

Atomic Structure

What is an atom?

Smallest particle of an element that has all the properties of that element is called atom.

Dalton's atomic theory

- 1) All elements are composed of tiny indivisible particles called atom.
- 2) The atom can neither be created nor be destroyed i.e., it is indestructible.
- 3) All atoms of an element are identical but atoms of different elements vary in size and mass.
- 4) Atoms of different elements combine in simple whole number ratios to form chemical compounds.
- 5) In a chemical reaction atoms are combined or separated but never changed to atom of another element.

Drawbacks: It fails to explain why atoms of different kinds should differ in mass and valency etc. The discovery of isotopes and isobars showed that atoms of same elements may have different atomic masses (isotopes) and atoms of different kinds may have same atomic masses (isobars).

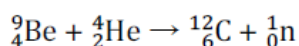
Fundamental sub-atomic particles:

The discovery of various sub-atomic particles like electrons, protons, neutrons etc. during late 19th century led to the idea that the atom was no longer an indivisible and the smallest particle of the matter.

The existence of electrons in atoms was first suggested, by J.J. Thomson. The conduction of electricity through gases at low pressures and at high voltage, which produces cathode rays consisting of negatively charged particles, named as electrons. The e/m ratio for cathode rays is fixed whose value is $1.76 \times 10^8 \text{ C/g}$.

Since, the atom is electrically neutral, it must also contain some positively charged particles. This was confirmed by Goldstein in his discharge tube experiment with perforated cathode. On passing high voltage between the electrodes of a discharge tube it was found that some rays were coming from the side of the anode which passed through the holes in the cathode. These anode rays (canal rays) consisted of positively charged particles formed by ionization of gas molecules by the cathode rays. The charge to mass ratio (e/m value) of positively charged particles was found to be maximum when the discharge tube was filled with hydrogen gas as hydrogen is the lightest element. These positively charged particles are called protons.

The electrically neutral charge particle, neutron was discovered by James Chadwick by bombarding boron or beryllium with α -particles.



Characteristics of the three fundamental particles:

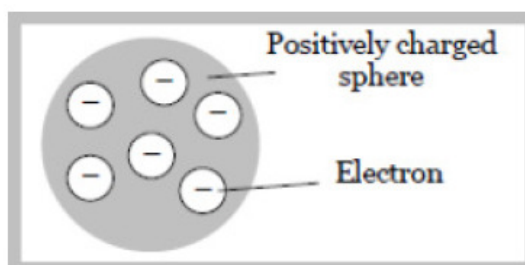
	Electron	Proton	Neutron
Symbol	e	p	n
Approximate relative mass	1/1836	1	1
Approximate relative charge	-1	+1	No charge
Mass in kg	9.109×10^{-31}	1.673×10^{-27}	1.675×10^{-27}
Mass in amu	5.485×10^{-4}	1.007	1.008
Actual charge (coulomb)	1.602×10^{-19}	1.602×10^{-19}	0
Actual charge (e.s.u.)	4.8×10^{-10}	4.8×10^{-10}	0

The atomic mass unit (amu) is 1/12 of the mass of an ${}^{12}_6\text{C}$ atom = 1.660×10^{-27} kg.

Atomic Models

Thomson's model: Plum pudding model

J.J. Thomson gave the first idea regarding structure of atom. According to this model - An atom is a solid sphere in which entire and positive charge and its mass is uniformly distributed in which negative charge (*i.e.* electron) is embedded like seeds in watermelon.



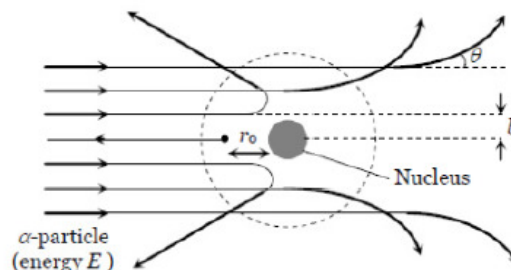
Success and failure

The model can successfully explain the phenomenon of thermionic emission, photoelectric emission and ionization.

The model fails to explain the α -particles scattering and it cannot explain the origin of spectral lines observed in the spectrum of hydrogen and other atoms.

Rutherford's model: Nuclear model

Rutherford's α -particle scattering experiment:



Rutherford performed experiments on the scattering of alpha particles by extremely thin gold foils and made the following observations:

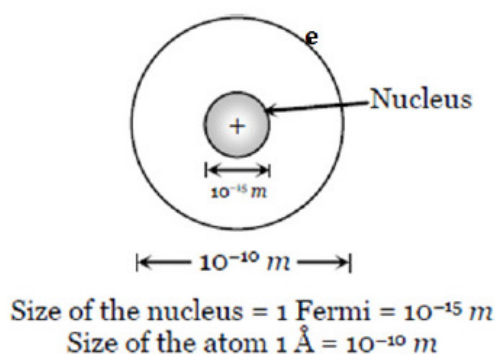
- (i) Most of the α -particles pass through the foil straight away undeflected.
- (ii) Some of them are deflected through small angles.
- (iii) A few α -particles (1 in 1000) are deflected through the angle more than 90° .
- (iv) A few α -particles (very few) returned back *i.e.* deflected by 180° .
- (v) Distance of closest approach (Nuclear dimension) is the minimum distance from the nucleus up to which the α -particle approaches (r_0). When the α -particle approaches close to the nucleus, its direction is reversed at a stage when its kinetic energy is just balanced by potential energy, *i.e.*

$$\frac{1}{2}mv^2 = \frac{Zeq}{4\pi\epsilon_0} \times \frac{1}{r_0} \text{ or, } r_0 = \frac{Zeq}{4\pi\epsilon_0 \left(\frac{1}{2}\right)mv^2}$$

- (vi) Impact parameter (b): The perpendicular distance of the velocity vector (\vec{v}) of the α -particle from the centre of the nucleus when it is far away from the nucleus is known as impact parameter. It is given as:

$$b = \frac{Zeq \cot\left(\frac{\theta}{2}\right)}{4\pi\epsilon_0 mv^2}$$

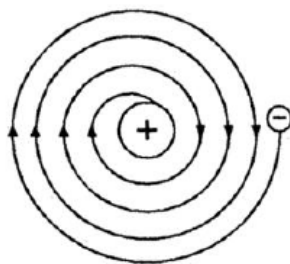
Conclusion:



- (1) Most of the mass and all of the positive charge of an atom concentrated in a very small region is called atomic nucleus.
- (2) Dimension of the nucleus is extremely small in comparison to the size of the atom. Its size (radius) is of the order of $10^{-15} \text{ m} \sim 1 \text{ Fermi}$. Most part of the atom is empty.
- (3) Electrons are present outside the nucleus and the number of electron is equal to the nuclear positive charge to maintain electrical neutrality of the atom.
- (4) Electrons revolve around the nucleus in a circular orbit in the same way as the planets revolve around the sun. The centrifugal force and electrostatic force balance each other to give a stable orbit: $\frac{mv^2}{r} = \frac{Ze^2}{4\pi\epsilon_0 r^2}$

Draw backs:

- (i) Stability of atom: It could not explain stability of atom because according to electromagnetic theory an accelerated charged particle should continuously radiate energy. Thus, an electron moving in a circular path around the nucleus should also radiate energy and thus move into smaller and smaller orbits of gradually decreasing radius and it should ultimately fall into nucleus.
- (ii) According to this model the spectrum of atom must be continuous where as practically it is a line spectrum.
- (iii) It did not explain the distribution of electrons outside the nucleus.



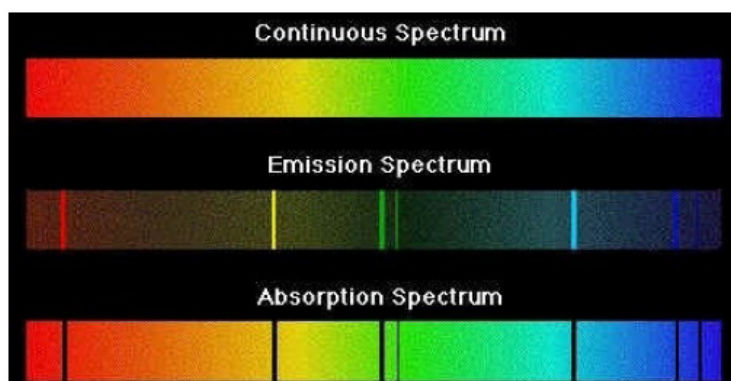
Atomic Spectrum

If the atom gains energy the electron passes from a lower energy level to a higher energy level, energy of specific wave length is absorbed. Consequently, when electron come back from a higher energy level to a lower energy level, energy of specific wave length is released. That means a specific wave length is absorbed or released, a dark line will appear in the spectrum. This dark line constitutes the atomic spectrum (absorption or emission spectrum).

Types of emission spectra

(i) Continuous spectra: When white light from any source such as sun or bulb is analysed by passing through a prism, it splits up into seven different wide bands of colour from violet to red (like rainbow). These colours also continuous that means each of them merge into the next. Hence the spectrum is called as continuous spectrum.

(ii) Line spectra: When an electric discharge is passed through a gas at low pressure light is emitted. If this light is resolved by a spectroscope, it is found that some isolated coloured lines are obtained on a photographic plate separated from each other by dark spaces. This spectrum is called line spectrum. Each line in the spectrum corresponds to a particular wavelength. Each element gives its own characteristic spectrum.



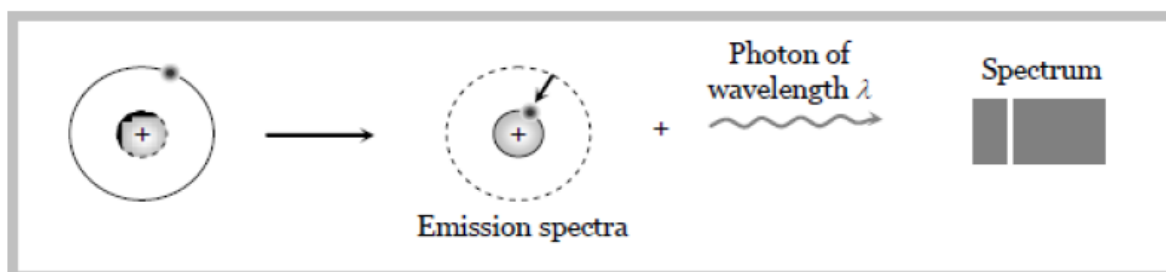
Hydrogen Spectrum and Spectral Series

If an electric discharge is passed through hydrogen gas taken in a discharge tube under low pressure H-atom become excited to higher energy state. When, come back to ground lower energy state it emits radiation which is analysed with the help of spectrograph. It is found to consist of a series of sharp lines in the UV, visible and IR regions. This series of lines is known as line or atomic spectrum of hydrogen. The lines in the visible region can be directly seen on the photographic film. Each line of the spectrum corresponds to a light of definite wavelength. The entire spectrum consists of six series of lines each series, known after their discoverer as the Balmer, Paschen, Lyman, Brackett, Pfund and Humphrey series.

The wavelength of all these series can be expressed by a single formula.

$$\frac{1}{\lambda} = \bar{\nu} = R \left[\frac{1}{n_1^2} - \frac{1}{n_2^2} \right]$$

Where, λ = wave length, $\bar{\nu}$ = wave number, R = Rydberg constant (109678 cm^{-1}) and n_1 and n_2 is integer define various energy levels.

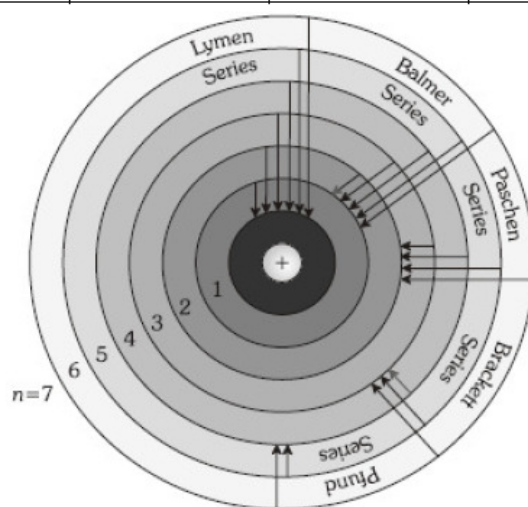


Spectral Series:

$$\frac{1}{\lambda} = R \left[\frac{1}{n_1^2} - \frac{1}{n_2^2} \right] \text{ or } \lambda = \frac{n_1^2 n_2^2}{R(n_2^2 - n_1^2)} = \frac{n_1^2}{R(1 - \frac{n_1^2}{n_2^2})}$$

When $n_1 = n$ and $n_2 = (n+1)$, $\lambda = \lambda_{\max} = \frac{n^2(n+1)^2}{(2n+1)R}$ and when $n_1 = n$ and $n_2 = \infty$, $\lambda = \lambda_{\min} = \frac{n^2}{R}$

Series	n_1	n_2	λ_{\max}	λ_{\min}	Region
Lyman	1	2, 3, 4... ∞	$\frac{4}{3R}$	$\frac{1}{R}$	Ultra Violet
Balmer	2	3, 4, 5... ∞	$\frac{36}{5R}$	$\frac{4}{R}$	Visible
Paschen	3	4, 5, 6... ∞	$\frac{144}{7R}$	$\frac{9}{R}$	Infra Red
Brackett	4	5, 6, 7... ∞	$\frac{400}{9R}$	$\frac{16}{R}$	Infra Red
Pfund	5	6, 7, 8... ∞	$\frac{900}{11R}$	$\frac{25}{R}$	Infra Red
Humphrey	6	7, 8, 9... ∞	$\frac{1512}{13R}$	$\frac{36}{R}$	Infra Red

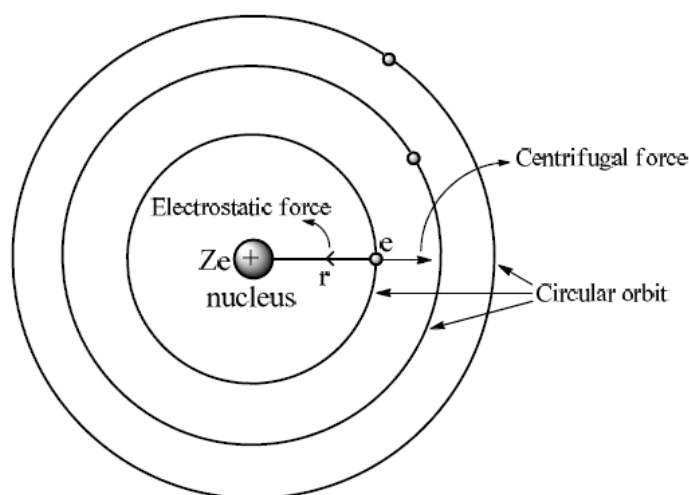


Bohr's Model

Bohr proposed a model for hydrogen atom which is also applicable for some lighter atoms in which a single electron revolves around a stationary nucleus of positive charge Ze (called hydrogen like atom)

Bohr's model is based on the following postulates:

- (1) Electron can revolve only in certain specified orbits around the nucleus, for which total angular momentum of the revolving electrons is an integral multiple of $\frac{h}{2\pi}$, i.e., $\frac{nh}{2\pi} = L = mvr$ where $n = 1, 2, 3, \dots$ = principal quantum number.
- (2) When an electron is revolving in a permitted orbit, it will neither accept nor radiate any energy. This situation is called stationary state and orbits are called stationary orbits.
- (3) When an electron jumps from one permitted orbit to another it radiates energy of certain frequency. When electron jumps from higher energy orbit (E_1) to lower energy orbit (E_2) then difference of energies of these orbits *i.e.* $E_1 - E_2$ emits in the form of photon. But if electron goes from E_2 to E_1 it absorbs the same amount of energy. The frequency (ν) of the radiation will be given by the relation: $E_1 - E_2 = h\nu$



Radius of the Bohr orbit

For an electron in an orbit of radius r around a nucleus with Z units of positive charge, then centrifugal force will be balanced by electrostatic force.

$$\frac{mv^2}{r} = \frac{Ze^2}{r^2} \text{ or, } mv^2 = \frac{Ze^2}{r} \text{ or, } (mv)^2 = \frac{mZe^2}{r} \dots\dots\dots(1)$$

At the same time, Bohr condition of angular momentum requires $mvr = \frac{nh}{2\pi}$ or, $mv = \frac{nh}{2\pi r}$

From equation (1), $\frac{n^2 h^2}{4\pi^2 r^2} = \frac{mZe^2}{r}$ or, $r = \frac{n^2 h^2}{4\pi^2 mZe^2}$ (in CGS) and $r = \frac{\epsilon_0 n^2 h^2}{\pi mZe^2}$ (in SI)

This is the desired expression of the radii of the permitted Bohr orbits.

For H atom, $Z = 1$. The radius of the smallest possible orbit (r_0) will be when $n = 1$.

$$r_0 = \frac{\epsilon_0 h^2}{\pi m e^2} = \frac{8.854 \times 10^{-12} \text{C}^2 \text{N}^{-1} \text{m}^{-2} \times (6.626 \times 10^{-34})^2 \text{J}^2 \text{s}^2}{3.141 \times 9.109 \times 10^{-31} \text{kg} \times (1.602 \times 10^{-19})^2 \text{C}^2} = 5.293 \times 10^{-11} \text{ m (0.05293 nm)}.$$

This is the radius of first Bohr orbit (a_0). Clearly, $r_n = r_0 \times n^2$. The value of the first Bohr radius of the hydrogen atom, i.e., 0.05293 nm is by definition the atomic unit of length, called Bohr.

Velocity and orbital frequency of an electron

The speed (v) of an electron in Bohr orbit can simply be written as,

$$v = \frac{nh}{2\pi mr} \text{ or } v = \frac{nh}{2\pi m} \times \frac{4\pi^2 mZe^2}{n^2 h^2} = \frac{2\pi Ze^2}{nh} \text{ (in CGS) and } v = \frac{Ze^2}{2\epsilon_0 nh} \text{ (in SI)}$$

$$\text{The orbital frequency (f) of an electron is } = \frac{\text{electron speed}}{\text{circumference of the orbit}} = \frac{v}{2\pi r} = \frac{4\pi^2 mZ^2 e^4}{n^3 h^3}$$

Energy of an electron in a Bohr orbit

An electron in an atom possesses (i) kinetic energy by virtue of its motion and (ii) potential energy due to its attachment to the nucleus. The total energy is the sum of these two energies.

$$\text{Kinetic energy: } E_k = \frac{1}{2}mv^2 = \frac{Ze^2}{2r}$$

Potential energy: The potential energy of an electron in an atom is calculated with reference to its position at infinity from the nucleus. At this point potential energy is assigned zero. The potential energy is then given by the total work done in bringing the electron from infinity to its position in the orbit of radius r . The force involved is the Coulombic force of attraction by the nucleus, $\frac{Ze^2}{r^2}$. The work done (W) and hence the potential energy (E_p) is then given as:

$$E_p = W = \int_{r=\infty}^{r=r} \frac{Ze^2}{r^2} = -\frac{Ze^2}{r}$$

$$\text{Now, the total energy of the electron, } E = \frac{Ze^2}{2r} - \frac{Ze^2}{r} = -\frac{Ze^2}{2r}$$

$$\text{Or, } E = -\frac{Ze^2}{2} \times \frac{4\pi^2 mZe^2}{n^2 h^2} = -\frac{2\pi^2 mZ^2 e^4}{n^2 h^2} \text{ (in CGS) and } E = -\frac{mZ^2 e^4}{8\epsilon_0^2 n^2 h^2} \text{ (in SI)}$$

The negative sign implies that work has to be done to remove the electron away from the nucleus. That means that electron is actually bound to the atomic system by a definite amount of energy. If the electron is to be removed from the influence of the nucleus, work equal to the magnitude of E has to be done on it. Due to negative sign of E , the energy of the electron increases with increasing value of n . Thus an orbit with a higher n value corresponds to higher energy of the electron.

The energy of an electron in the first Bohr orbit of hydrogen ($n = 1$, $Z = 1$) will be:

$$E = -\frac{mZ^2 e^4}{8\epsilon_0^2 n^2 h^2} = -\frac{9.109 \times 10^{-31} \text{ kg} \times (1.602 \times 10^{-19})^4 \text{ C}^4}{8 \times (8.854 \times 10^{-12})^2 \text{ C}^4 \text{ N}^{-2} \text{ m}^{-4} \times (6.626 \times 10^{-34})^2 \text{ J}^2 \text{ s}^2} = -2.18 \times 10^{-18} \text{ J} = 13.6 \text{ eV.}$$

This is often called the ground state energy. The energy of any other orbit having principal

$$\text{quantum number } n \text{ is given as: } E_n = -\frac{mZ^2 e^4}{8\epsilon_0^2 n^2 h^2} = -\frac{mZ^2 e^4}{8\epsilon_0^2 h^2} \times \frac{1}{n^2} = -\frac{E_1}{n^2} = -\frac{13.6}{n^2}$$

$$\text{And for other hydrogenic species, } E_n = -13.6 \frac{Z^2}{n^2}$$

Interpretation of the spectrum of atomic hydrogen

Consider two orbits with quantum numbers n_1 and n_2 in a Bohr type atom, such that $n_2 > n_1$.

Let the corresponding energy values be E_{n_2} and E_{n_1} where $E_{n_2} > E_{n_1}$

So, the energy difference between these two levels will follow the equation below ($Z=1$):

$$E_{n_2} - E_{n_1} = h\nu = \frac{me^4}{8\varepsilon_0^2 h^2} \left[\frac{1}{n_1^2} - \frac{1}{n_2^2} \right] \text{ or, } \nu = \frac{me^4}{8\varepsilon_0^2 h^3} \left[\frac{1}{n_1^2} - \frac{1}{n_2^2} \right] \text{ and } \bar{\nu} = \frac{1}{\lambda} = \frac{me^4}{8\varepsilon_0^2 ch^3} \left[\frac{1}{n_1^2} - \frac{1}{n_2^2} \right]$$

Substituting the value of m , e , ε_0 and h , $\bar{\nu} = 1.096775 \times 10^7 \left[\frac{1}{n_1^2} - \frac{1}{n_2^2} \right] \text{ m}^{-1}$

This expression agrees excellently with the experimentally established relation of Rydberg for the spectrum of atomic hydrogen: $\bar{\nu} = R \left[\frac{1}{n_1^2} - \frac{1}{n_2^2} \right]$ where $R = 1.096775 \times 10^7 \text{ m}^{-1}$.

Bohr correspondence principle

Though the wave numbers of spectral lines were given by the Bohr's theory, no inference regarding the nature and intensity of the lines could be made from it. Bohr, therefore, established a principle linking the classical theory and quantum theory. The principle states that for large quantum numbers, the behaviour of the atom would be same as predicted by both the quantum theory and classical theory. Accordingly, for very large values of n , the frequencies of the emitted radiation are nearly the same as the orbital frequency.

We know, the orbital frequency (f) of an electron is $= \frac{\text{electron speed}}{\text{circumference of the orbit}} = \frac{v}{2\pi r}$

$$\text{Or, } f = \frac{Ze^2}{2\varepsilon_0 nh} \times \frac{1}{2\pi} \times \frac{\pi m Ze^2}{\varepsilon_0 n^2 h^2} = \frac{mZ^2 e^4}{4\varepsilon_0^2 n^3 h^3}$$

Now, let us consider the frequency (ν) of radiation for the transition from n_i to n_f where n is

very large value of principal quantum number. $\nu = \frac{mZ^2 e^4}{8\varepsilon_0^2 h^3} \left[\frac{1}{n_f^2} - \frac{1}{n_i^2} \right]$ Let us consider, $n_i = n$ and

$n_f = n - p$ where $p = 1, 2, 3, \dots$. Hence, $\nu = \frac{mZ^2 e^4}{8\varepsilon_0^2 h^3} \left[\frac{1}{(n-p)^2} - \frac{1}{n^2} \right]$ or, $\nu = \frac{mZ^2 e^4}{8\varepsilon_0^2 h^3} \left[\frac{2pn - p^2}{n^2(n-p)^2} \right]$

Now, if $n \gg p$, then $2pn - p^2 \approx 2pn$ and $(n-p)^2 \approx n^2$. Thus, $\nu = \frac{mZ^2 e^4}{8\varepsilon_0^2 h^3} \left(\frac{2p}{n^3} \right)$. For $p = 1$, $f = \nu$.

Therefore, the frequency of radiation is equal to the frequency of revolution.

Merits of Bohr's theory

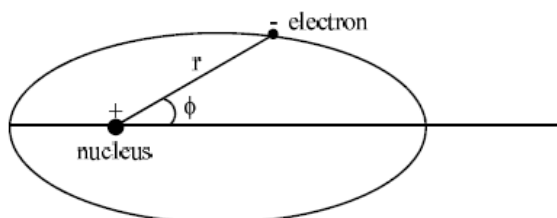
- (i) The experimental value of radii and energies in hydrogen atom are in good agreement with that calculated on the basis of Bohr's theory.
- (ii) Bohr's concept of stationary state of electron explains the stability of atoms and the emission and absorption spectra of hydrogen like atoms.
- (iii) The experimental values of the spectral lines of the hydrogen spectrum are in close agreement with the calculated by Bohr's theory.

Limitations of Bohr's Theory

- (i) Bohr introduces an integer (n) in selecting the stable orbits for electrons arbitrarily. There was no theoretical justification for it.
- (ii) It does not explain the spectra of atoms or ions having more than one electron.
- (iii) Bohr's atomic model failed to account for the effect of magnetic field (Zeeman effect) or electric field (Stark effect) on the spectra of 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.
- (iv) de-Broglie suggested that electrons like light have dual character. It has particle and wave character. Bohr treated the electron only as particle.
- (v) 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". But in Bohr's model, electrons revolve in well defined orbits around the nucleus with well defined velocities. So, it is not attainable.

Sommerfeld's Model

Bohr's theory was inadequate to explain the fine structure of emission spectrum. Fine structure suggests the presence of more energy levels for any given value of n . This indicates the existence of sub energy levels corresponding to each Bohr orbit.



According to Sommerfeld:

(i) Elliptical orbit – Electrons are revolving around the nucleus in some specified elliptical orbit with different eccentricities. That means corresponding to each principal quantum number (n) several orbit of varying ellipticity were possible. The nucleus was positioned at the focus of the ellipse. The circular orbit is only special case of Sommerfeld elliptic orbits.

(ii) Quantum restriction – The position of a revolving electron around the nucleus in an elliptical orbit is determined by radius vector (r) measured from the nucleus and the angle (ϕ) between radius vector and semi major axis. ϕ is called azimuthal angle. Only certain elliptical orbits will be allowed which satisfy the condition $\oint p_{\phi} d\phi = kh$ and $\oint p_r dr = n_r h$. Here, p_{ϕ} and p_r are the angular and radial momentum of the electron, h Planck constant, k and n_r are the two positive integers called the azimuthal and radial quantum numbers respectively.

(iii) Requirement of two quantum restrictions: There are two quantum numbers (a) radial quantum number (n_r) and (b) azimuthal quantum number (k). These are related to principal quantum number (n) and ellipticity of the orbit by the following relation:

$$(i) n = n_r + k \text{ and } (ii) \frac{n}{k} = \frac{\text{length of semi major axis } (a_n)}{\text{length of semi minor axis } (b_n)}$$

The ellipticity of the orbits was thus determined by the relative values of n and k . The eccentricities of the ellipse, ϵ is expressed as $\frac{b_n}{a_n} = \frac{k}{n} = \sqrt{1 - \epsilon^2}$. For any given value of n , permissible values of n_r and k are: $n_r = (n-1), (n-2), (n-3), \dots, 0$ and

$$k = 1, 2, 3, \dots, n$$

When $k = 0$, $b_n = 0$ and as a result, the ellipse gets converted into a straight line leading the moving electron to pass through the nucleus. So, $k = 0$ is not acceptable.

❖ It is worth mentioning that the azimuthal quantum number, k has subsequently been replaced by symbol ' l ' for certain mathematical advantages. The values of l are fixed in relation to k as $l = k-1$. Thus, for any given value of n , l may have values $0, 1, \dots$ to $(n-1)$.

Detailed mathematical calculation gives the value of a_n , b_n and E_n as follows:

Semi major axis, $a_n = \frac{\epsilon_0 n^2 h^2}{\pi m Z e^2}$ or, $a_n = \frac{n^2}{Z} a_0$ and Semi minor axis, $b_n = \frac{\epsilon_0 n k h^2}{\pi m Z e^2}$ or $b_n = \frac{n k}{Z} a_0$

$E_n = -\frac{m Z^2 e^4}{8 \epsilon_0^2 n^2 h^2}$ or, $E_n = -\frac{m Z^2 e^4}{8 \epsilon_0^2 (n_r + k)^2 h^2}$. This implies that the energy of an electron would be same in any orbit of principal quantum number, n whatever is the ellipticity. At this point Sommerfeld considered relativistic variation of mass of the electron during its motion in an elliptical orbit and showed that the energy of the electron will be different with variation of k . It has been calculated that relativistic variation of the electron mass is significant that causes differences in energy of the electron in orbits of varying ellipticity:

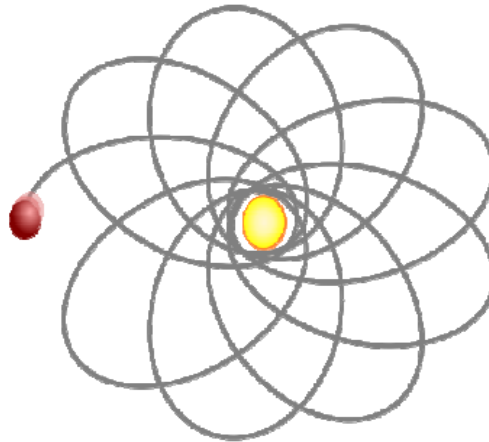
$$E = -\frac{\mu Z^2 e^4}{8 \epsilon_0^2 n^2 h^2} \left[1 + \frac{\alpha^2 Z^2}{n} \left(\frac{1}{k} - \frac{3}{4n} \right) \right] \text{ where } \alpha = \frac{e^2}{2 \epsilon_0 h c} \text{ is called fine structure constant.}$$

Relativistic effect:

When electron is moving in an elliptical orbit, electrostatic force is varying with the distance of electron from the nucleus. To balance the varying electrostatic force, velocity of the electron changes with its position. The velocity is greatest when the electron is closest to the nucleus and decreases gradually as the electron moves farther. According to the theory of relativity, the mass of the electron also changes according to the relation $m = \frac{m_0}{\sqrt{1 - \frac{v^2}{c^2}}}$ where m_0

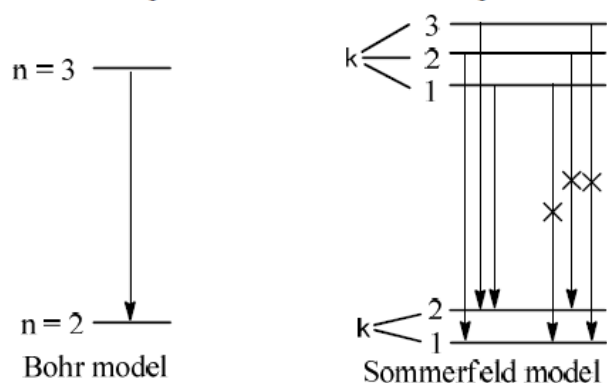
is the rest mass of the electron, m is its mass at velocity v and c is velocity of light. With change of velocity (v), mass (m) of electron is changing.

Relativistic variation of the mass of the electron has a further consequence. Each time the electron passes near the nucleus, the equilibrium force between the electron and nucleus is slightly perturbed and semi major axis of the ellipse shifts, i.e., undergoes precession. The resulting path of the electron appears like a rosette.



Explanation of fine structure:

The energy expression shows that total energy of the electron now depends on the value of both n and k for a particular value of principal quantum number, n . The fine structure of the spectra was now understood by assuming transition involving orbits of different n and k values. There are n different energy levels for a particular value of n , because of n number of permitted values of k . Say, H_α line in Balmer series i.e., $n = 3$ to $n = 2$ transition, there should be six line. But experimentally less number of transitions was observed. This is why, quantum restriction, i.e., selection was introduced as $\Delta k = \pm 1$, $\Delta n = \text{any value}$. This restriction leading to three lines (triplet) for Balmer series and five lines (quintet) for Paschen series and the α -line in the Lyman series should show no fine structure (single line). Unfortunately, the number of components predicted from the theory does not agree with the experimental results. So, further quantum numbers were required to explain the spectrum.

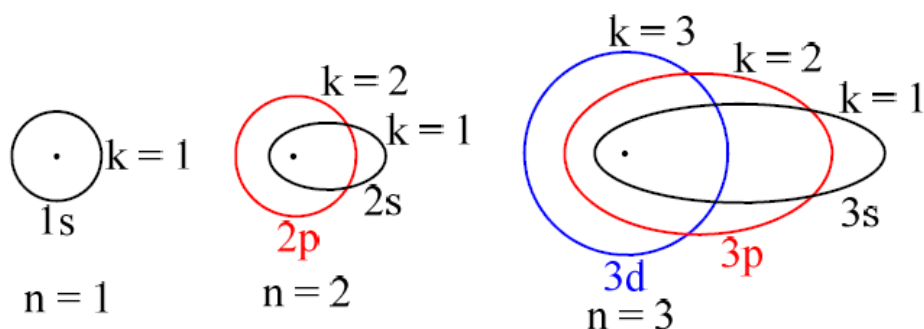


Shape of orbits for a particular value of n :

We have the relation, $\frac{b_n}{a_n} = \frac{k}{n} = \sqrt{1 - \epsilon^2}$. For a particular value of n , it appears that as the value of k increases the ellipticity of the orbit decreases and for the highest allowed value of k , it becomes a circular orbit. So, for the minimum values of k , orbit is the most elliptical.

Name of the orbit: s, p, d, f, ... and

The values of k : 1, 2, 3, 4, ...



Achievements and drawbacks of Sommerfeld model:

Achievements:

In addition to the merits in Bohr's theory, some additional successes have been achieved.

(i) Fine spectra: Sommerfeld's modification can explain the origin of fine spectra by introducing two quantum numbers k and n_r , though it fails to predict the exact number of the fine lines.

(ii) Penetrating and screening power: The eccentricities of different orbits of same principal quantum number are different because of different k values. These orbits experience different amount of positive charge of the nucleus because of their different penetrating power. The binding force for different electrons lies in the sequence, $s > p > d > f$ electrons. This prediction is verified in many properties like ionisation potentials, electron affinity, etc.

Drawbacks:

(i) Components of fine structure: It can't predict the correct number of fine structure lines.

(ii) Relative intensity: It can't say anything regarding the relative intensities of the fine lines.

(iii) Azimuthal quantum number: Sommerfeld's azimuthal quantum number (k) is different from one (l) obtained in wave mechanics.

(iv) Uncertainty principle: According to the uncertainty principle, simultaneous consideration of the exact position and velocity of the revolving electron can't be supported.

(v) Poly-electronic system: It mainly deals with hydrogen like systems.

de Broglie hypothesis:

In quantum theory, the energy of photon of frequency ν is related as, $E = h\nu$. According to the Einstein's law of mass-energy equivalence, $E = mc^2$. Comparing the above two equations, $mc^2 = h\nu$ or, $mc = h \frac{\nu}{c}$ or, $mc = \frac{h}{\lambda}$ or, $p = \frac{h}{\lambda}$

Thus, momentum of photon ($p = mc$) is related with its wavelength (λ) as $p = \frac{h}{\lambda}$.

In other words, the fundamental law of relativity gives the relation $E = \sqrt{p^2c^2 + m_0^2c^4}$. Now for photon, the rest mass (m_0) is zero. Hence, $E = pc$ or, $p = \frac{E}{c}$ or, $p = \frac{h\nu}{c} = \frac{h}{\lambda}$

The French scientist, de Broglie generalized the idea and applies equally to both photons and material particle. He assumed that a moving body has also associated matter wave. For a particle of mass m moving with a velocity v is related as $\lambda = \frac{h}{mv}$ where λ is wave length of matter called de Broglie wave length of the particle.

Wave length of a moving subatomic particle:

The electron in a hydrogen atom moved with a velocity, $v = 2.3 \times 10^6 \text{ m s}^{-1}$. Thus, the wave length, $\lambda = \frac{h}{mv} = \frac{6.626 \times 10^{-34} \text{ J s}}{9.1 \times 10^{-31} \text{ kg} \times 2.3 \times 10^6 \text{ ms}^{-1}} = 3.16 \times 10^{-10} \text{ m} = 3.16 \text{ \AA}$

This value of wave length is comparable to that of X-rays and it is measurable as well as believable.

Wave length of a moving macroscopic particle:

A bullet of mass $2 \times 10^{-3} \text{ kg}$ is moving with a speed of 300 m s^{-1} . Thus, wave length, λ will be:

$$\lambda = \frac{h}{mv} = \frac{6.626 \times 10^{-34} \text{ J s}}{2 \times 10^{-3} \text{ kg} \times 300 \text{ ms}^{-1}} = 1.1 \times 10^{-33} \text{ m} = 1.1 \times 10^{-23} \text{ \AA}$$

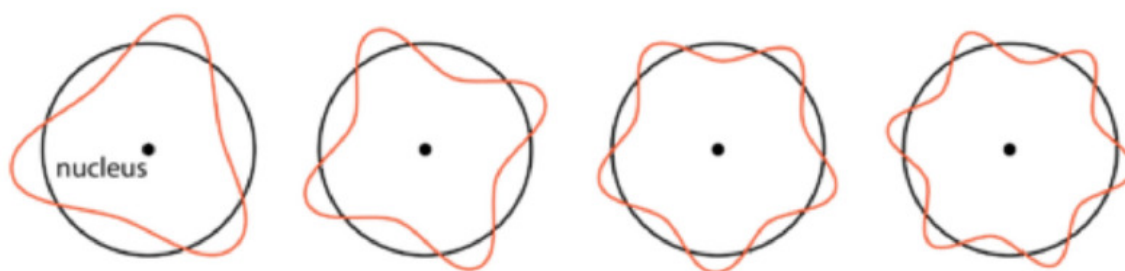
The value of wave length is exceeding small and not measurable. Besides this, due to this exceedingly high frequency, the energy of the bullet becomes so high that it is unbelievable in our sense. That's why the de Broglie's wave equation has not meaningful for macroscopic particle.

Bohr's quantum restriction from de Broglie concept:

According to Bohr's theory, the stationary orbits are defined by the relation, $mvr = n \frac{h}{2\pi}$.

Now, considering wave-particle dualism, the revolving electron in a particular stationary orbit can be considered as a stationary wave, i.e., the position of its maxima and minimum do not change with time. Such wave can be obtained, if the two ends of an electron wave meet in the same phase. To satisfy this condition, the circumference of the Bohr's circular orbit must be an integral multiple of the wave length (λ). So,

$2\pi r = n\lambda$ or, $2\pi r = n \frac{h}{p}$ or, $2\pi r = n \frac{h}{mv}$ or, $mvr = n(\frac{h}{2\pi})$ It is the Bohr's quantum restriction to define a stationary orbit.



The uncertainty principle:

Considering wave-particle dualism of matter, W. Heisenberg stated: it is not possible to determine simultaneously both position and the momentum of a body with any arbitrary desired accuracy. In other words, it is impossible to know both the exact position and exact momentum of an object at the same time. Mathematically, uncertainty principle as follows:

$$\Delta x \cdot \Delta p \geq \frac{h}{4\pi}$$

where Δx and Δp represent the uncertainties in determining the position and momentum of the particle respectively at the same time. The relation indicates that the product of two uncertainties is approximately of the order of Planck's constant. Thus, a certainty in one quantity introduces an uncertainty in its conjugate quantity.

The uncertainty in determining the velocity can be obtained as follows:

$$\Delta x \cdot \Delta p \geq \frac{h}{4\pi} \text{ or, } \Delta x \cdot m \Delta v \geq \frac{h}{4\pi} \text{ or } \Delta x \cdot \Delta v \geq \frac{h}{4\pi m}$$

Uncertainty in energy and time:

The uncertainty relation holds between any two conjugate properties like energy and time. If Δt and ΔE is the uncertainty in time and energy measurement then $\Delta E \cdot \Delta t \geq \frac{h}{4\pi}$

Suppose, we want to measure energy, E of a free particle moving with a velocity v in the x -direction. The energy, E is equal to the kinetic energy of the particle:

$$E = \frac{1}{2}mv^2 \text{ or, } E = \frac{p^2}{2m} \text{ (m = mass and p = momentum)}$$

$$\text{Or, } \Delta E = \frac{2p}{2m} \Delta p \text{ or, } \Delta E = \frac{p}{m} \Delta p \text{ or, } \Delta E = v \cdot \Delta p$$

$$\text{But, velocity } v = \frac{\text{displacement}}{\text{time}} = \frac{\Delta x}{\Delta t}$$

$$\text{So, now } \Delta E = \frac{\Delta x}{\Delta t} \Delta p \text{ or, } \Delta E \cdot \Delta t = \Delta x \cdot \Delta p. \text{ Therefore, } \Delta E \cdot \Delta t \geq \frac{h}{4\pi}$$

❖ Consider a ball of mass 2 g whose uncertainty in position is equal to 10^{-8} cm. Hence, the corresponding uncertainty in its velocity would be:

$$\Delta v = \frac{h}{4\pi m \cdot \Delta x} = \frac{6.626 \times 10^{-34} \text{ J s}}{4 \times 3.14 \times 2 \times 10^{-3} \text{ kg} \times 10^{-10} \text{ m}} = 0.26 \times 10^{-21} \text{ m s}^{-1}.$$

This uncertainty is definitely negligible to the usual velocity of the ball.

❖ Consider position of the electron from the nucleus can be determined with uncertainty of 4 pm i.e., 4×10^{-12} m. Hence, the corresponding uncertainty in defining the velocity would be:

$$\Delta v = \frac{h}{4\pi m \Delta x} = \frac{6.626 \times 10^{-34} \text{ J s}}{4 \times 3.14 \times 9.1 \times 10^{-31} \text{ kg} \times 4 \times 10^{-12} \text{ m}} = 1.45 \times 10^7 \text{ m s}^{-1}$$

Now, this uncertainty in velocity is huge and even more than that the velocity of electron in the first Bohr's orbit. Thus, this principle strikes at the fundamental root of the Bohr's concept to have the existence of well defined orbits.

An electron can't exist in the nucleus:

A typical nucleus have radius less than 10^{-14} m. Hence, an electron to exist in the nucleus, its uncertainty in position can't exceed the limit, 10^{-14} m i.e., $\Delta x = 10^{-14}$ m. So, the corresponding uncertainty in its momentum will be:

$$\Delta p = \frac{h}{4\pi \Delta x} = \frac{6.626 \times 10^{-34} \text{ J s}}{4 \times 3.14 \times 10^{-14} \text{ m}} = 0.55 \times 10^{-20} \text{ kg m s}^{-1}. \text{ This is the minimum uncertainty of}$$

momentum. Now, if an electron possesses a momentum of the order of $10^{-20} \text{ kg m s}^{-1}$, its classical kinetic energy ($p^2/2m$) becomes much greater than the rest mass energy ($m_0 c^2$).

Under such condition, the relativistic kinetic energy = $pc = 0.55 \times 10^{-20} \times 3 \times 10^8 \text{ m s}^{-1}$

$$= 1.65 \times 10^{-12} \text{ J} = 10.3 \text{ MeV}$$

Therefore, it concludes that, if the electron is to be considered as a nuclear constituent, it will have energy at least more than 10.3 MeV. But, experimentally, it has been established that even for the most unstable atoms, an electron can never get associated with more than a fraction of this energy. Based on this, it can be firmly concluded that an electron can't exist in a nucleus.

Schrodinger wave equation

E. Schrodinger introduced a mathematical concept of wave-particle dualism to the electron in an atom by considering the electron as a standing wave as in the case of a vibrating string fixed at both ends. This mathematical expression is called Schrodinger wave equation. The equation can be applied to many cases such as to the electrons to describe the atomic model, to the harmonic oscillators to define their energy levels, to the diatomic molecules to define their rotational and vibrational energy levels etc. The equation with respect to space can be written in the Cartesian coordinate system for stationary waves (time independent) as follows

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

Here Ψ is called wave function. Ψ represents the amplitude of the matter associated with the particle at various points defined by x, y, z space coordinates, m stands for mass of the particle, h is the Planck constant, E represents the total energy while V stands for the potential energy of the particle at the position x, y, z.

The above second order differential equation is very often represented as:

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

The term ∇^2 is called Laplacian operator.

The Schrodinger equation is also expressed in the following form:

$$\nabla^2 \Psi + \frac{8\pi^2 m}{h^2} (E - V) \Psi = 0 \text{ Or, } -\nabla^2 \Psi + \frac{8\pi^2 m}{h^2} V \Psi = \frac{8\pi^2 m}{h^2} E \Psi$$

$$\text{Or, } \left[-\frac{h^2}{8\pi^2 m} \nabla^2 + V \right] \Psi = E \Psi \text{ Or, } \left[-\frac{\hbar^2}{2m} \nabla^2 + V \right] \Psi = E \Psi \quad (\text{where } \hbar = h/2\pi)$$

Or, $\hat{H} \Psi = E \Psi$ where $\hat{H} = \left[-\frac{\hbar^2}{2m} \nabla^2 + V \right]$ called Hamiltonian operator which is a function of various coordinates and potential energy.

Physical significance of the wave function:

The wave function(Ψ) has no physical significance as it is not associated with any physical wave. It is an abstract mathematical entity though it provides information on physical quantities which may be verified experimentally.

On the other hand Ψ^2 bears a meaningful significance. In classical mechanics, the square of amplitude of the wave associated with electromagnetic radiation is interpreted as a measure of intensity effect at any point. $\Psi \Psi^*$ or Ψ^2 may be used as a measure of density of electric charge or particle at a particular point.

Another statistical interpretation of $\Psi\Psi^*$ or Ψ^2 was given by Max Born where $\Psi\Psi^*d\tau$ or $\Psi^2d\tau$ is considered as a measure of probability of finding particle in small volume $d\tau$ ($dx.dy.dz$) at a particular point. Thus, $\Psi^2d\tau$ is proportional to the probability of finding particle in the volume $d\tau$. The total probability over the whole space is unity, i.e., $\int_{-\infty}^{+\infty} \Psi\Psi^*d\tau = 1$

Ψ may be both real and complex. If Ψ is complex then Ψ^2 will contain a imaginary term which have no physical significance. In such cases $\Psi\Psi^*$ is to be considered where Ψ^* is the complex conjugate of Ψ , [if $\Psi = (a + ib)$ then $\Psi^* = (a - ib)$]. If Ψ is real then $\Psi = \Psi^*$ and thus $\Psi\Psi^*$ becomes Ψ^2 . This is why in general $\Psi\Psi^*$ are considered for interpretation.

Eigen function and Eigen values:

The time independent Schrödinger equation can be written as $\hat{H}\Psi = E\Psi$ where \hat{H} is Hamiltonian operator or energy operator since it yields energy of the system when applied on Ψ . In general, when an operator \hat{A} , operates on a function Ψ_i , to give back the function multiplied by some constant a_i , that is,

$$\hat{A}\Psi_i = a_i\Psi_i \text{ [operator (function) = constant x same function]}$$

Then, Ψ_i is an eigen function of the operator \hat{A} and a_i is its eigen value. In the case of Hamiltonian operator \hat{H} , $\Psi(x)$ is an eigen function and several values of E that are obtained for various wave functions are eigen values.

Well behaved wave function:

The Schrodinger equation provides many solution of a system but many of them have no physical reality. Only those solutions give information on physical measurable properties of the system are acceptable. Such acceptable solutions for the wave function are selected according to the following conditions.

- 1) Ψ must be single valued i.e., Ψ may have one and only one value at any point in space.
- 2) Ψ must be finite. The probability density at any point in space must be finite.
- 3) Ψ must be continuous. Certain properties like momentum are calculated by taking the derivative of Ψ . If Ψ is discontinuous at a point, its 1st derivative at that point will be infinite.
- 4) Ψ must be square integrable. This allows multiplication of Ψ by a constant to make it normalized. This means the total probability of finding a particle described by Ψ over entire space must be equal to unity. $\int_{-\infty}^{+\infty} \Psi^2 d\tau = 1$ or $\int_{-\infty}^{+\infty} \Psi\Psi^* d\tau = 1$

** If Ψ_1 and Ψ_2 are two acceptable wave functions, they are orthogonal. Condition of orthogonality is as follows: $\int_{-\infty}^{+\infty} \Psi_1\Psi_2d\tau = 0$

Schrodinger equation for hydrogen atom

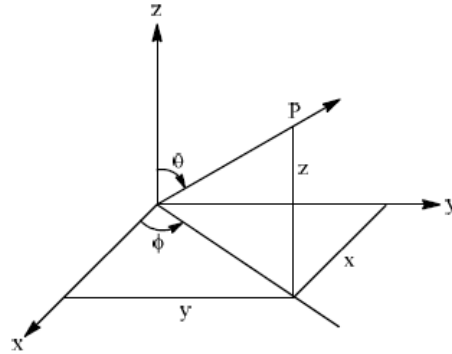
The time independent Schrodinger equation with the wave function of the electron Ψ , which is a function of the space coordinates x, y, z and potential energy V written as:

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

E is the total energy of the electron. The potential energy V of the electron at a distance r from the nucleus is, $V = -\frac{e^2}{r}$ or $(-\frac{e^2}{4\pi\epsilon_0 r})$ in SI). Since, V is a function of r and in Cartesian coordinates $r = \sqrt{x^2 + y^2 + z^2}$. So $V = -\frac{e^2}{\sqrt{x^2 + y^2 + z^2}}$. The final Schrodinger equation will be

$$\nabla^2\Psi + \frac{8\pi^2m}{h^2}(E + \frac{e^2}{\sqrt{x^2 + y^2 + z^2}})\Psi = 0.$$

But, it is more realistic to express the Schrodinger equation for hydrogen atom in spherical polar coordinates. Interrelation of Cartesian and polar coordinates is as follows.



$$r = \sqrt{x^2 + y^2 + z^2}, \theta = \cos^{-1} \frac{z}{\sqrt{x^2 + y^2 + z^2}} \text{ and } \phi = \tan^{-1} \frac{y}{x}$$

$$x = r\sin\theta\cos\phi, y = r\sin\theta\sin\phi \text{ and } z = r\cos\theta$$

$$\text{Accordingly, } \nabla^2 = \frac{1}{r^2} \frac{\partial}{\partial r} (r^2 \frac{\partial}{\partial r}) + \frac{1}{r^2 \sin\theta} \frac{\partial}{\partial \theta} (\sin\theta \frac{\partial}{\partial \theta}) + \frac{1}{r^2 \sin^2\theta} \frac{\partial^2}{\partial \phi^2}$$

Using the expression for ∇^2 and $V = -\frac{Ze^2}{r}$, the Schrodinger equation is transformed into spherical coordinates as:

$$\frac{1}{r^2} \frac{\partial}{\partial r} (r^2 \frac{\partial \Psi}{\partial r}) + \frac{1}{r^2 \sin\theta} \frac{\partial}{\partial \theta} (\sin\theta \frac{\partial \Psi}{\partial \theta}) + \frac{1}{r^2 \sin^2\theta} \frac{\partial^2 \Psi}{\partial \phi^2} + \frac{8\pi^2m}{h^2} (E + \frac{Ze^2}{r}) \Psi = 0$$

The wave function Ψ is a function of three variables r, θ and ϕ . The wave function can be expressed as a product of three functions $R(r)$ or $\Psi(r)$, $\Theta(\theta)$ or $\Psi(\theta)$ and $\Phi(\phi)$ or $\Psi(\phi)$ which depend only on r, θ and ϕ respectively.

$$\Psi(r, \theta, \phi) = R(r) \Theta(\theta) \Phi(\phi)$$

$R(r)$ is a function of r , the radial distance from the nucleus. This is called radial part of the wave function or radial function. $\Theta(\theta)$ is a function of θ and $\Phi(\phi)$ is a function of ϕ . These two functions represent the angular part of the wave function. They may also be combined into a single function $\Psi(\theta, \phi)$.

$$\Psi(r, \theta, \phi) = R(r) \Psi(\theta, \phi)$$

Therefore, we can write the Schrodinger equation as follows by putting $\Psi = R(r) \Theta(\theta) \Phi(\phi)$:

$$\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) R(r) \Theta(\theta) \Phi(\phi) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) R(r) \Theta(\theta) \Phi(\phi) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2}{\partial \phi^2} R(r) \Theta(\theta) \Phi(\phi) + \frac{8\pi^2 m}{h^2} \left(E + \frac{Ze^2}{r} \right) \Psi = 0$$

By solving this equation we will get three differential equations each containing one variable.

$$\Phi \text{ equation: } \frac{1}{\Phi(\phi)} \frac{\partial^2}{\partial \phi^2} \Phi(\phi) = -m^2$$

$$\Theta \text{ equation: } \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \Theta(\theta) \right) + \left(\beta - \frac{m^2}{\sin^2 \theta} \right) \Theta(\theta) = 0$$

$$R \text{ equation: } \frac{1}{R(r)} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} R(r) \right) + \frac{8\pi^2 m}{h^2} \left(E + \frac{Ze^2}{r} \right) r^2 = \beta \text{ where } \beta = l(l+1)$$

Clearly, it is seen that the solution of Schrodinger equation leads to three quantum number principal quantum number (n), azimuthal quantum number (l) and magnetic quantum number (m) to describe the electron. For a given energy state, the radial function $R(r)$ depends on n and l , $\Theta(\theta)$ depends on l and m while $\Phi(\phi)$ depends on m only. Summarily, the wave function are written as: $\Psi(r, \theta, \phi) = R_{nl}(r) \Theta_{lm}(\theta) \Phi_m(\phi)$

The final solutions of these above three differential equations are as follows:

$$\Phi(\phi) = \frac{1}{\sqrt{2\pi}} e^{im\phi} \text{ where } m = 0, \pm 1, \pm 2, \pm 3, \dots \text{ and } \frac{1}{\sqrt{2\pi}} \text{ is normalization constant.}$$

$$\Theta(\theta) = \frac{\sqrt{(2l+1)(l-|m|)!}}{\sqrt{2(l+|m|)!}} P_l^{|m|} \cos(\theta) \text{ where } m = 0, \pm 1, \pm 2, \pm 3, \dots \pm l$$

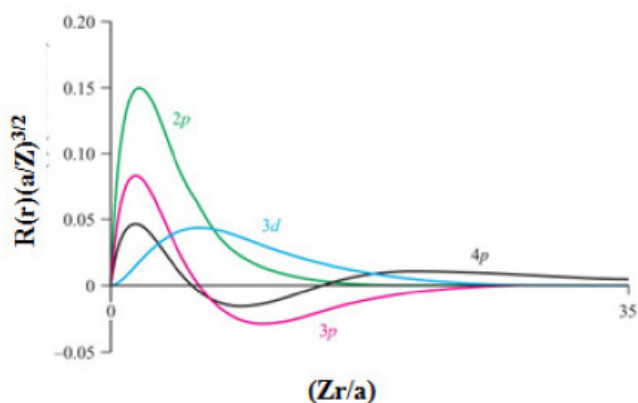
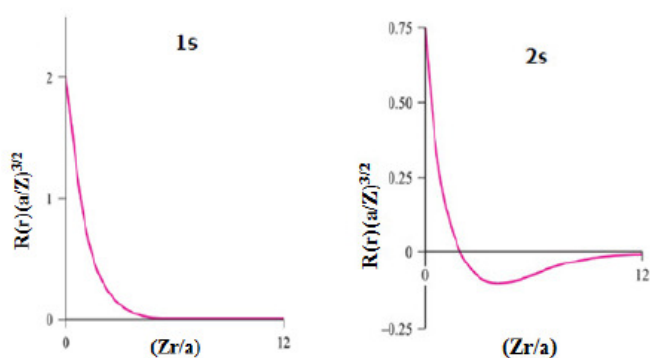
$$R(r) = - \left[\left(\frac{2Z}{na_0} \right)^3 \frac{(n-l-1)!}{2n[(n+l)!]^3} \right]^{\frac{1}{2}} e^{-\frac{x}{2}} x^l L_{n+l}^{2l+1}(x) \text{ where } x = \frac{2Zr}{na_0} \text{ and } a_0 = \frac{h^2}{4\pi^2 me^2}$$

By putting the different values of n , l and m we finally obtained the value of $\Phi(\phi)$, $\Theta(\theta)$, $R(r)$.

	n	l	m	$\Theta(\theta)$	$\Phi(\phi)$	R(r)
1s	1	0	0	$\frac{1}{\sqrt{2}}$	$\frac{1}{\sqrt{2\pi}}$	$2\left(\frac{Z}{a_0}\right)^{\frac{3}{2}} e^{-\frac{Zr}{a_0}}$
2s	2	0	0	$\frac{1}{\sqrt{2}}$	$\frac{1}{\sqrt{2\pi}}$	$\frac{1}{2\sqrt{2}} \left(\frac{Z}{a_0}\right)^{\frac{3}{2}} \left(2 - \frac{Zr}{a_0}\right) e^{-\frac{Zr}{a_0}}$
2p _z	2	1	0	$\frac{\sqrt{6}}{2} \cos\theta$	$\frac{1}{\sqrt{2\pi}}$	$\frac{1}{2\sqrt{16}} \left(\frac{Z}{a_0}\right)^{\frac{3}{2}} \left(\frac{Zr}{a_0}\right) e^{-\frac{Zr}{2a_0}}$
2p _x	2	1	± 1	$\frac{\sqrt{3}}{2} \sin\theta$	$\frac{1}{\sqrt{\pi}} \cos\phi$	$\frac{1}{2\sqrt{16}} \left(\frac{Z}{a_0}\right)^{\frac{3}{2}} \left(\frac{Zr}{a_0}\right) e^{-\frac{Zr}{2a_0}}$
2p _y	2	1		$\frac{\sqrt{3}}{2} \sin\theta$	$\frac{1}{\sqrt{\pi}} \sin\phi$	$\frac{1}{2\sqrt{16}} \left(\frac{Z}{a_0}\right)^{\frac{3}{2}} \left(\frac{Zr}{a_0}\right) e^{-\frac{Zr}{2a_0}}$
3s	3	0	0	$\frac{1}{\sqrt{2}}$	$\frac{1}{\sqrt{2\pi}}$	$\frac{2}{81\sqrt{3}} \left(\frac{Z}{a_0}\right)^{\frac{3}{2}} \left[27 - 18\frac{Zr}{a_0} + 2\left(\frac{Zr}{a_0}\right)^2\right] e^{-\frac{Zr}{3a_0}}$
3p _z	3	1	0	$\frac{\sqrt{6}}{2} \cos\theta$	$\frac{1}{\sqrt{2\pi}}$	$\frac{4}{81\sqrt{6}} \left(\frac{Z}{a_0}\right)^{\frac{3}{2}} \left[6\frac{Zr}{a_0} - \left(\frac{Zr}{a_0}\right)^2\right] e^{-\frac{Zr}{3a_0}}$
3p _x	3	1	± 1	$\frac{\sqrt{3}}{2} \sin\theta$	$\frac{1}{\sqrt{\pi}} \cos\phi$	$\frac{4}{81\sqrt{6}} \left(\frac{Z}{a_0}\right)^{\frac{3}{2}} \left[6\frac{Zr}{a_0} - \left(\frac{Zr}{a_0}\right)^2\right] e^{-\frac{Zr}{3a_0}}$
3p _y	3	1		$\frac{\sqrt{3}}{2} \sin\theta$	$\frac{1}{\sqrt{\pi}} \sin\phi$	$\frac{4}{81\sqrt{6}} \left(\frac{Z}{a_0}\right)^{\frac{3}{2}} \left[6\frac{Zr}{a_0} - \left(\frac{Zr}{a_0}\right)^2\right] e^{-\frac{Zr}{3a_0}}$
3d _{z²}	3	2	0	$\sqrt{\frac{5}{8}}(3\cos^2\theta-1)$	$\frac{1}{\sqrt{2\pi}}$	$\frac{4}{81\sqrt{30}} \left(\frac{Z}{a_0}\right)^{\frac{3}{2}} \left(\frac{Zr}{a_0}\right)^2 e^{-\frac{Zr}{3a_0}}$
3d _{xz}	3	2	± 1	$\sqrt{\frac{15}{4}} \sin\theta \cos\theta$	$\frac{1}{\sqrt{\pi}} \cos\phi$	$\frac{4}{81\sqrt{30}} \left(\frac{Z}{a_0}\right)^{\frac{3}{2}} \left(\frac{Zr}{a_0}\right)^2 e^{-\frac{Zr}{3a_0}}$
3d _{yz}	3	2		$\sqrt{\frac{15}{4}} \sin\theta \cos\theta$	$\frac{1}{\sqrt{\pi}} \sin\phi$	$\frac{4}{81\sqrt{30}} \left(\frac{Z}{a_0}\right)^{\frac{3}{2}} \left(\frac{Zr}{a_0}\right)^2 e^{-\frac{Zr}{3a_0}}$
3d _{xy}	3	2	± 2	$\sqrt{\frac{15}{16}} \sin^2\theta$	$\frac{1}{\sqrt{\pi}} \sin 2\phi$	$\frac{4}{81\sqrt{30}} \left(\frac{Z}{a_0}\right)^{\frac{3}{2}} \left(\frac{Zr}{a_0}\right)^2 e^{-\frac{Zr}{3a_0}}$
3d _{x²-y²}	3	2		$\sqrt{\frac{15}{16}} \sin^2\theta$	$\frac{1}{\sqrt{\pi}} \cos 2\phi$	$\frac{4}{81\sqrt{30}} \left(\frac{Z}{a_0}\right)^{\frac{3}{2}} \left(\frac{Zr}{a_0}\right)^2 e^{-\frac{Zr}{3a_0}}$

Variation of Radial wave function:

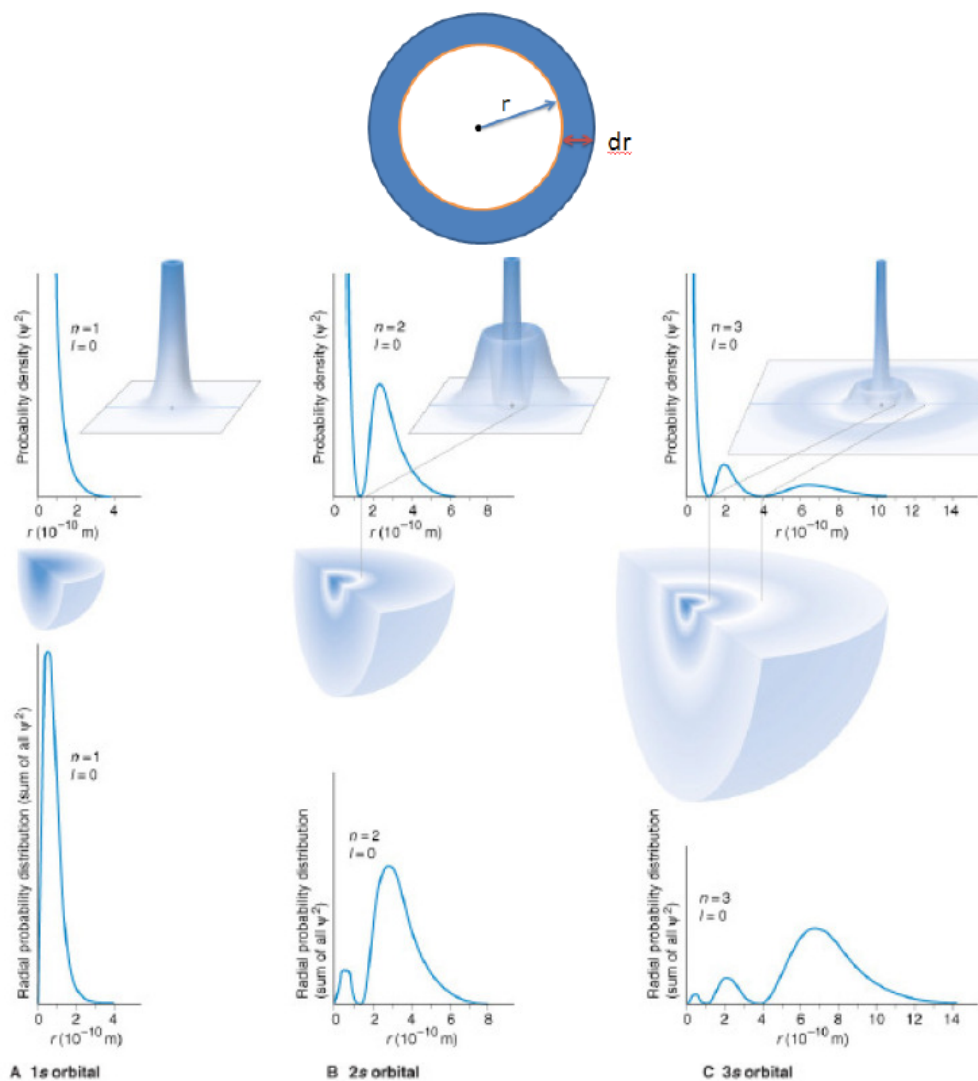
- i) All the functions contains an exponential term, $e^{-\frac{Zr}{na_0}}$, which decreases with r . So, $R(2s)$ has slower rate of decay with r than $R(1s)$. Thus, the wave function of an orbital with higher n extends to a larger distance from the nucleus.
- ii) The R -function for the $2s$ orbital passes through zero when $(2 - \frac{Zr}{a_0}) = 0$ i.e., at $r = \frac{2a_0}{Z}$, $R(2s) = 0$. The point at $r = \frac{2a_0}{Z}$ represents a radial node. The function changes its sign beyond this point.
- iii) The orbital designated by n and l has $n-l-1$ number of radial nodes. Node is a surface where the wave function passes through zero as it changes sign.



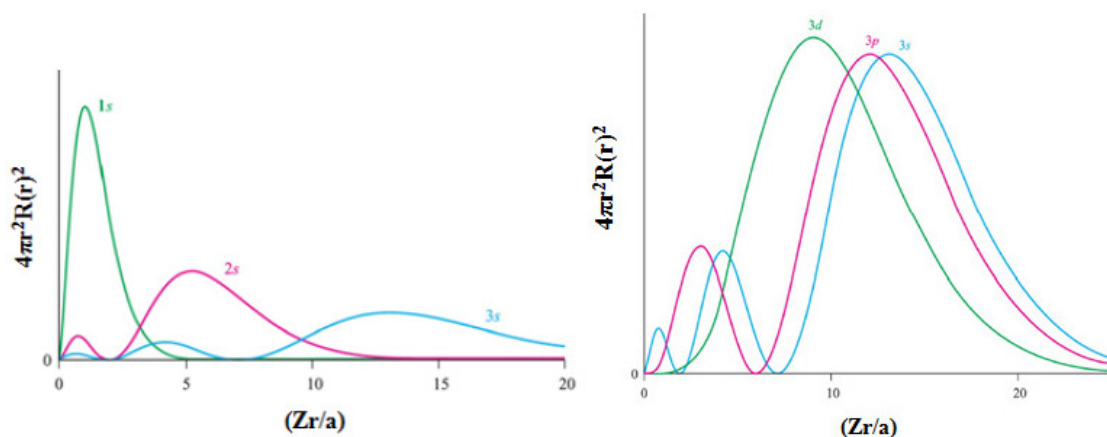
Radial distribution function (RDF)

Radial distribution function gives the idea of total probability of finding the electron in the spherical shell bounded by the spheres of radius r and $r + dr$. It measures the probability per unit length at the distance r . RDF is different from the radial probability density, $P(r)$, which measures the probability density per unit volume. Generally, $P(r) = R(r)^2$ or $\Psi(r)^2$ and $RDF = R(r)^2 dv = 4\pi r^2 R(r)^2 dr$ where $dv = 4\pi r^2 dr$.

Suppose, the atom is composed by concentric spheres. Now, if dv is the volume in between those sphere of radius r and $r + dr$, then $dv = 4\pi r^2 dr$ (where $v = 4/3\pi r^3$).



For, s-orbital, the radial probability density is maximum at the nucleus but for all other orbitals this probability is zero at the nucleus. However, for s-orbital, the total probability i.e., radial probability distribution function ($4\pi r^2 R(r)^2 dr$) is zero at $r = 0$ because the volume element dv become zero at $r = 0$.



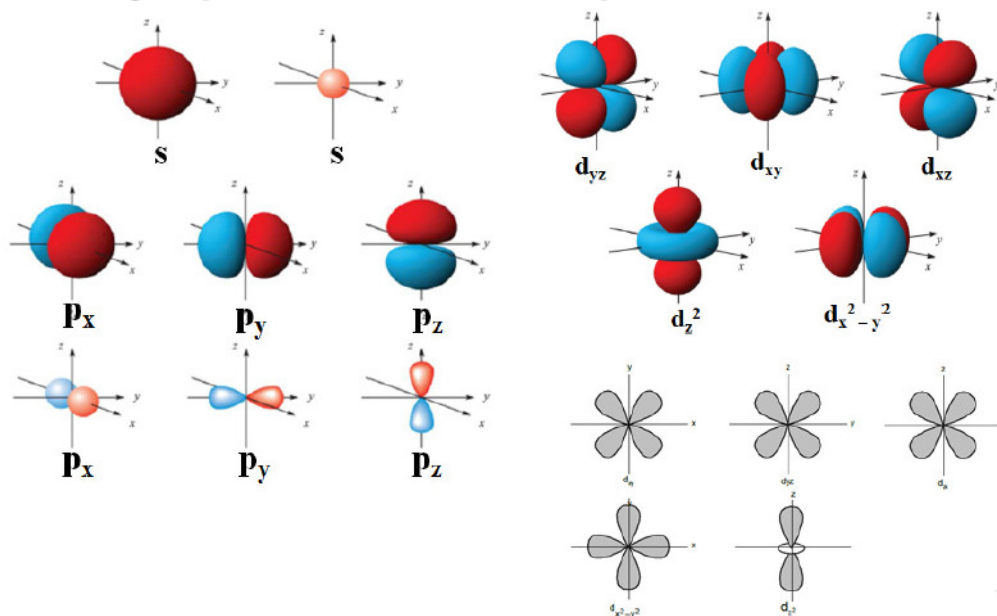
Characteristic features of Radial distribution function:

- (i) RDF at $r = 0$: $4\pi r^2 R^2$ becomes zero at $r = 0$.
- (ii) Probability at $r = \infty$: As $r \rightarrow \infty$, the probability tends to be zero. In practical sense, at the larger values of r , the probability approaches to almost zero.
- (iii) Maximum probability regions: As r increases, the probability increases and at a particular value of r , the probability becomes maximum then it falls down. Except the orbitals appearing first as 1s, 2p, 3d, 4f, in all other cases, more than one value of r , the maxima appear. The r_{\max} values for different orbitals are 1s (a_0), 2s ($0.77a_0, 5.23a_0$), 2p ($4a_0$) etc.
- (iv) Intra-nodal maxima and penetrating power: For, 3s, sp, 3d orbitals, the r_{\max} for the largest maximum probability region lies in the sequence $r_{\max}(3s) > r_{\max}(3p) > r_{\max}(3d)$ but, for 3s and 3p orbitals, there are two and one additional intra-nodal maxima at lower distances from the nucleus. By considering these intra-nodal nodes, it is found that the 3s orbital electron spends a larger fraction of its time closer to the nucleus compared to 3p electron. The 3d electron spends relatively its least time close to nucleus compared to 3s and 3p electrons. By combining all of these maxima the average r_{\max} of the orbitals runs as $\langle r_{\max}(3s) \rangle < \langle r_{\max}(3p) \rangle < \langle r_{\max}(3d) \rangle$. This is why, the 3s electrons are most tightly bound to the nucleus followed by 3p and 3d electrons.

Again, the radial distribution functions of orbitals like 2s, 3s, 3p, 4d etc has intra-nodes that means the electrons of these orbital can spread into the inner orbital or comes closer to nucleus. This distribution into the inner core is termed as 'penetration'. The sequence of penetrating power as follows: $s > p > d > f$.

Characteristic features of Angular wave functions:

- (i) Relation with quantum numbers: The angular part of the wave function is dependent on the two quantum numbers l and m that determine the shape of the orbitals.
- (ii) Orbital shape: All s-orbitals ($l = 0$) are spherically symmetrical, as angular part is not dependent on θ and ϕ but, other orbitals angular part dependent on θ and/or ϕ . The boundary surfaces of the angular part of the wave function are represented below:



- (iii) Angular node: Angular node appears when the angular functions become zero and are planar or conical. Except the s-orbitals, for any other orbitals the angular wave function has zero values. The number of angular nodes for any orbital = l . The number of angular nodes for s, p and d-orbitals are as follows:

s-orbital = 0; p-orbitals = 1 (plane) and d orbitals = 2 (plane) and $d_{z^2} = 2$ conical surface.

Quantum numbers

(1) Principal quantum number (n):

It was introduced in Bohr's atomic model as $mvr = n(h/2\pi)$ where $n = 1, 2, 3, 4$, and so on.

Significance:

(i) Energy of the electron: In Bohr's model energy of the electron in hydrogen like system is governed by the principal quantum number as follows:

$E_n = -\frac{2\pi^2 m Z^2 e^4}{n^2 h^2}$ i.e., E_n proportional to $(1/n^2)$. The shells or energy levels are designated by capital letters as K ($n = 1$), L ($n = 2$), M ($n = 3$), N ($n = 4$) and so on.

(ii) Radius of the orbital: In Bohr's model, the position of the electron measured from the nucleus is governed by n as follows: $r_n = \frac{n^2 h^2}{4\pi^2 m Z e^2}$

(iii) Total capacity of electron in a particular shell: The total number of electrons can be accommodated in a particular shell related with principal quantum number as $2n^2$ formulae.

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

(2) Azimuthal quantum number (l):

In Sommerfeld's atomic model, the azimuthal quantum number (k) is originated from the hypothesis of elliptical locus for moving electron. But in wave mechanical model, it comes to make the function, $\Theta(\theta)$ acceptable. k and l is related by the relation $l = k-1$. The acceptable values of l are $0, 1, 2, \dots, (n-1)$. It is also called angular momentum quantum number.

Significance:

(i) Shape of the orbit or orbital: In Sommerfeld's model, the azimuthal quantum number determines the shape i.e., the ellipticity of the orbit. In the wave mechanical model, the angular part of the wave function gives l and m (magnetic quantum number) determines the shape of the orbitals.

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

l	0	1	2	3
Orbital	s	p	d	f

These names are comes from spectroscopic terms sharp, principal, diffuse and fundamental.

(iii) Number of radial nodes and nodal surfaces: The number of radial nodes of the orbital is given by $(n-l-1)$ and angular nodes given by l .

(iv) Penetrating power of the orbit or orbital: From the ellipticity of the orbit and radial probability distribution in wave mechanics, the penetrating power of the orbitals in the sequence $s > p > d > f$ for a particular principal quantum number.

(v) Orbital angular momentum: The orbital angular momentum p_l is quantized as follows:

$$\vec{l} = p_l = l(h/2\pi) \text{ (classical mechanics)}$$

$$= \sqrt{l(l+1)}(h/2\pi) \text{ (wave mechanics)}$$

(3) Magnetic quantum number: To have acceptable solutions of $\Phi(\phi)$, the magnetic quantum number (m) comes to the picture. In vector model, it appeared to explain the Zeeman effect and Stark effect. The magnetic quantum number, m have values as: $m = \pm l, \pm(l-1), \pm(l-2), \dots 0$. Therefore, for a particular value of l , it can have $(2l+1)$ values.

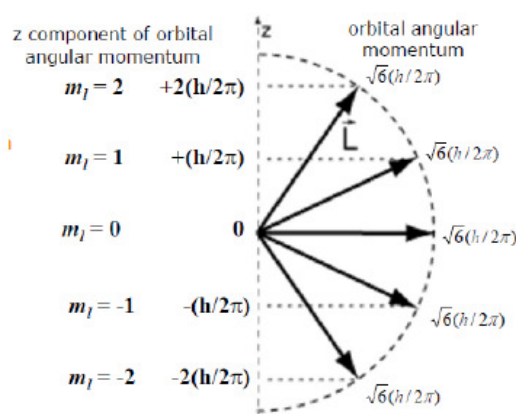
Significance:

(i) Number of sub-energy levels or orbitals:

	s-orbital ($l = 0$)	p-orbital ($l = 1$)	d-orbital ($l = 2$)	f-orbital ($l = 3$)
m	0	0, ± 1	0, $\pm 1, \pm 2$	0, $\pm 1, \pm 2, \pm 3$
	One orbital	A set of three orbital	A set of five orbital	A set of seven orbital

(ii) Shape of the orbitals: The angular part of the wave function, $\Theta_{l,m}(\theta) \times \Phi_m(\phi)$, determine the shape of the orbitals. Thus, l and m jointly determine the shape of the orbitals.

(iii) Splitting of the orbitals in presence of an external field: In absence of any external field (magnetic or electric), the orbitals generated for different values of m having a particular value of l are degenerate. For example, three p-orbital ($m = 0, \pm 1$) or five d-orbitals ($m = 0, \pm 1, \pm 2$). But, in presence of external field orbitals are splitted having different m values that explain Zeeman and Stark effect.



The acceptable values of θ (angle of \vec{l} with z-axis) for which $\vec{l} \cos\theta = m_l (h/2\pi)$. For example, for d-orbital $l = 2$, $\vec{l} \cos\theta = 2(h/2\pi)\cos\theta = m_l (h/2\pi)$ or, $m_l = 2\cos\theta$. Now, $\theta = 0$, $m_l = +2$; $\theta = 90^\circ$, $m_l = 0$; $\theta = 180^\circ$, $m_l = -2$ etc.

(4) Spin quantum number:

In Dirac's relativistic wave mechanical model, the spin quantum number appears to make the solutions acceptable. In vector model, the concept of a spinning electron was introduced by Uhlenbeck and Goudmit. It has non-integral value $\frac{1}{2}$. It actually measures the angular momentum of the electron due to its spinning motion. In magnetic field, it has only two quantized orientations giving rise to the magnetic spin quantum number (m_s) = $\pm 1/2$.

Significance:

(i) Spin angular moment: The spin angular momentum (p_s) developed due to the spinning motion of the electron around its own axis is given by:

$$\vec{S} = p_s = s(h/2\pi) \text{ (classical mechanics)}$$

$$= \sqrt{s(s+1)}(h/2\pi) \text{ (wave mechanics)}$$

(ii) Spectral selection rule: During electronic transition between the states, the selection rule, $\Delta S = 0$ where S = resultant spin quantum number, is obeyed.

Pauli Exclusion Principle:

The simplest wave of the two electron system is given by: $\Psi' = \Psi_a(1)\Psi_b(2)$ where Ψ terms represents one electron spatial wave function and, 1 and 2 represents the electrons. Now, electron can exchange its position giving two states as:

$$\Psi_I = \Psi_a(1)\Psi_b(2) \text{ and } \Psi_{II} = \Psi_a(2)\Psi_b(1)$$

Thus, the true wave function will be the linear combination of these two states.

$$\Psi_s = \frac{1}{\sqrt{2}}[\Psi_I + \Psi_{II}] = \frac{1}{\sqrt{2}}[\Psi_a(1)\Psi_b(2) + \Psi_a(2)\Psi_b(1)]$$

$$\Psi_a = \frac{1}{\sqrt{2}}[\Psi_I - \Psi_{II}] = \frac{1}{\sqrt{2}}[\Psi_a(1)\Psi_b(2) - \Psi_a(2)\Psi_b(1)] \text{ where } \frac{1}{\sqrt{2}} \text{ is the normalization constant.}$$

Ψ_s is symmetric as it does not change sign due to interchange of electron but Ψ_a is antisymmetric as it changes sign.

Now, to characterise the electron in an orbital, it is necessary to consider both orbital and spin wave function. Thus, total wave function will be: $\Psi_{\text{total}} = \Psi_{\text{orbital}} \times \Psi_{\text{spin}}$

Regarding the spin wave function, it is known that only two types of spin exist say, α and β . In two electron system, electrons can be arranged either same or opposite spin giving four possible results as follows:

$$\Psi_{\text{spin}}(\text{I}) = \alpha(1)\alpha(2) [M_s = +1]$$

$$\Psi_{\text{spin}}(\text{II}) = \beta(1)\beta(2) [M_s = -1]$$

$$\Psi_{\text{spin}}(\text{III}) = \frac{1}{\sqrt{2}}[\alpha(1)\beta(2) + \alpha(2)\beta(1)] [M_s = 0]$$

$$\Psi_{\text{spin}}(\text{IV}) = \frac{1}{\sqrt{2}}[\alpha(1)\beta(2) - \alpha(2)\beta(1)] [M_s = 0]$$

It is evident that first three functions $\Psi_{\text{spin}}(\text{I})$, $\Psi_{\text{spin}}(\text{II})$ and $\Psi_{\text{spin}}(\text{III})$ are symmetric while $\Psi_{\text{spin}}(\text{IV})$ is antisymmetric with respect to the exchange of electrons.

Therefore, there will be eight possible combination of total wave function as follows:

$\Psi_I = \Psi_s \times \Psi_{\text{spin}}(\text{I})$	(symmetric x symmetric)	} symmetric
$\Psi_{II} = \Psi_s \times \Psi_{\text{spin}}(\text{II})$	(symmetric x symmetric)	
$\Psi_{III} = \Psi_s \times \Psi_{\text{spin}}(\text{III})$	(symmetric x symmetric)	
$\Psi_{IV} = \Psi_s \times \Psi_{\text{spin}}(\text{IV})$	(symmetric x antisymmetric)	} antisymmetric
$\Psi_V = \Psi_a \times \Psi_{\text{spin}}(\text{I})$	(antisymmetric x symmetric)	
$\Psi_{VI} = \Psi_a \times \Psi_{\text{spin}}(\text{II})$	(antisymmetric x symmetric)	
$\Psi_{VII} = \Psi_a \times \Psi_{\text{spin}}(\text{III})$	(antisymmetric x symmetric)	
$\Psi_{VIII} = \Psi_a \times \Psi_{\text{spin}}(\text{IV})$	(antisymmetric x antisymmetric)	} symmetric

It is experimentally established that the total wave function for a system of two-electron must be antisymmetric with respect to the simultaneous exchange of spatial coordinates and spin between the electrons. Hence, out of eight possibilities, only four antisymmetric wave functions.

Pauli Exclusion Principle: This principle states that the total wave function ($\Psi_{\text{spin}} \times \Psi_{\text{spatial}}$) of a two electron system must be antisymmetric with respect to interchange of the positions of the two electrons.

(This antisymmetric criterion is followed by all the particles which are having a half-integral spin as electrons, protons, neutrons. These particles are called Fermions. Another kind of particles called Bosons which have integral spin as photon. These particles follow symmetric criterion)

Familiar form of Pauli Exclusion Principle: No two electrons in a given system can have all the four quantum numbers identical.

Say, $1s$ orbital of He atom ($1s^2$). Thus, the two electrons have same n , l and m values. The allowed four antisymmetric total wave functions are given as:

$$\Psi_{IV} = \frac{1}{\sqrt{2}}[\Psi_{1s}(1)\Psi_{1s}(2) + \Psi_{1s}(2)\Psi_{1s}(1)] \times \frac{1}{\sqrt{2}}[\alpha(1)\beta(2) - \alpha(2)\beta(1)]$$

$$\Psi_V = \frac{1}{\sqrt{2}}[\Psi_{1s}(1)\Psi_{1s}(2) - \Psi_{1s}(2)\Psi_{1s}(1)] \times \alpha(1)\alpha(2)$$

$$\Psi_{VI} = \frac{1}{\sqrt{2}}[\Psi_{1s}(1)\Psi_{1s}(2) - \Psi_{1s}(2)\Psi_{1s}(1)] \times \beta(1)\beta(2)$$

$$\Psi_{VII} = \frac{1}{\sqrt{2}}[\Psi_{1s}(1)\Psi_{1s}(2) - \Psi_{1s}(2)\Psi_{1s}(1)] \times \frac{1}{\sqrt{2}}[\alpha(1)\beta(2) + \alpha(2)\beta(1)]$$

Here, Ψ_V , Ψ_{VI} and Ψ_{VII} are zero, only Ψ_{IV} is acceptable in which the electrons are in different spin state. Thus, if the electrons have the same orbital wave functions i.e., same n , l and m values, they must have the opposite spin.

shell	n	<i>l</i>	<i>m_l</i>	<i>m_s</i>	Set of quantum no.	Sub shell	Total electron	
K	1	0	0	+1/2, -1/2	(1,0,0,+1/2) & (1,0,0,-1/2)	1s ²	2	
L	2	0	0	+1/2, -1/2	(2,0,0,+1/2) & (2,0,0,-1/2)	2s ²	8	
		1	+1	+1/2, -1/2	(2,1,+1,+1/2) & (2,1,+1,-1/2)	2p ⁶		
			0	+1/2, -1/2	(2,1,0,+1/2) & (2,1,0,-1/2)			
			-1	+1/2, -1/2	(2,1,-1,+1/2) & (2,1,-1,-1/2)			
M	3	0	0	+1/2, -1/2	(3,0,0,+1/2) & (3,0,0,-1/2)	3s ²	18	
			1	+1	+1/2, -1/2	(3,1,+1,+1/2) & (3,1,+1,-1/2)		3p ⁶
				0	+1/2, -1/2	(3,1,0,+1/2) & (3,1,0,-1/2)		
				-1	+1/2, -1/2	(3,1,-1,+1/2) & (3,1,-1,-1/2)		
		2	+2	+1/2, -1/2	(3,2,+2,+1/2) & (3,2,+2,-1/2)	3d ¹⁰		
			+1	+1/2, -1/2	(3,2,+1,+1/2) & (3,2,+1,-1/2)			
			0	+1/2, -1/2	(3,2,0,+1/2) & (3,2,0,-1/2)			
			-1	+1/2, -1/2	(3,2,-1,+1/2) & (3,2,-1,-1/2)			
			-2	+1/2, -1/2	(3,2,-2,+1/2) & (3,2,-2,-1/2)			
L	4	0	0	+1/2, -1/2	(4,0,0,+1/2) & (4,0,0,-1/2)	4s ²	32	
		1	+1	+1/2, -1/2	(4,1,+1,+1/2) & (4,1,+1,-1/2)	4p ⁶		
			0	+1/2, -1/2	(4,1,0,+1/2) & (4,1,0,-1/2)			
			-1	+1/2, -1/2	(4,1,-1,+1/2) & (4,1,-1,-1/2)			
		2	+2	+1/2, -1/2	(4,2,+2,+1/2) & (4,2,+2,-1/2)	4d ¹⁰		
			+1	+1/2, -1/2	(4,2,+1,+1/2) & (4,2,+1,-1/2)			
			0	+1/2, -1/2	(4,2,0,+1/2) & (4,2,0,-1/2)			
			-1	+1/2, -1/2	(4,2,-1,+1/2) & (4,2,-1,-1/2)			
			-2	+1/2, -1/2	(4,2,-2,+1/2) & (4,2,-2,-1/2)			
		3	+3	+1/2, -1/2	(4,3,+3,+1/2) & (4,3,+3,-1/2)	4f ¹⁴		
			+2	+1/2, -1/2	(4,3,+2,+1/2) & (4,3,+2,-1/2)			
			+1	+1/2, -1/2	(4,3,+1,+1/2) & (4,3,+1,-1/2)			
			0	+1/2, -1/2	(4,3,0,+1/2) & (4,3,0,-1/2)			
			-1	+1/2, -1/2	(4,3,-1,+1/2) & (4,3,-1,-1/2)			
			-2	+1/2, -1/2	(4,3,-2,+1/2) & (4,3,-2,-1/2)			
			-3	+1/2, -1/2	(4,3,-3,+1/2) & (4,3,-3,-1/2)			

Aufbau Principle: (Building up principle)

The orbital of lowest energy will be occupied by the electron first then the orbitals of higher energy will start to accommodate the electrons.

The energy of the orbital increases with increasing value of principal quantum number (n). Again, for a particular value of n , the energy sequence of the orbital is $s < p < d < f$. This order can be explained from the penetrating power of different orbital. For a particular value of n , as the value of l decreases, the probability of existence of the corresponding electron at a closer distance towards the nucleus increases experiencing greater attraction by the nucleus and consequently energy decreases with decrease of l value.

$(n + l)$ rule:

(a) The energy of the orbitals increases with increasing value of $(n + l)$.

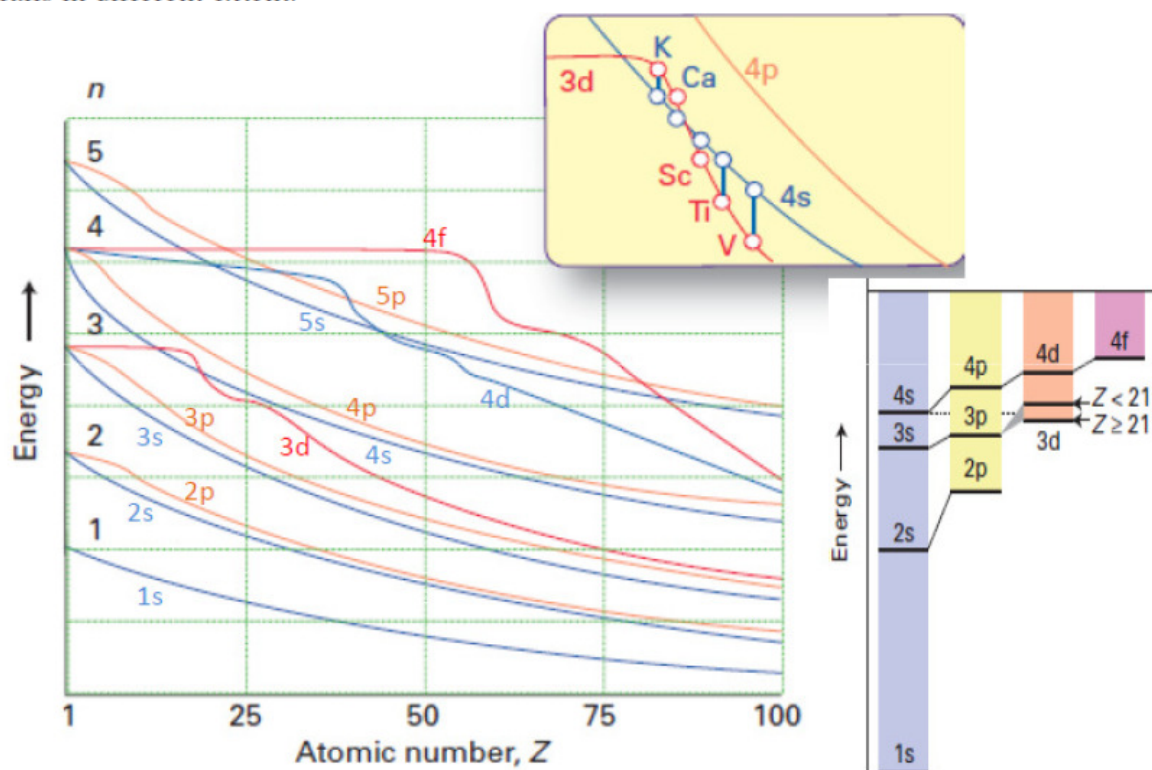
(b) For same value of $(n + l)$, energy increases with increase of n .

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

$(n + l)$: $1 < 2 < 3 \sim 3 < 4 \sim 4 < 5 \sim 5 \sim 5 < 6 \sim 6 < 7 \sim 7 \sim 7 \sim 7$

This generalization is valid only for the one electron wave function for each separate orbital.

It is seen that this energy sequence is strictly followed by the lighter elements. But, for heavier elements, with the increase of effective nuclear charge, the sequence becomes modified. Generally, with the increase of effective nuclear charge, the energy of the orbitals falls in different extent.



Exception of $(n + l)$ rule:

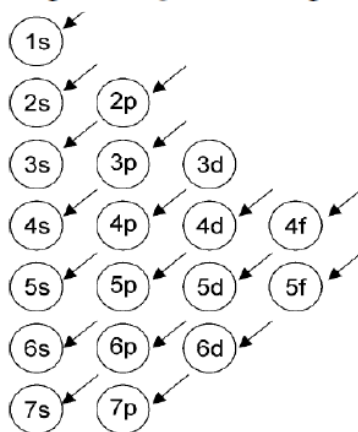
(i) Anomaly for elements, $Z = 57-58$: Ba ($Z = 56$), configuration is $[\text{Xe}]6s^2$. La ($Z = 57$) should have configuration $[\text{Xe}]4f^1 6s^2$, but it is $[\text{Xe}]4f^0 5d^1 6s^2$.

(ii) Anomaly in energy order of 5f and 6d in the range of $Z = 90$: Ra ($z = 88$), configuration is $[\text{Rn}]7s^2$. Ac ($Z = 89$) should have configuration $[\text{Rn}]5f^1 6d^0 7s^2$, but it is $[\text{Rn}]5f^0 6d^1 7s^2$.

(iii) $(n-1)d$ level vs. ns level and $(n-2)f$ level vs. $(n-1)d$ level:

According to $(n + l)$ rule, for the transition elements the $(n-1)d$ orbitals lies above the ns orbital, but with the filling of $(n-1)d$ orbital, its energy become close to ns level and also lower down with increase of effective nuclear charge.

(iv) Half filled and full filled level: The aufbau principle is not obeyed for the system where half filled or full filled electronic configuration produces higher stability.



Exchange energy (E_{ex})

Exchange energy is a quantum mechanical phenomenon which tells that the electrons in an orbital (same n and l values) with parallel spin can exchange their positions. More correctly, the wave functions associated with them are exchangeable. The configuration having higher exchange energy is more stable compared to other configuration with equal number of electron. It is measured by the number of sets of two electrons.

$$N = {}^x C_2 = \frac{x!}{2!(x-2)!} = \frac{x(x-1)}{2} \text{ and } E_{ex} = K \left[\frac{x(x-1)}{2} \right]$$

$$x = 1 \quad 2 \quad 3 \quad 4 \quad 5 \quad 6$$

$$E_{ex} (K) = 0 \quad 1 \quad 3 \quad 6 \quad 10 \quad 15$$

configuration	Exchange energy	configuration	Exchange energy
p^2	${}^2C_2 = 1K$	d^4	${}^4C_2 = 6K$
p^3	${}^3C_2 = 3K$	d^5	${}^5C_2 = 10K$
p^4	${}^3C_2 + {}^1C_2 = (3 + 0)K = 3K$	d^6	${}^5C_2 + {}^1C_2 = (10 + 0)K = 10K$
p^5	${}^3C_2 + {}^2C_2 = (3 + 1)K = 4K$	d^7	${}^5C_2 + {}^2C_2 = (10 + 1)K = 11K$
p^6	${}^3C_2 + {}^3C_2 = (3 + 3)K = 6K$	d^8	${}^5C_2 + {}^3C_2 = (10 + 2)K = 12K$

Examples of half filled and full filled configurations:

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

Hund's rule of maximum multiplicity:

(I) Rule of spin multiplicity: Ground state will be determined by the highest spin multiplicity, $(2S + 1)$ that means, in degenerate orbitals electrons remains unpaired with parallel spin as long as possible. Here, $S = \Sigma m_s$.

m_l	+1	0	-1
	↑	↑	
(i)			

m_l	+1	0	-1
	↑↓		
(ii)			

m_l	+1	0	-1
	↑	↓	
(iii)			

m_l	+1	0	-1
	↑		↓
(iv)			

m_l	+1	0	-1
	↑		↑
(v)			

According to this rule, only (i) and (v) are allowed for p^2 configuration.

(II) Rule of orbital multiplicity: With considering maximum spin multiplicity, the ground state will be determined by highest possible orbital multiplicity $(2L + 1)$ i.e., the highest possible value of L . Generally highest $M_L (\Sigma m_l)$ is calculated as M_L ranges from $+L$ to $-L$.

Now, only arrangement (i) is allowed.

(III) Rule of J: With considering 1st and 2nd rule, ground state will be determined by J values where $J = |L + S|$ to $|L - S|$. For less than half filled ground state will have lowest J value and for more than half filled, the ground state will have highest J values.

Derivation of ground state term symbol:

Term symbol represented as:

$$(2S + 1)_L^J$$

L value	0	1	2	3	4	5	6
symbol	S	P	D	F	G	H	I

s^1 configuration:

m_l	0
	↑

$S = \Sigma m_s = 1/2$; Spin multiplicity $(2S+1) = [(2 \times 1/2) + 1] = 2$

$L = \Sigma m_l = 0$

$J = |L + S|$ to $|L - S|$

$J = (0 + 1/2)$ to $(0 - 1/2) = 1/2$.

Therefore, Term symbol for s^1 will be $^2S_{1/2}$.

s^2 configuration:

m_l	0
	↑↓

$S = \Sigma m_s = 1/2 - 1/2 = 0$. Spin multiplicity $(2S+1) = [(2 \times 0) + 1] = 1$

$L = \Sigma m_l = 0$

$J = |L + S|$ to $|L - S|$

$J = (0 + 0)$ to $(0 - 0) = 0$.

Therefore, Term symbol for s^2 will be 1S_0 .

p² configuration:

m_l	+1	0	-1
	↑	↑	

$S = \Sigma m_s = \frac{1}{2} + \frac{1}{2} = 1$. Spin multiplicity $(2S+1) = [(2 \times 1) + 1] = 3$

$L = \Sigma m_l = 1 + 0 = 1$

$J = |L + S|$ to $|L - S|$

$J = (1 + 1)$ to $(1 - 1) = 2$ to $0 = 2, 1, 0$. Since it is less than half filled J will be 0

Therefore, Term symbol for p² will be ³P₀.

d⁶ configuration:

m_l	+2	+1	0	-1	-2
	↑↓	↑	↑	↑	↑

$S = \Sigma m_s = 4 \times \frac{1}{2} = 2$. Spin multiplicity $(2S+1) = [(2 \times 2) + 1] = 5$

$L = \Sigma m_l = (2 \times 2) + 1 + 0 - 1 - 2 = 2$

$J = |L + S|$ to $|L - S|$

$J = (2 + 2)$ to $(2 - 2) = 4$ to $0 = 4, 3, 2, 1, 0$. Since it is more than half filled J will be 4.

Therefore, Term symbol for d⁶ will be ⁵D₄.

f⁹ configuration:

m_l	+3	+2	+1	0	-1	-2	-3
	↑↓	↑↓	↑	↑	↑	↑	↑

$S = \Sigma m_s = 5 \times \frac{1}{2} = 5/2$. Spin multiplicity $(2S+1) = [(2 \times 5/2) + 1] = 6$

$L = \Sigma m_l = (2 \times 3) + (2 \times 2) + 1 + 0 - 1 - 2 - 3 = 5$

$J = |L + S|$ to $|L - S|$

$J = (5 + 5/2)$ to $(5 - 5/2) = 15/2$ to $5/2$. Since it is more than half filled J will be 15/2.

Therefore, Term symbol for d⁶ will be ⁶H_{15/2}.

²⁴Cr: [Ar] 4s¹ 3d⁵ configuration:

	m_l	0			m_l	+2	+1	0	-1	-2	
		↑				↑	↑	↑	↑	↑	

$S = \Sigma m_s = 6 \times \frac{1}{2} = 3$. Spin multiplicity $(2S+1) = [(2 \times 3) + 1] = 7$

$L = \Sigma m_l = 0 + 0 = 0$

$J = |L + S|$ to $|L - S|$

$J = (3 + 0)$ to $(3 - 0) = 3$.

Therefore, Term symbol of Cr will be ⁷S₃.

²³V: [Ar] 4s² 3d³ configuration:

	m_l	0			m_l	+2	+1	0	-1	-2	
		↑↓				↑	↑	↑			

$S = \Sigma m_s = 3 \times \frac{1}{2} = 3/2$. Spin multiplicity $(2S+1) = [(2 \times 3/2) + 1] = 4$

$L = \Sigma m_l = 2 + 1 = 3$

$J = |L + S|$ to $|L - S|$

$J = (3 + 3/2)$ to $(3 - 3/2) = 9/2$ to $3/2$. Since it is less than half filled J will be 3/2.

Therefore, Term symbol of Cr will be ⁴F_{3/2}.

Config.	m l values							$S = \Sigma m_s$	$2S + 1$	$L = \Sigma m_l$	J	Term symbol
	+3	+2	+1	0	-1	-2	-3					
p ¹			↑					1/2	2	1	1/2	² P _{1/2}
p ²			↑	↑				1	3	1	0	³ P ₀
p ³			↑	↑	↑			3/2	4	0	3/2	⁴ S _{3/2}
p ⁴			↑↓	↑	↑			1	2	1	2	² P ₂
p ⁵			↑↓	↑↓	↑			1/2	2	1	3/2	² P _{3/2}
p ⁶			↑↓	↑↓	↑↓			0	1	0	0	¹ S ₀
d ¹		↑						1/2	2	2	3/2	² D _{3/2}
d ²		↑	↑					1	3	3	2	³ F ₂
d ³		↑	↑	↑				3/2	4	3	3/2	⁴ F _{3/2}
d ⁴		↑	↑	↑	↑			2	5	2	0	⁵ D ₀
d ⁵		↑	↑	↑	↑	↑		5/2	6	0	5/2	⁶ S _{5/2}
d ⁶		↑↓	↑	↑	↑	↑		2	5	2	4	⁵ D ₄
d ⁷		↑↓	↑↓	↑	↑	↑		3/2	4	3	9/2	⁴ F _{9/2}
d ⁸		↑↓	↑↓	↑↓	↑	↑		1	3	3	4	³ F ₄
d ⁹		↑↓	↑↓	↑↓	↑↓	↑		1/2	2	2	5/2	² D _{5/2}
d ¹⁰		↑↓	↑↓	↑↓	↑↓	↑↓		0	1	0	0	¹ S ₀
f ¹	↑							1/2	2	3	5/2	² F _{5/2}
f ²	↑	↑						1	3	5	4	³ H ₄
f ³	↑	↑	↑					3/2	4	6	9/2	⁴ I _{9/2}
f ⁴	↑	↑	↑	↑				2	5	6	4	⁵ I ₄
f ⁵	↑	↑	↑	↑	↑			5/2	6	5	5/2	⁶ H _{5/2}
f ⁶	↑	↑	↑	↑	↑	↑		3	7	3	0	⁷ F ₀
f ⁷	↑	↑	↑	↑	↑	↑	↑	7/2	8	0	7/2	⁸ S _{7/2}
f ⁸	↑↓	↑	↑	↑	↑	↑	↑	3	7	3	6	⁷ F ₆
f ⁹	↑↓	↑↓	↑	↑	↑	↑	↑	5/2	6	5	15/2	⁶ H _{15/2}
f ¹⁰	↑↓	↑↓	↑↓	↑	↑	↑	↑	2	5	6	8	⁵ I ₈
f ¹¹	↑↓	↑↓	↑↓	↑↓	↑	↑	↑	3/2	4	6	15/2	⁴ I _{15/2}
f ¹²	↑↓	↑↓	↑↓	↑↓	↑↓	↑	↑	1	3	5	6	³ H ₆
f ¹³	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑	1/2	2	3	7/2	² F _{7/2}
f ¹⁴	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	0	1	0	0	¹ S ₀