

Chemistry Class 11 Chapter 2 Structure of Atom

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 namely electrons, protons and neutrons,

Electron

Electron was discovered as a result of study of cathode rays by JJ Thomson. It was named by Stoney

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 rays 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 – their path.
3. These produce X-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.

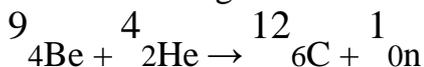
The e/m ratio of proton is 9.58×10^{-4} C/g. (e/m ratio is maximum for

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 a 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 a-particle scattering experiment. Rutherford presented that

1. Most part of the atom is empty.
2. Atom possesses a highly dense, positively charged center, 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 orbits.
5. Electrons and the nucleus are held together by electrostatic forces of attraction.

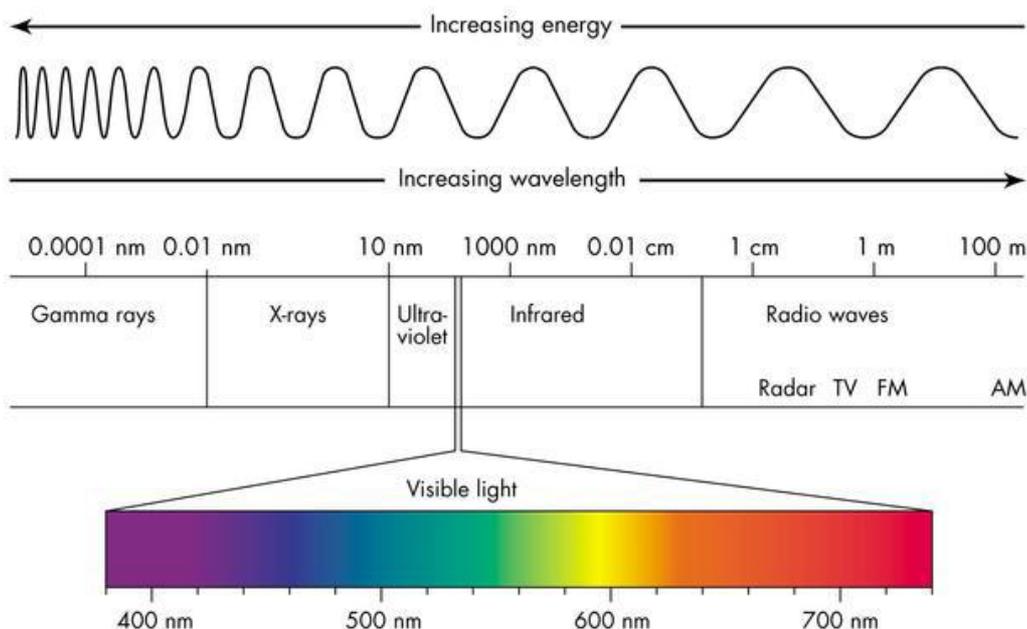
Drawbacks of Rutherford's Model

1. According to electromagnetic theory, when charged particles accelerated, they emit electromagnetic radiations, which control 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 presents the neutral atom



Different Types of Radiations and Their Sources

| Type of radiation | Wavelength (in Å) | Generation source |
|-------------------|------------------------------------|---|
| Gamma rays | 0.01 to 0.1 | Radioactive disintegration |
| X-rays | 0.1 to 150 | From metal when an electron strikes on it |
| UV-rays | 150 to 3800 | Sun rays |
| Visible rays | 3800 to 7600 | Stars, arc lamps |
| Infrared rays | 7600 to 6×10^6 | Incandescent objects |
| Micro waves | 6×10^6 to 3×10^9 | Klystron tube |
| Radio waves | 3×10^4 | 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 spectra 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 phenomenon in which a beam of light of certain frequency falls on the surface of metal and electrons are ejected from it.

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

$$W_0 \leq h\nu_0$$

$$W_0 \leq hc / \lambda_{\max}$$

Threshold frequency (ν_0) = minimum frequency of the radiation

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

$$E = KE + W_0$$

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

[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 explained the distribution of intensity of the radiation from a black body as a function of frequency or wavelength at different temperatures.

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

where, h = Planck's constant = 6.63×10^{-34} J-s

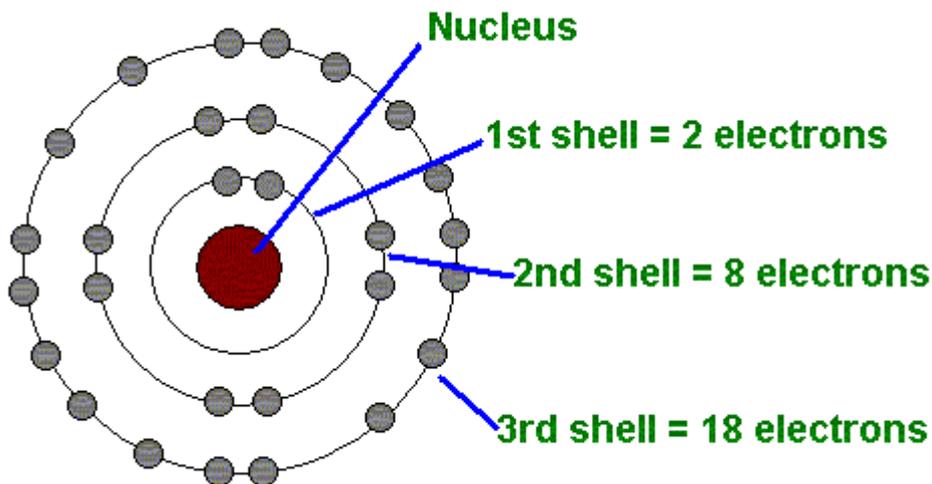
E = energy of photon or quantum

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 1931. Bohr's model is applicable only for one electron system like H, He⁺, Li²⁺ etc.



Assumptions of Bohr's model are

1. Electrons 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.

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 electrons 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 are

(i) Velocity of an electron in n th Bohr orbit (v_n) = $2.165 * 10^6 Z / n \text{ m / s}$

(ii) Radius of n th Bohr orbit

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

$$\begin{aligned}
 \text{(iii) } E_n &= -2.178 \times 10^{-18} \frac{Z^2}{m^2} \text{ J/atom} \\
 &= -1312 \frac{Z^2}{n^2} \text{ kJ/mol} \\
 &= -13.6 \frac{Z^2}{n^2} \text{ eV/atom} \\
 \Delta E &= -2.178 \times 10^{-18} \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) Z^2 \text{ J/atom}
 \end{aligned}$$

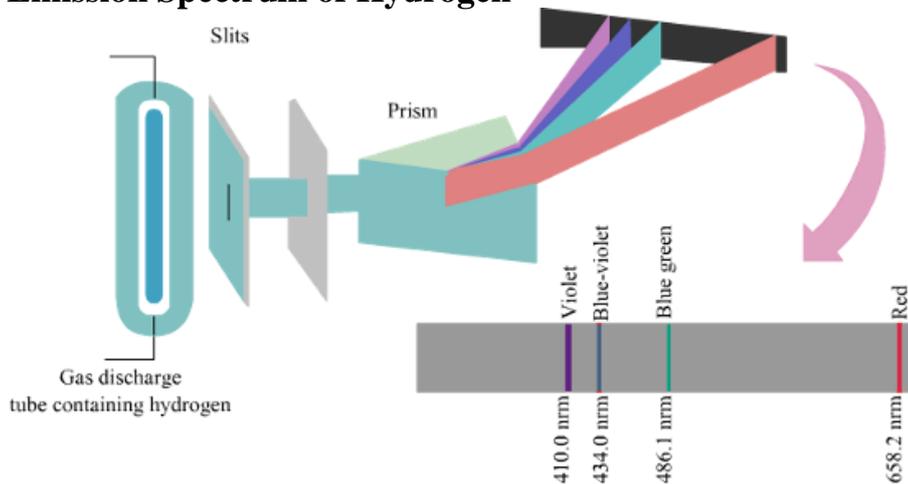
where, n = number of shell; Z = atomic number

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

Thus,

$$E_2 - E_1 > E_3 - E_2 > E_4 - E_3 > E_5 - E_4 \text{ etc.}$$

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 = $n(n - 1) / 2$

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, ... |

Wave number ν is defined as reciprocal of the wavelength.

$$\nu = 1 / \lambda$$

$$\nu = RZ^2 (1 / n_1^2 - 1 / n_2^2)$$

Here, λ = wavelength

$$R = \text{Rydberg constant} = 109677.8 \text{ cm}^{-1}$$

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

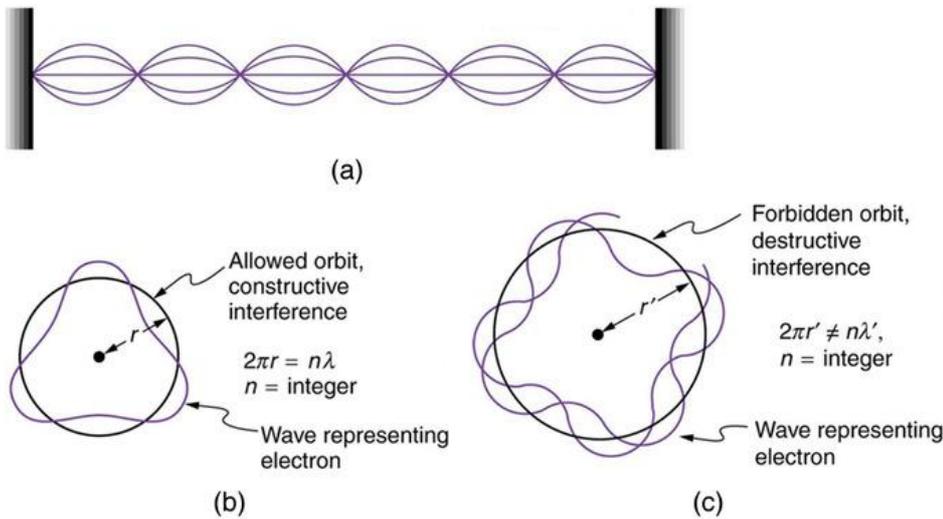
De-Broglie explains the dual nature of electron i.e., both particle as well as wave nature.

$$\lambda = h / mv$$

where, λ = wavelength: v = velocity of particle; m = mass of particle

$$\lambda = h / \sqrt{2m * K E}$$

where, KE = kinetic energy.



Heisenberg's Uncertainty Principle

According to this principle, "it is impossible to specify at any given instant both the momentum and the position of subatomic particles like electrons."

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

where, Δx = uncertainty in position; Δp = uncertainty in momentum

Quantum Mechanical Model of Atom

It is the branch of chemistry which deals with the dual behavior of matter. It is given by Werner Heisenberg and Erwin Schrodinger.

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 (Psi) = 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,

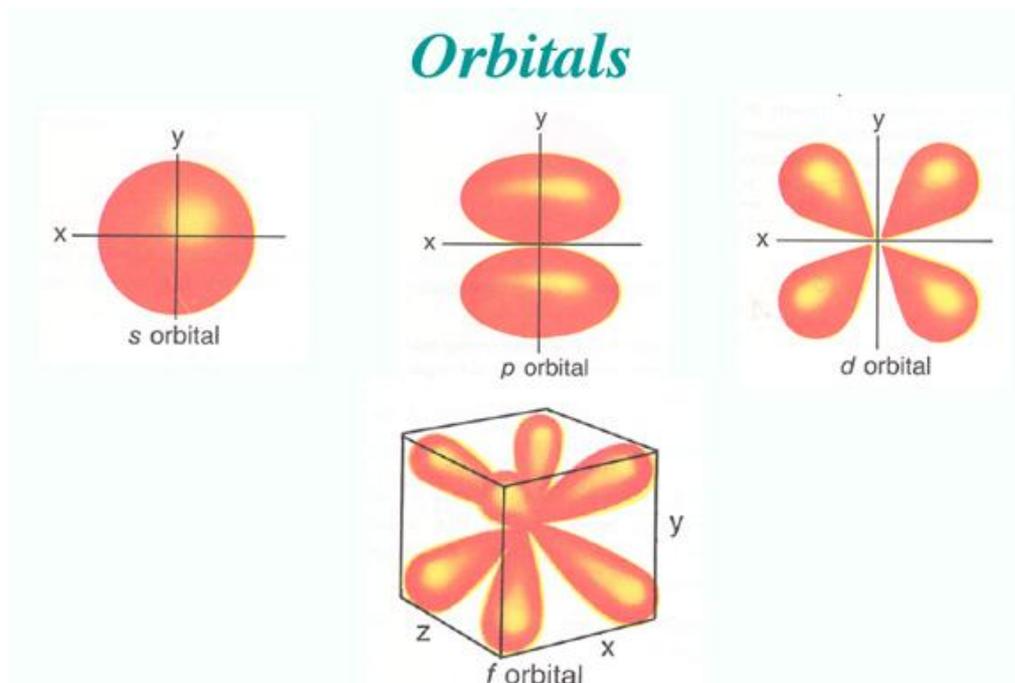
$$H = T + U$$

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

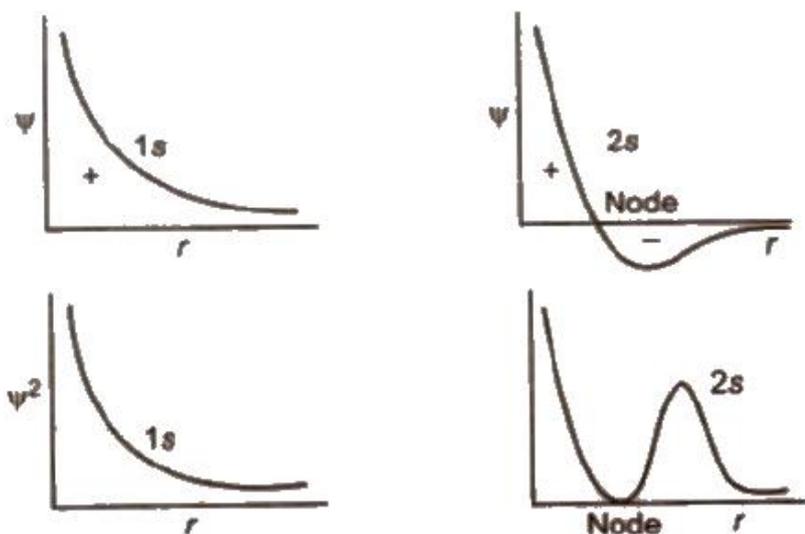
[The atomic orbitals can be represented by the product of two wave functions (i) radial wave function (ii) angular wave function.

The orbital 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 diagrams.



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 for Various Orbitals

S. No. Type of orbital Number of peaks

| | | | |
|---|---|-------|-------|
| 1 | s | n | n - 1 |
| 2 | p | n - 1 | n - 2 |
| 3 | d | n - 2 | n - 3 |
| 4 | f | n - 3 | n - 4 |

Quantum Numbers

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

Principal Quantum Number (Neil's 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 $n = \text{any integer}$.

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 represent 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 orbitals in each subshell = $(2l + 1)$

| S. No. | Subshell | Orbital |
|--------|----------|---------|
| 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 Orbital

| ORBIT | ORBITAL |
|---|---|
| It is path around the nucleus in which the electron revolves. | It is the region around the nucleus where probability of finding electron is maximum. |
| orbit is circular or elliptical in shape | Orbital may be spherical, dumb-bell or double dumb-bell in shape. |
| It represent the movement of electron in one plane | It represent the movement of electron in three dimensional plane |

Electronic Configuration

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

Pauli Exclusion Principle

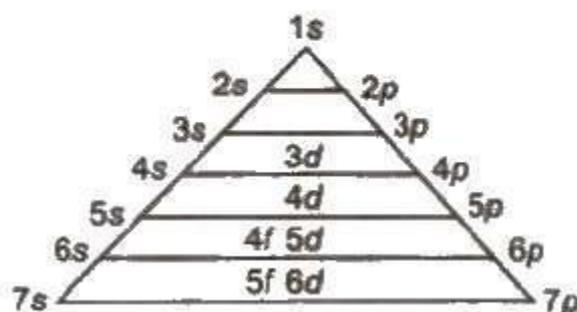
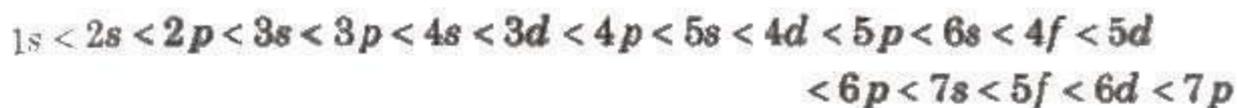
It states, no two electrons in an atom can have identical set of four quantum numbers.

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

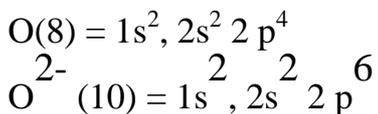
According to this principle, in the ground state of an atom, the electrons occupy the lowest energy orbitals available to them, i.e., the orbitals are filled in order of increasing value of $n + l$. For the orbitals having the same value of $n + l$, the orbital having lower value of n is filled up first.

The general order of increasing energies of the orbital is



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 multielectron atom. the electron 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

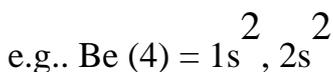
$$Z_{\text{eff}} = Z - \sigma$$

where σ = screening constant

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

Slater 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 $\sigma = 0.35$ each
4. All electrons of (n - 1) s and p shell contribute $\sigma = 0.85$ each
- 5 All electrons 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



$$\begin{aligned} & \text{(for } 2s) \quad \text{for } 1s \\ \sigma &= 0.35 + 2 \times 0.85 \\ &= 2.05 \end{aligned}$$

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

Different Types of Atomic Species

(a) **Isotopes:** Species with same atomic number but different mass number are called

isotopes, e.g., ${}^1_1\text{H}$, ${}^2_1\text{H}$.

(b) **Isobars:** Species with same mass number but different atomic number are called

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

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

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

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 atoms and same number of electrons, are called isostere, e.g., N_2 and CO .

