertainty of velocity if uncertainties of position and momentum are equal?