

Chapter \Rightarrow 2

Structure of Atom

\Rightarrow Atom :-

John Dalton proposed (in 1808) that atom is the smallest indivisible particle of matter. Atomic radii are of the order of 10^{-8} cm. It contains three subatomic particles of namely electrons, protons and neutrons,

\Rightarrow Electron :-

Electron was discovered as a result of study of Cathode rays by JJ Thomson. It was named by stony

It carries a unit negative charge $(-1.6 * 10^{-19}$

C.)

Mass of electron is $9.11 * 10^{-31}$ kg and mass of one mole of electron is 0.55 mg.

Some of the Characteristics of Cathode ray are :

1. These travel in straight line away from Cathode and produce fluorescence when strike the glass wall of discharge tube.
2. These cause mechanical motion in a small pin wheel placed in their path.
3. These produce α -rays when strike with metal and are deflected by electric and magnetic field.

→ Proton :-

Rutherford discovered proton on the basis of anode ray experiment.

It carries a unit positive charge ($+1.6 \times 10^{-19}$ C).

The mass of proton is 1.007276 u.



The e/m ratio of proton is $9.58 \times 10^{-7} \text{ C/g}$
(e/m ratio is maximum for hydrogen gas.)

Some of the Characteristics of anode rays are :

1. These travel in straight line and possess mass many times the mass of an electron.
2. These are not originated from anode.
3. These also cause mechanical motion and are deflected by electric and magnetic field.
4. Specific charge (e/m) for these rays depends upon the nature of the gas taken and is maximum for H_2

⇒ Neutron :-

Neutrons are neutral particles. It was discovered by Chadwick (1932). The mass of neutron is 1.675×10^{-24} g or 1.008665 amu or u.



→ Some uncommon subatomic particles :-

a) Positron :- Positive electron (${}^0_{+1}\text{e}$), discovered by Dirac (1930) and Anderson (1932).

(b) Neutrino and antineutrino :- Particles of small mass and no charge as stated by Fermi (1934).

⇒ (c) Meson :- Discovered by Yukawa (1935) and Kemmer. They are unstable particles and include pi ions [pi^+ , pi^- or pi^0].

(d) Anti-proton :- It is negative proton produced by Segre and Weigand (1955).

⇒ Thomson's Atomic Model :-

Atom is positive sphere with a number of electrons distributed within the sphere. It is also known as plum pudding model. It explains the neutrality of an atom. This model could not explain the results of Rutherford scattering experiment.

⇒ Rutherford's Nuclear Model of Atom :-

It is based upon α -particle scattering experiment. Rutherford presented that

1. Most part of the atom is empty.
2. Atom possesses a highly dense, positively charged centre, called nucleus of the order 10^{-13} cm.
3. Entire mass of the atom is concentrated inside the nucleus.



4. Electrons revolve around the nucleus in circular orbitals.

5. Electrons and the nucleus are held together by electrostatic force of attraction.

⇒ Drawbacks of Rutherford's Model :-

1. According to electromagnetic theory, when charged particles accelerated, they emit electromagnetic radiations, which ~~CODE~~ by electronic motion and thus orbit continue to shrink, so atom unstable. It doesn't explain the stability of atom.

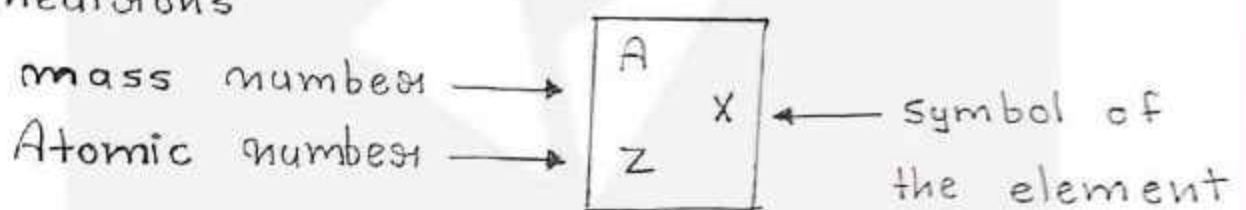
2. It doesn't say anything about the electronic distribution electrons around nucleus.

⇒ Atomic Number :-

Atomic number of an element corresponds to the total number protons present in the nucleus or total number of electrons present the neutral atom.

⇒ Mass number :-

Mass number of an element
= number of protons + number of neutrons



⇒ Electromagnetic Wave Theory:- (Maxwell)

The energy is emitted from source continuously in the form of radiations and magnetic field. All electromagnetic waves travel with the velocity of light ($3 \times 10^8 \text{ m/s}$) and do not require any medium for their propagation.

An electromagnetic wave has the following

Characteristics :

(i) wavelength :- It is the distance between two successive crests or troughs of a wave. It is denoted by the Greek letter λ (lambda).

(ii) frequency :- It represents the number of waves which pass through a given point in one second. It is denoted by ν (nu).

(iii) velocity :- (v) It is defined as the distance covered in one second by the waves. Velocity of light is $3 \times 10^{10} \text{ cm s}^{-1}$.

= (iv) wave number :- It is the reciprocal of wavelength and has units cm^{-1} . It is denoted by ν (nu bar).

= (v) Amplitude :- (a) It is the height of the crest or depth of the trough of a wave.

Wavelength (λ), frequency (ν) and velocity (c) of any electromagnetic radiation are related to each other as $c = \nu\lambda$

→ Electromagnetic Spectrum :-

The different types of electromagnetic radiations differ only in their wavelengths and hence, frequencies. When these electromagnetic radiation are arranged in order to their, increasing wavelengths or decreasing frequencies, the complete spectrum obtained is called electromagnetic spectrum.

→ Different Types of Radiations and Their Sources :-

Type of Radiation	wavelength(in \AA)	Generation Source
Gamma rays	0.01 to .1	Radiative disintegration
X-rays	0.01 to 150	from metal when an electron strikes on it
UV-rays	150 to 3800	Sun rays
Visible rays	3800 to 7600	Star, arc lamps
Infrared rays	7600 to 6×10^4	Incandescent objects
Micro waves	6×10^6 to 3×10^8	Klystron tube
Radio waves	3×10^{14}	from an alternating current of high frequency



Electromagnetic spectra may be emission or absorption spectrum on the basis of energy absorbed or emitted. An emission spectrum is obtained when a substance emits radiation after absorbing energy. An absorption spectrum is obtained when a substance absorbs certain wavelengths and leave dark spaces in bright continuous spectrum.

Electromagnetic wave theory was successful in explaining the properties of light such as interference, diffraction etc., but it could not explain the following

1. Black body - radiation
2. Photoelectric effect

These phenomena could be explained only if electromagnetic waves are supposed to have particle nature.

→ 1. Black Body Radiation :-

If the substance being heated is a Black body. the radiation emitted is called black body radiation.

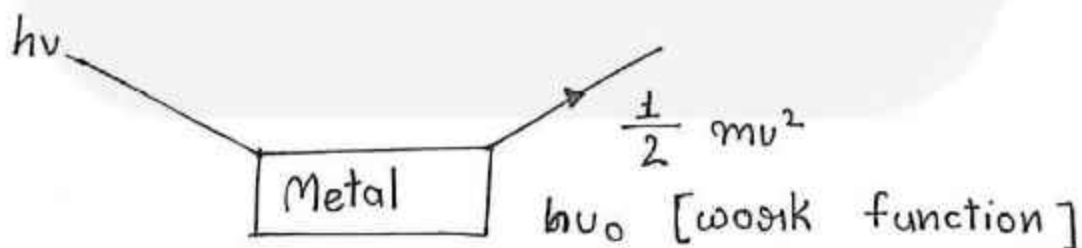
⇒ 2. Photoelectric Effect :-

It is the phenomena in which beam of light of certain frequency falls on the surface of metal and electrons are ejected from it.

This phenomenon is known as photoelectric effect. It was first observed by Hertz.

$$W_{0c} = h\nu_0$$

$$W_{0c} = hc / \lambda_{max}$$



Threshold frequency (ν_0) = minimum frequency of the radiation

Work function (W_0) = required minimum energy of the radiation

$$E = K_e + W_0$$

$$\therefore \frac{1}{2} Mv^2 = h(\nu - \nu_0)$$

[Kinetic energy of ejected electron = $h(\nu - \nu_0)$]

Where; ν = frequency of incident radiation

ν_0 = threshold frequency

▶ Particle Nature of Electromagnetic Radiation:

▶ Planck's Quantum Theory :-

Planck explain the distribution of intensity of the radiation from black body as a function of frequency or wavelength at different temperature.

$$E = h\nu = hc / \lambda$$

Where, h = Planck's constant = $6.63 \times 10^{-34} \text{ J-s}$

E = energy of photon or quantum

ν = frequency of emitted radiation



If n is the number of quanta of a particular frequency and E_T be Total energy then $E_t = nh\nu$

⇒ Bohr's Model :-

Neils Bohr proposed his model in 1913. Bohr's model is applicable only for one electron system like H, He^+, Li^{2+} etc.

Assumptions of Bohr's model are

1. Electron keep revolving around the nucleus in certain fixed permissible orbits where it doesn't gain or lose energy. These orbits are known as stationary orbits.

Number of waves in an orbit = Circumstances of orbit / wavelength

2. The electrons can move only in those orbits for which the angular momentum is an integral multiple of $h / 2\pi$, i.e.,

$$mvr = nh / 2\pi$$



Where, m = mass of electron ; v = velocity of electron ;

r = radius of orbit

n = number of orbit in which electron are present

3. Energy is emitted or absorbed only when an electron jumps from higher energy level to lower energy level and vice-versa.

$$\Delta E = E_2 - E_1 = h\nu = hc / \lambda$$

4. The most stable state of an atom is its ground state or normal state,

from Bohr's model, energy, velocity and radius of an electron in n th Bohr orbit

$$(v_n) = 2.165 * 10^6 Z / n \text{ m/s}$$

(i) velocity of an electron in n th Bohr orbit

(ii) Radius of n th Bohr orbit

$$(r_n) = 0.53 * 10^{-10} n^2 / Z \text{ m} = 0.53 n^2 / Z \text{ \AA}$$



$$(iii) E_n = -2.178 \times 10^{-18} \frac{Z^2}{n^2} \text{ J/atom}$$

$$= -1312 \frac{Z^2}{n^2} \text{ KJ/mol}$$

$$= -13.6 \frac{Z^2}{n^2} \text{ eV/atom}$$

$$\Delta E = -2.178 \times 10^{-18} \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) Z^2$$

J/atom

Where, n_1 = number of shell; Z = atom number

As we go away from the nucleus, the energy levels come closer; i.e., with increase in the value of n , the difference of energy between successive orbits decreases.

Thus, $E_2 - E_1 > E_3 - E_2 > E_4 - E_3 > E_5 - E_4$ etc.

⇒ Sommerfeld Extension to Bohr's Model :-

According to this theory, the angular momentum of revolving electron in all elliptical orbit is an integral multiple of $h/2\pi$, i.e.,



$$m_{\text{max}} = kh / 2\pi$$

from Bohr model, $m_{\text{max}} = nh / 2\pi$

for K shell, $n = 1$, $k = 1$ Circular shape

L shell, $n = 2$, $k = 1, 2$ Circular

M shell, $n = 3$, $k = 1, 2, 3$ Elliptical

N shell, $n = 4$, $k = 1, 2, 3, 4$ Elliptical

⇒ Emission spectrum of Hydrogen :-

According to Bohr's theory, when an electron jumps from ground states to excited state.

It emits a radiation of definite frequency (or wavelength), corresponding to the wavelength of each photon of light emitted, a bright line appears in the spectrum.

The number of spectral lines in the spectrum when the electron comes from n th level to the ground level = $n(n-1)$

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Hydrogen spectrum consist of line spectrum.

Series	Region	n_1	n_2
(i) Lyman	UV	1	2, 3, 4
(ii) Balmer	Visible	2	3, 4, 5
(iii) Paschen	IR	3	4, 5, 6
(iv) Brackett	IR	4	5, 6, 7
(v) Pfund	far IR	5	6, 7
(vi) Humphrey	far IR	6	7, 8, 9

wave number ν is defined as reciprocal of the wavelength

$$\nu = 1/\lambda$$

$$\nu = RZ^2 \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

Here, λ = wavelength

R = Rydberg constant = 109677.8 cm^{-1}

first line of a series is called line of longest wavelength (shortest energy) and last line of a series is the line of shortest wavelength highest energy, ($n_2 = \infty$).

Limitations of Bohr's Theory :-

1. It is unable to explain the spectrum of atom other than hydrogen like doublets or multielectron atoms.
2. It could not explain the ability of atom to form molecules by chemical bonds. Hence, it could not predict the shape of molecules.
3. It is not in accordance with the Heisenberg uncertainty principle and could not explain the concept of dual character of matter.
4. It is unable to explain the splitting of spectral lines in the presence of magnetic field (Zeeman effect) and electric field (Stark effect).

→ de - Broglie principle :-

de - Broglie explains the dual nature of electron i.e., both particle as well as wave nature.

$$\lambda = h / mv$$

Where, λ = wavelength ; v = velocity of particle

m = mass of particle

$$\lambda = h / \sqrt{2m \cdot KE}$$

Where, KE = kinetic energy.

⇒ Heisenberg's uncertainty principle :-

According to this principle, "It is impossible to specify at any give instant both the momentum and the position of subatomic particles like electron".

$$\Delta x \cdot \Delta p \geq h / 4\pi$$

Where, Δx = uncertainty in position ; Δp = uncertainty in momentum.

⇒ Quantum Mechanical Model of Atom :-

It is the branch of Chemistry which deals with dual behaviour of matter. It is given by Werner Heisenberg and Erwin Schrödinger.

Schrodinger's wave equation is

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

Where x, y, z = cartesian coordinates

m = mass of electron, E = total energy of electron

U = Potential energy of electron, h = Planck's constant

ψ (Ψ) = wave function which gives the amplitude of wave

ψ^2 = Probability function

for H-atom. The equation is solved as

$$H\psi = E\psi$$

Where, H is the total energy operator, called Hamiltonian. If the sum of kinetic energy operator (T) and potential energy operator (U) is the total energy E of the system,

$$H = T + U$$

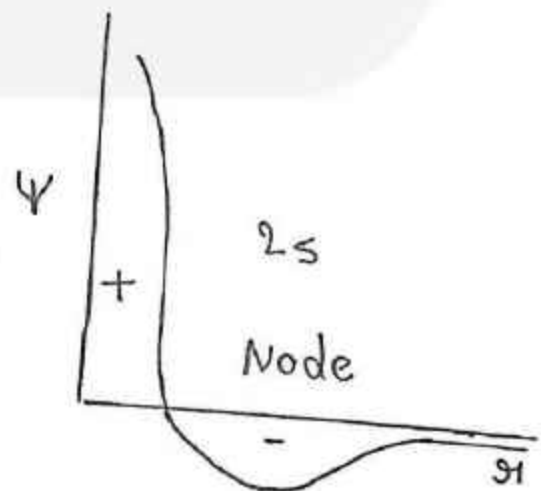
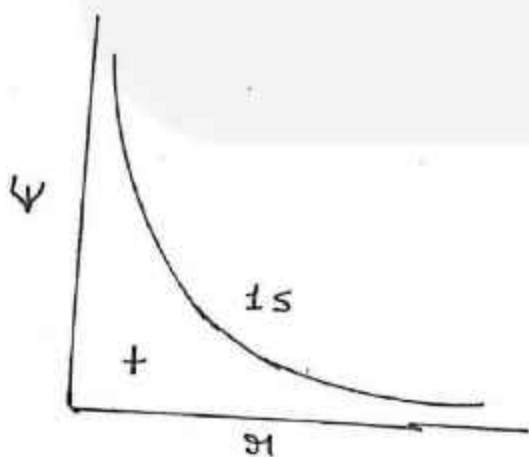
$$(T + U)\Psi = E\Psi$$

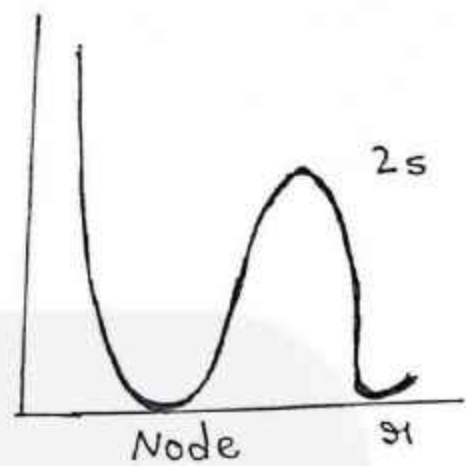
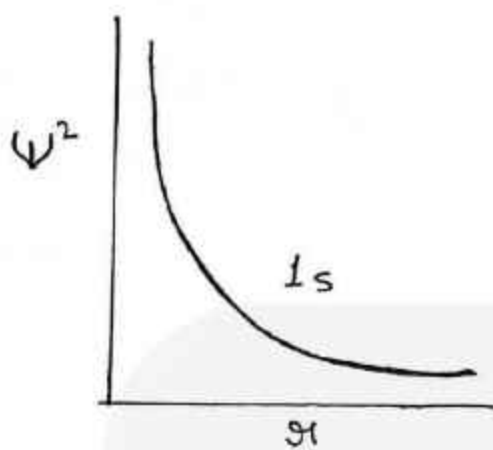
[The atomic orbitals can be represented by the product of two wave functions (i) radial wave function (ii) angular wave function.

The orbitals wave function, Ψ has no significance, but Ψ^2 has significance, it measures the electron probability density at a point in an atom. Ψ can be positive or negative but ' Ψ^2 ' is always positive.

⇒ Probability Diagrams :-

The graph plotted between Ψ^2 and distance from nucleus is called probability diagram.





→ Node :-

A region or space, where probability of finding an electron is maximum is called a peak, while zero probability space is called node. Nodes are of two types.

(a) Radial nodes

(b) Angular nodes

(i) $(n - l - 1)$ = radial node

(ii) (l) = angular node

(iii) $(n - 1)$ = total + node

⇒ Number of Peaks and Nodes of various orbitals :-

S.NO.	Type of Orbital	Number of peaks	
1	s	n	$\frac{1}{2}$
2	p	$n - 1$	$\frac{2}{2}$
3	d	$n - 2$	$\frac{3}{2}$
4	f	$n - 3$	$\frac{4}{2}$

⇒ Quantum Numbers :-

Each electron in an atom is identified in terms of four quantum numbers.

⇒ Principal Quantum Number (Niels Bohr) :-

It is denoted by n . It tells us about the main shell in which electron resides.

it also gives an idea about the energy of shell and average distance of the electron from the nucleus.

Value of $n =$ any integer.

⇒ Azimuthal Quantum Number (Sommerfeld):

It is denoted by l . It tells about the number of subshells (s, p, d, f) in any main shell. It also represents the angular momentum of an electron and shapes of subshells. The orbital angular momentum of an

$$\text{electron} = \sqrt{l(l+1)} \frac{h}{2\pi}$$

Value of $l = 0$ to $n-1$.

$l = 0$ for s, $l = 1$ for p, $l = 2$ for d

$l = 3$ for f

Number of subshells in main energy level = n .

⇒ Magnetic Quantum Number (Lande):

is denoted by m . It tells about the number of orbitals and orientation of each subshell.

value of $m = -l$ to $+l$ including zero.
 Number of orbital in each subshell
 $= (2l + 1)$

S. No.	Subshell	Orbitals
1	s	1
2	p	3
3	d	5
4	f	7

Number of orbitals in main energy level $= n^2$

Spin Quantum Number :- (Uhlenbeck and Goldsmith)

" It is denoted by m_s or s . It indicates the direction of spinning of electron, i.e., Clockwise or anti-clockwise.

Maximum number of electrons in main energy level $= 2n^2$

→ Difference between Orbit and Orbitals :-

Orbit	Orbital
1. An orbit is a well defined circular path around the nucleus in which the electron revolves.	1. An orbital is the three dimensional space around the nucleus within which the probability of finding an electron is maximum.
2. The maximum number of electrons in any orbit is given by $2n^2$ Where n is the number of the orbit.	2. The maximum of electron present in any orbital is two.

→ Electronic Configuration :-

Arrangement of electrons in the space around nucleus in an atom known as electronic configuration.



⇒ Pauli Exclusion Principle :-

It states, no two electrons in an atom can have identical set of four quantum numbers.

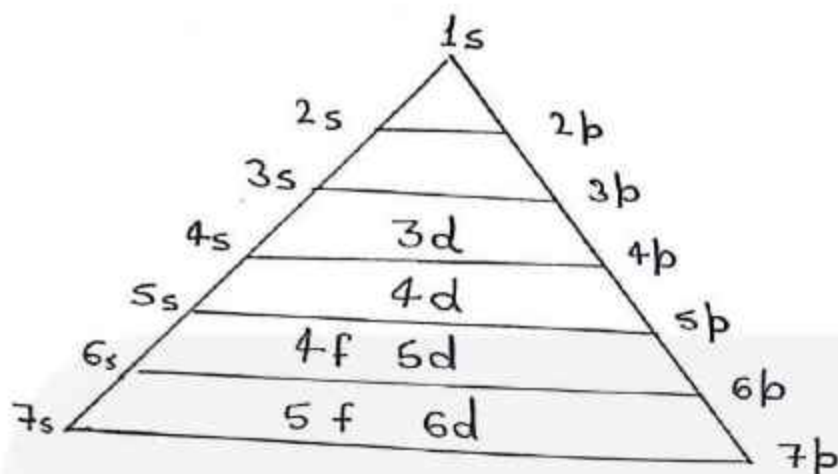
The maximum number of electrons in s subshell is 2, p subshell is 6, d subshell is 10 and f subshell is 14.

⇒ Aufbau Principle :-

According to this principle, in the ground state of an atom, the electrons occupy the lowest energy orbitals available to them, i.e., the orbitals are filled in order of increasing value of $n + l$. For the orbitals having lower value of n is filled up first.

The general order of increasing energies of the orbital is

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



The energy of atomic orbitals for H-atom varies as

$$1s < 2s = 2p < 3s \quad 3p = 3d < 4s = 4p = 4d = 4f$$

Half-filled and completely filled electronic configurations are more stable hence. Outer configurations of Cr is $3d^5 4s^1$ and Cu is $3d^{10} 4s^1$.

Hund's Rule of Maximum Multiplicity :- It states.

(i) in an atom no electron pairing takes place in the p, d or f orbital until each orbital of the given subshell contain

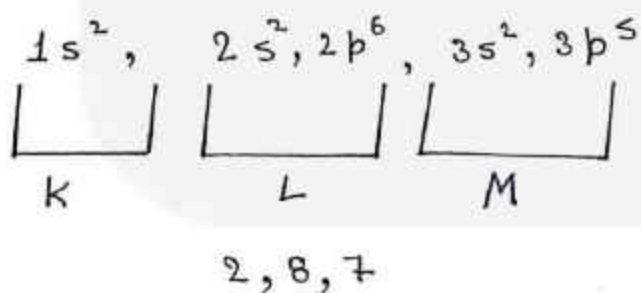
one electrons.

(ii) The unpaired electron present in the various orbitals of the same subshell should have parallel spin.

⇒ Methods of Writing Electronic configuration

(i) orbital Method : In this, the electrons present in respective orbitals are denoted.
e.g. Cl (17) = $1s^2, 2s^2, 2p^6, 3s^2, 3p^5$.

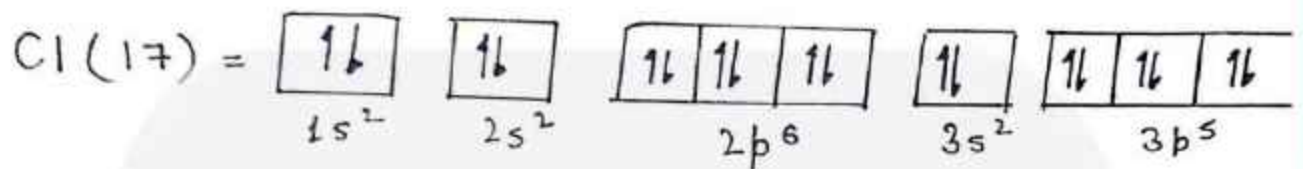
(ii) Shell Method : In this, the number of electrons in each shell is continuously written.
e.g. Cl (17) =



(iii) Box . method :- In this method, each orbital is denoted by a box and electrons are

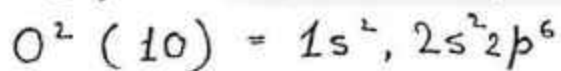
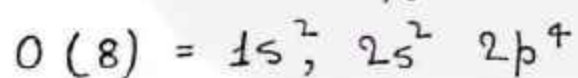
represented by half-headed (\uparrow) or full-headed ($\uparrow\downarrow$) arrows. An orbital can accommodate a maximum of two electrons.

e.g.,



⇒ Electronic configuration of ions :-

To write the electronic configuration of ions, first write the electronic configuration of neutral atom and then add (for negative charge) or remove (for positive charge) electrons in outer shell according to the nature and magnitude of charge present on the ion. e.g.:



⇒ Effective Nuclear Charge :- (Slater's rule)

In a multi-electron atom, the electrons of the inner-shell decrease the force of

attraction exerted by the nucleus on the valence electrons. This is called shielding effect. Due to this, the nuclear charge (Z) actually present on the nucleus, reduces and is called effective nuclear charge (Z_{eff}). It is calculated by using the formula

$$Z_{eff} = Z - \sigma$$

Where σ = screening constant :-

The magnitude of σ is determined by Slater's rules.

Slater's Rules :-

1. Write the electronic configuration in the following order and groups.
 $(1s) (2s, 2p) (3s, 3p) (3d), (4s, 4p) (4d) (4f)$
 $(5s, 5p)$ etc
2. Electrons of $(l+1)$ shell (shell higher than considering electrons) do not contribute in shielding i.e., $\sigma = 0$

3. All other electrons in (ns, np) group contribute $\sigma = 0.85$ each
4. All electrons of $(n-1)$ s and p shell contribute $\sigma = 0.85$ each
5. All electron of $(n-2)$ s and p shell or lower shell contribute $\sigma = 1.00$ each
6. All electrons of nd and nf orbital contribute $\sigma = 0.35$ and those of $(n-1)$ and f or lower orbital contribute $\sigma = 1.00$ each

e.g... Be (4) = $1s^2, 2s^2$

(for 2s)

$$\sigma = 0.35 + 2 \times 0.85$$

$$= 2.05$$

$$Z_{\text{eff}} = Z - \sigma = 4 - 2.05 = 1.95$$

→ Different Types of Atomic Species :-

(a) Isotopes : Species with same atomic number but different mass numbers are called isotopes, e.g. ${}_1\text{H}^1$, ${}_1\text{H}^2$

(b) Isobars : Species with same mass number but different atomic number are called isobars. e.g., ${}_{18}\text{Ar}^{40}$, ${}_{19}\text{K}^{40}$.

⇒ (c) Isotones : Species having same number of neutrons are called isotones,
e.g., ${}_1\text{H}^3$ and ${}_2\text{He}^4$ are isotones.

⇒ (d) Isodiaphers : Species having with same isotopic number are called isodiaphers, e.g., ${}_{19}\text{K}^{39}$, ${}_9\text{F}^{19}$

Isotopic number = mass number - 2 * atomic number.

(e) Isoelectronic: Species with same Number of electrons are called isoelectronic species, e.g., Na^+ Mg^{2+} .

(f) Isostere: Species having same number of atom and same number of electrons, are called isostere, e.g., N_2 and CO .