

ATOMIC STRUCTURE

CLASS XI

THE FORMULLAE WHICH IS REQUIRED WHILE STUDYING ATOMIC STRUCTURE.

$M_e = 9.1 \times 10^{-31}$ kg. Charge of electron = 1.6×10^{-19} Coulomb

$h = 6.625 \times 10^{-34}$ Joule-sec; $c = 3 \times 10^8$ m/s

Proton- E. Goldstein Electron – J.J. Thompson. Neutron – James Chadwick.

Increase of λ ; Decrease of frequency

[Cosmic rays – X rays – UV rays – Visible rays – IR rays – Microwaves – Radio waves].

1 photon = 1 quantum; 1 Einstein = 6.022×10^{23} quantum.

WaveNumber ($\tilde{\nu}$) = $109677 \times Z^2 (1/n_1^2 - 1/n_2^2)$ cm^{-1} .

Wavelength (λ) = $1/\tilde{\nu} = 1/109677 \times (n_1 n_2)^2 / Z^2 (n_2^2 - n_1^2) = [9.11 \times 10^{-6} \times (n_1 n_2)^2 / Z^2 (n_2^2 - n_1^2)] \text{cm}$.

Frequency (ν) = $3.29 \times 10^{18} (1/n_1^2 - 1/n_2^2)$ hertz or s^{-1} .

Energy (E) = $-2.18 \times 10^{-18} (1/n_1^2 - 1/n_2^2)$ J/atom. (1 eV = 1.6×10^{-19} J).

Radius (r) = $(0.05291 n^2 / Z)$ nm = $(5.29 \times 10^{-11} n^2 / Z)$ m.

Angular Momentum $mvr = nh/2\pi$.

Velocity (V) = $nh/2\pi mr$.

No. of revolutions = $2\pi m v Z e^2 / n^2 h^2$.

[**Plank** $E \rightarrow h\nu = hc/\lambda$]; [**Einstein** $\rightarrow E = mc^2$], Hence $hc/\lambda = mc^2$ or $\lambda = h/mc$.

$\lambda = h/mv = h/P = h/\sqrt{2mE}$ de Broglie.

$\Delta x \cdot \Delta v \geq h/4\pi m$ or $\Delta x \cdot \Delta v \geq h/4\pi m \Delta v$.

$R_n = n^2 h^2 / (4\pi^2 m Z e^2) = [0.529 n^2 / Z] \text{Å}$

$E_n = (-2 \pi^2 m k^2 Z^2 e^4) / (n^2 h^2)$; ($E_n = 13.6 Z^2 / n^2$ eV/atom)

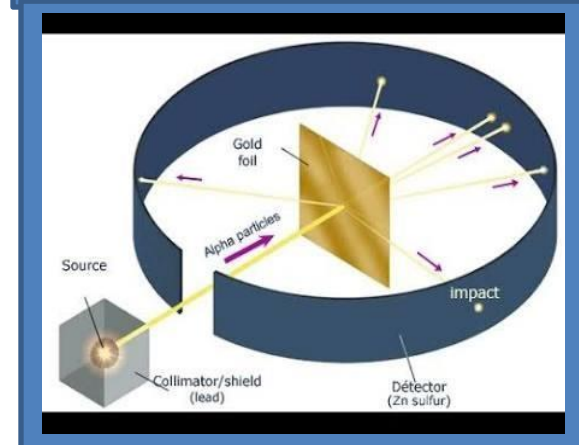
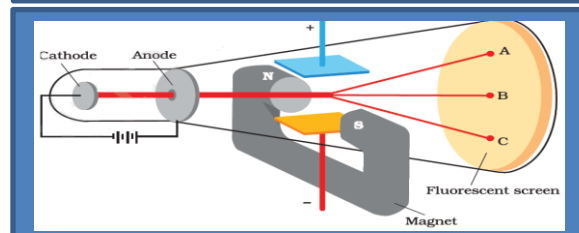
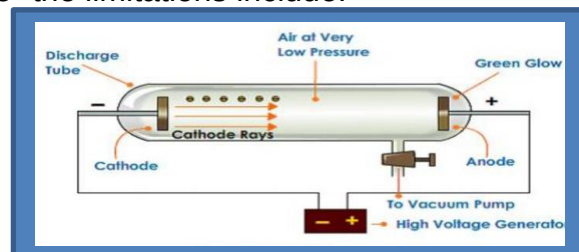
or ($E_n = 2.18 \times 10^{-18} Z^2 / n^2$ Joule /atom);

or ($E_n = 1312 Z^2 / n^2$) kJ/mole.

No. of revolutions per sec = $V_n / (2\pi r_n)$

Atomic Theory [John Dalton-1808]: An atom is the ultimate particle of matter, it is indestructible, indivisible particle. With the discovery of the subatomic particle- the limitations include:

- 1) to account for the stability of atom.
- 2) to compare the behaviour of one element from term of both physical and chemical



Michael Faraday cathode ray experiment - 1850

Thomson Model of Atom - 1898

Rutherford Atomic model (Hans Geiger, Ernest Marsden)

Experiment: A stream of high energy alpha particles from a radioactive source was directed at a thin foil of metal. A fluorescent screen smeared with ZnS was kept behind the gold foil.

Observation:

- i) whenever alpha particles struck the screen;
- i) A tiny flash of light was produced at that point
- ii) Most of the alpha particles passed through gold foil.
- iii) A small fraction of the alpha particles was deflected by small angles
- iv) A very few alpha particles (1 out of every 20000) bounced back in the same path deflecting nearly by 180° .

Inference:

- i) Most of the space in an atom is empty.
- ii) The positive charge was concentrated in a very small volume and that repelled and deflected the positively charged alpha particles.
- iii) The positive charge and most of the mass of an atom was densely concentrated in an extremely small region called nucleus.
- iv) The size of the nucleus is comparatively small as compared to the volume of the atom as a whole. The radius of atom = 10^{-10} m and radius of nucleus = 10^{-15} m.
- v) The nucleus is surrounded by electrons that move around the nucleus with a very high speed in circular paths called orbits.
- vi) Electrons and nucleus are held together by electrostatic forces of attraction.

Limitations:

- i) It failed to discuss about the electronic structure of atom – the distribution of electrons around the nucleus.
- ii) energy distribution- energies present in each shell.
- iii) According to Maxwell's electromagnetic theory, a charged particle when accelerated should emit electromagnetic radiation. Hence, electron being negatively charged will emit radiation and thereby will shrink the radius continuously and fall in the nucleus by 10^{-8} s. So, there leads to the instability of atom.

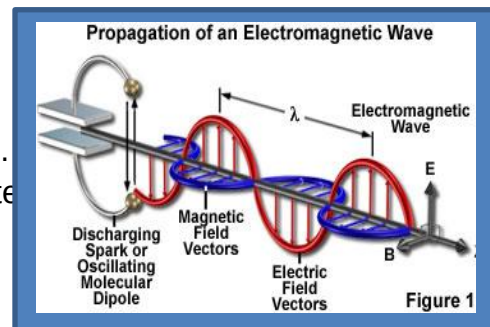
• Corpuscular Theory:

According to Newton, light was regarded as a stream of particles (corpuscles of light). The particle nature could explain- reflection, refraction of light but not diffraction.



• **Maxwell's Theory:** Electromagnetic Radiation [C. Huygens- Wave Theory]

1. The absorption or emission of energy occurs continuously in the form of radiation.
2. The radiations possess wave character and travel with $3 \times 10^8 \text{ ms}^{-1}$.
3. The radiations consist of electric and magnetic fields which oscillate and both perpendicular to the direction of propagation of radiation.
4. Electromagnetic waves do not require any material medium for propagation.
5. The colour of emitted radiation is related to its frequency.

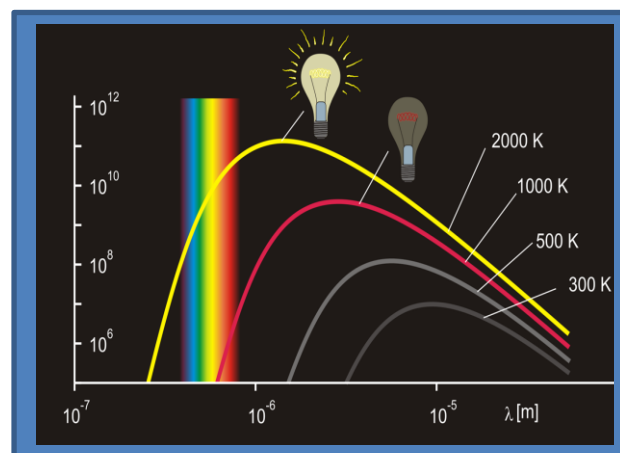
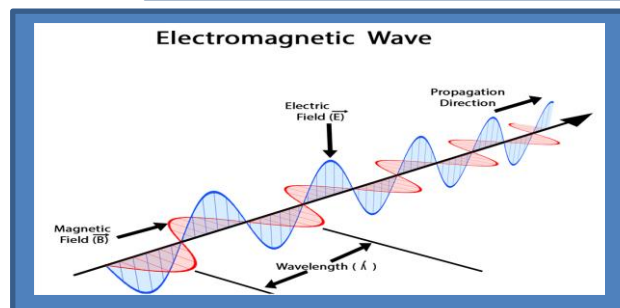


Limitations:

1. It could explain – refraction, diffraction, interference etc.
2. It could not explain- blackbody radiations, photoelectric

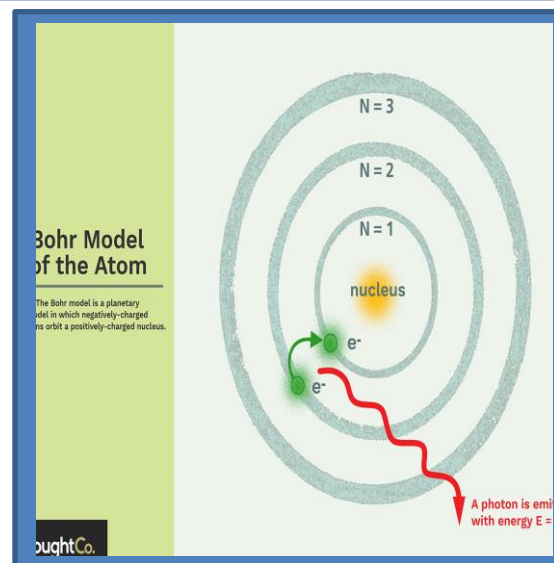
• **Plank's Quantum Theory:**

1. Radiant energy is emitted or absorbed discontinuously in the form of small packets of energy.
2. Each packet of energy is known as quantum.
3. The amount of energy associated with each is proportional to the frequency of radiation ($E=h\nu$).
4. The amount of energy associated with each of but depends on the frequency radiation. [Energy is proportional to frequency]
5. Emission/absorption of energy takes place only integral multiples of Quanta.
6. [**Plank** $E \rightarrow h\nu = \frac{hc}{\lambda}$] ; [**Einstein** $\rightarrow E=mc^2$], $\frac{hc}{\lambda} = mc^2$ or $\lambda = \frac{h}{mc}$.



• **Bohr's Atomic Model:**

1. Electron in hydrogen atom revolves around the nucleus only in certain selected circular paths which are associated with definite energies. Only those orbits are permitted for the revolving electron in which the angular momentum is the integral multiple of $\frac{h}{2\pi}$. [$mvr = \frac{nh}{2\pi}$]
2. When an electron revolves in any selected orbit, it neither emits nor absorbs energy.
3. The energy of the orbit increases as the distance from nucleus increases [$K < L < M \dots$].
4. When an electron jumps from a higher shell to a lower shell – it emits a fixed amount of energy in the form of radiations and vice-versa. Electron can never occupy a position in between two successive orbits.



Achievements:

Calculation of Energy: $E_n = -2mk^2\pi^2Z^2e^4x1/(nh)^2 = -2.18 \times 10^{-18} Z^2/n^2 \text{ J/atom}$

Calculation of Radius: $r_n = (nh)^2 / 4mk\pi Ze^2 = 0.529n^2/Z \text{ \AA}$.

$$k = 9 \times 10^9$$

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

Z=atomic number of element

$$e = 1.6 \times 10^{-19} \text{ C}$$

$$h = 6.625 \times 10^{-34}$$

n = orbit number

Calculation of Velocity: $v_n = \frac{2\pi nZe^2}{nh} = (2.18 \times 10^6) \times \frac{Z}{n} \text{ m/s}$

- Energy in 1st orbit = $-(2.18/1) \times 10^{-18} Z^2 \text{ J/atom} = -1312 \text{ J/mole}$
- Energy in 2nd orbit = $-(2.18/4) \times 10^{-18} Z^2 = -0.545 \times 10^{-18} Z^2$
- Energy in 3rd orbit = $-(2.18/9) \times 10^{-18} Z^2 = -0.242 \times 10^{-18} Z^2$

Limitations:

1. Spectra of atoms or ions having two or more electrons cannot be explained with Bohr's theory.
2. It failed to explain- the splitting of spectral lines under the influence of Magnetic Field (Zeeman Effect) Electric Effect (Stark Effect).
3. Bohr's atomic model is 2- dimensional and hence fails to give any idea about the actual 3- dimensional electronic model of atoms.
4. According to de Broglie- electron has dual character – particle as well as wave nature. Bohr treated electron as particles.
5. According to Bohr, electrons move around the nucleus along a fixed path with definite velocity. According to Heisenberg – it is impossible to measure simultaneously, both position and velocity of electron with absolute accuracy.

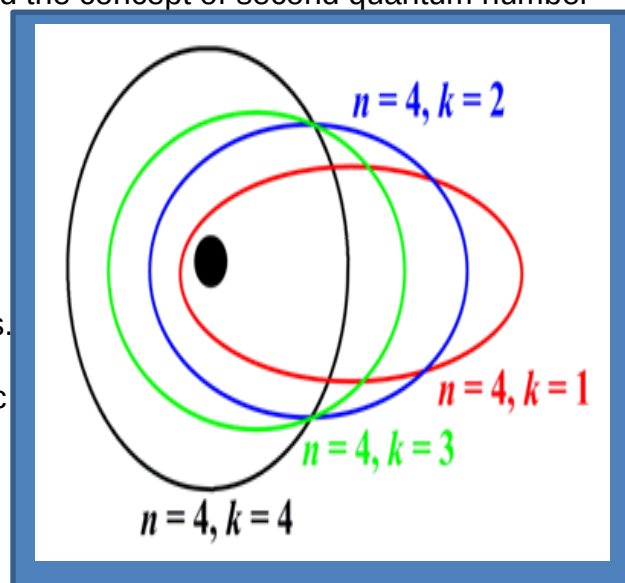
• Sommerfield's – Extended Bohr's Theory.

1. An electron moving around a positively charged nucleus might describe elliptical orbits with different ellipticity in addition to circular orbits.
2. When the electron moves in an elliptical orbit with different ellipticity, the nucleus remain at one of the foci.
3. During motion of electrons in circular paths, only the angle of revolution changes while the distance from the nucleus remains same. But in elliptical motion, both the angle of revolution (Φ - radial energy) and the distance (r- radial distance) of the electron from the nucleus change.
4. In order to describe an elliptical Sommerfield introduced the concept of second quantum number (azimuthal quantum number) called k and $[l = (k-1)]$; $[n/k = \text{length of major axis} / \text{length of minor axis}]$.
5. To explain the splitting of spectral lines under the influence of electric or magnetic field. Sommerfield suggested that the electronic orbits may lie in different planes.

Limitations:

1. It is two dimensional in nature.
2. It failed to explain the spectra of multi electro atoms.

Nuclear Isomers: Atoms which have the same atomic number and mass number but have differ in energy and manner of radioactive decay and that exist for a measurable interval of time
[lower Co $^{58}(t_{1/2}=71\text{day})$]. [higher Co $^{58}(t_{1/2}= 9 \text{ Hrs})$].



Isodiapher: atoms in which the difference between the number of neutrons and the number of protons are same. $[_{92}\text{U}^{238}]$ has $n-p = 146-92=54$; $[_{90}\text{Th}^{234}]$ has $n-p = 144-90=54$

Isoster: molecules or ions with same number of atoms and same number of electrons; [N_2O and CO_2^- has 3 atoms and number of electrons is 22]

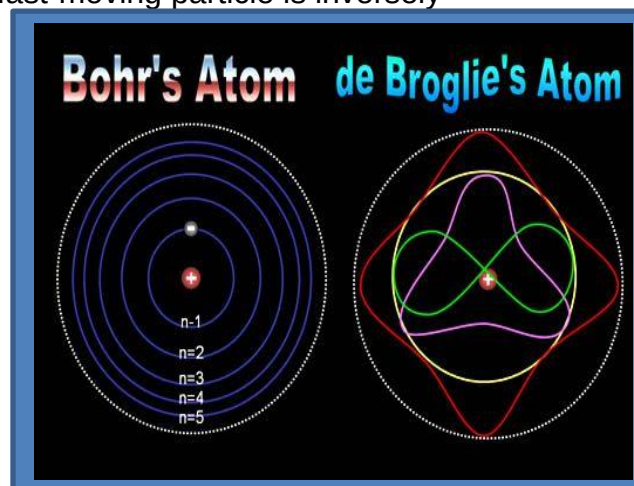
Quantum Mechanics: the branch of science that takes into account the dual behaviour of matter is called quantum mechanics. It is a theoretical science that deals with the study of motions of microscopic objects, that have both observable wave like and particle like properties.

[Werner Heisenberg, Erwin Schrodinger, de Broglie]

- **De-Broglie's Theory (dual nature of electrons):**

Like radiations, moving electrons are associated with both particle and wave nature [$\lambda = h/mv = h/P$ or $\lambda \propto 1/P$]. Wavelength of the wave is associated with the fast-moving particle is inversely proportional to its momentum.

- The wave associated with fast moving particle is called-matter wave or De-Broglie wave. It is different from electromagnetic waves. De-Broglie's equation is not applicable to moving particles having large mass because in such cases, the wave length of the wave associated with the moving particle is negligibly small.
- No. of Radial Nodes = $(n-l-1)$; No. of Planar Nodes = l ; Total Nodes = $(n-1)$; where "Node" means the probability of finding electrons is zero.

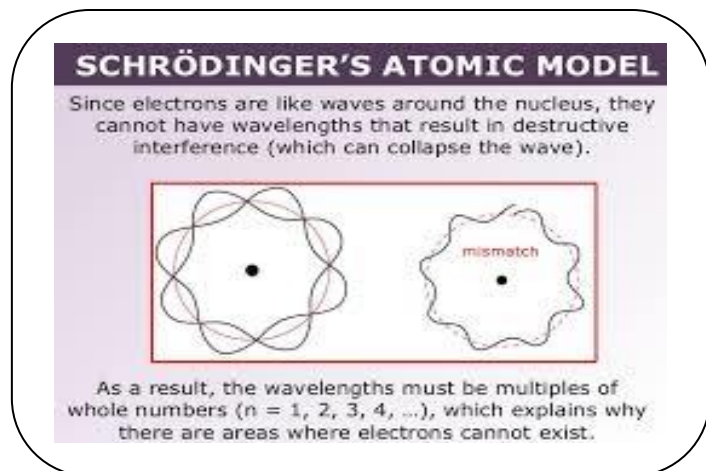


- **Heisenberg's Uncertainty Principle:**

It is impossible to measure simultaneously both the position and the velocity (or momentum) of a sub-atomic particle, like electron accurately at any particular moment [$\Delta x \cdot \Delta P \geq h/4\pi$] or [$\Delta x \cdot m\Delta v \geq h/4\pi$] or [$\Delta x \cdot \Delta v \geq h/4\pi m$].

- **Erwin Schrodinger's Wave Equation:-**

Schrodinger developed a new atomic model, based on De-Broglie's concept and Heisenberg Uncertainty Principle known as "Wave Mechanical Model". When an electron is any energy state, the wave function corresponding to that energy state contains all information about the electron like-principal, azimuthal and magnetic quantum number.



Second derivative with respect to Z

Schrodinger wave Function

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

Position

Energy

Potential Energy

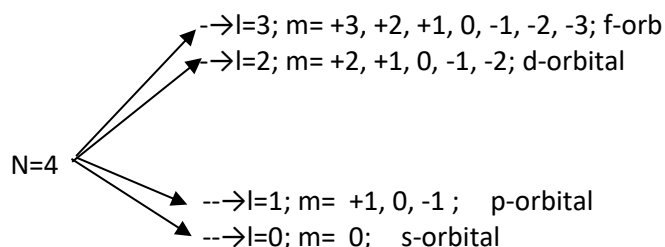
Principal Quantum number(n), azimuthal Quantum Number(l)=(n-1), m=2(l)+1

Heisenberg's Uncertainty Principle

$$\Delta x \Delta p \geq \frac{h}{4\pi} = \frac{\hbar}{2}$$

uncertainty in momentum
↑
uncertainty in position

The more accurately you know the position (i.e., the smaller Δx is), the less accurately you know the momentum (i.e., the larger Δp is); and vice versa



n= the size and to large extent the energy of the orbital

(l)= the three dimensional shape of the orbitals (s=0; p=1; d=2; f=3; g=4; h=5)

m= the spatial orientation of the orbital with respect to standard set of coordinate axis.

The probability of finding the electron at a point within an atom is proportional to the $|\psi|^2$ at that point. When Schrodinger's Equation is solved, different values of ψ are obtained. All the values may not be significant. The significant values of ψ are called Eigen Values. These functions give significant values of the total energy [Eigen Values]. Each permitted value corresponding to a definite energy level called Orbital [where ψ is the amplitude of the wave associated with the moving electron and ψ^2 is the measure of probability of finding an electron in a given region of space.

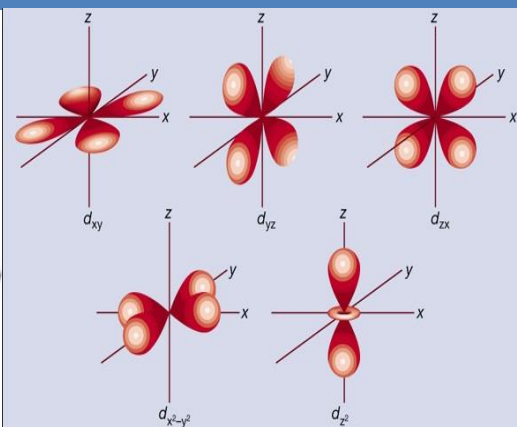
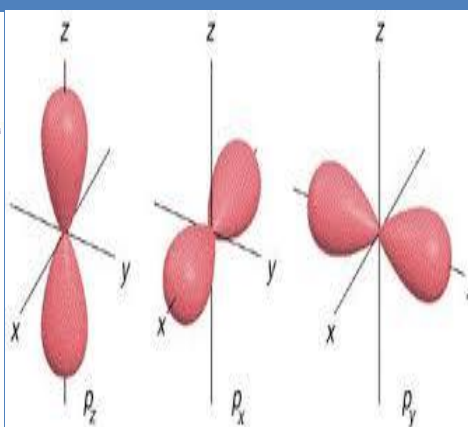
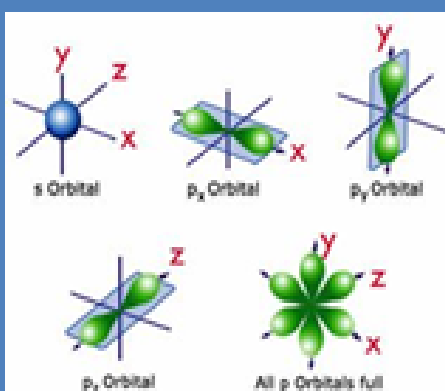
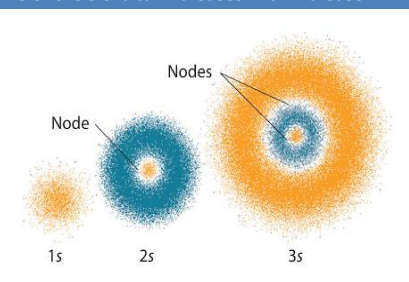
Nodes/nodal surface-

region where probability function reduces to zero.

p-orbitals consists of 2 sections called lobes that are on either side of the plane that passes through the nucleus. The probability density function is zero on the plane where the 2 lobes touch each other.

p-orbitals increase in size and energy with increase in n. The number of nodes are given by the n-2, so of radial node is 1 for 3p, 2 for 4p and so on.

"Size of the s orbital increases with increase in n"



All the 4 d orbitals (d_{xy} , d_{yz} , d_{zx} , $d_{x^2-y^2}$) have a similar shape but not d_{z^2} . But they all have similar energy. 4d, 5d also have similar shapes but differ in energy and size. 1 angular node for p orbital and 2 angular nodes for d orbitals. Total number of nodes=(n-1) which is the sum of the angular nodes and (n-l-1) radial nodes.

The increase in energies: $1s < 2s = 2p < 3s = 3p = 3d < 4s = 4p = 4d = 4f < \dots$. the orbitals having the same energy - **degenerate**.

Shielding effect: the stability of an electron is due to the total attractive interactions are more than the repulsive interaction. The attractive interaction increases in the increase in the positive charge in the nucleus. Due to the presence of the inner shell electrons, the electrons in the outer shell will not experience the full positive charge of the nucleus. It is lowered due to partial screening of positive charge on the nucleus by the inner shell electrons. the net positive charge experienced by outer electrons is called effective nuclear charge.

- Electrons present in spherical shaped s orbital shields the outer electrons from the nucleus more effectively as compared to electrons present in p orbitals. While electrons present in p orbitals shield the outer electrons more than that of d orbitals.
- S-orbital electron will be more tightly bound to the nucleus than p-orbital electrons which in turn will be better tightly bound than the d orbital electron.
- The lower the value of $n+l$ for an orbital, the lower is its energy. If the two orbitals have the same value of $(n+l)$, the orbital of lower value of n will have lower energy.
- Energies of the orbitals in the same subshell decrease with increase in the atomic number.
 $E_{2s}(\text{H}) > E_{2s}(\text{He}) > E_{2s}(\text{Na}) > E_{2s}(\text{K})$

- Pauli's Exclusion Principle:** No two electrons in an atom will have the same values for all the four quantum numbers. Only two electrons may exist in the same orbital and these electrons must have opposite spin [n - principal Q. No., l – azimuthal Q. No ; m - magnetic Q.No.; s - spin Q. No.]

- Hunds' Rule:** The pairing of electrons in the orbitals within the same sub-shell does not take place until the orbitals are singly filled up and the singly occupied orbitals must have all the electrons with parallel spin.

- Aufbau's principle:** Electrons are added progressively to the various orbitals in order of increasing energy starting with the orbital of the lowest energy.

[1s 2s 2p 3s 3p 4s 3d 4p 5s 4d 5p 6s 4f 5d 6p 7s].

Extra stability of half-filled and full filled orbitals:

- Symmetrical distribution of electrons- so they have lower energy which ultimately results in greater configuration.
- Exchange Energy – The electrons occupying degenerate orbitals can exchange their position with other electrons with the same spin. In this process exchange energy is released.

Stability of completely filled and half-filled subshell.

