Atomic Structure

Topics:

1. **Bohr's model and its limitations**
2. **The dual nature of matter and light, de Broglie's relationship**
3. **Heisenberg uncertainty principle**

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4. **Schrödinger wave equation (elementary idea only)**
5. **Concept of orbitals, quantum numbers, shapes of s, p and d orbitals**
6. **Rules for filling electrons in orbitals: Aufbau principle, Pauli exclusion principle and Hund's rule**
7. **Exchange energy, electronic configuration of atom, stability of half-filled, completely filled orbitals**

Bohr's model for hydrogen atom (H-like Atoms)

Postulates:

- 1. ***The electrons in an atom revolve around the nucleus only in certain selected circular paths which have a fixed value of radius and energy*. These paths are called orbits.**
- ***2. The energy of an electron in an orbit does not change with time, these orbits are known as stationary orbit.***
- ***3. Only those orbits are permitted in which the angular momentum of the electron is a whole number multiple of $h/2\pi$ (where h is Planck's constant)***

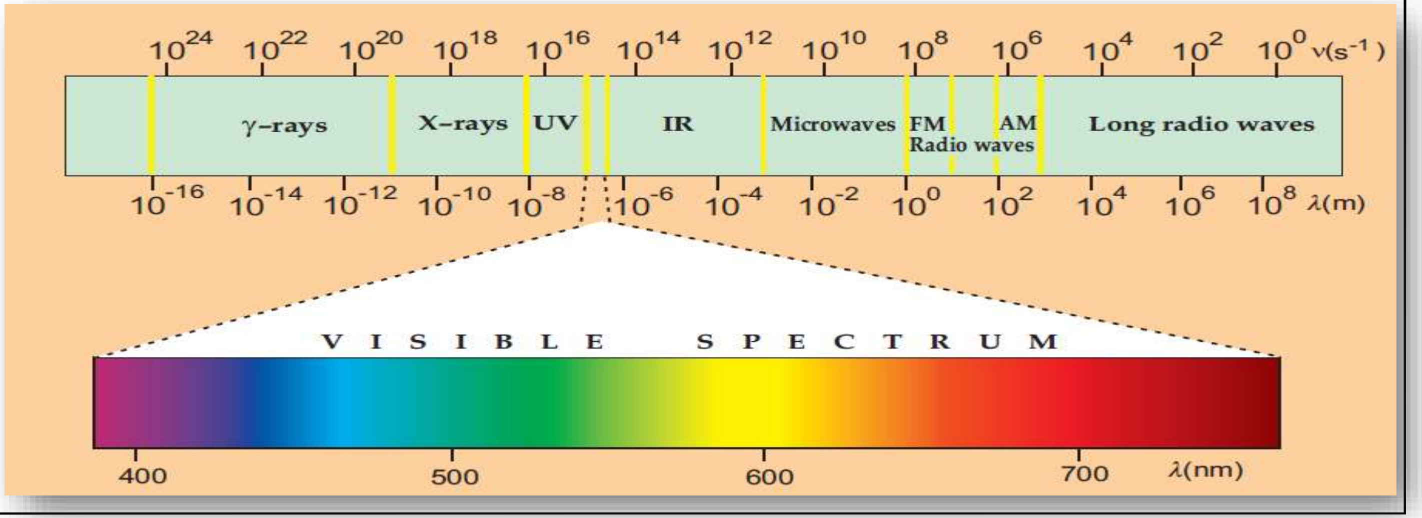
  i.e., $mvr = nh/2\pi$ **where** $n = 1, 2, 3 \ldots$

- ***4. The energy is emitted or absorbed only when the electrons jump from one energy level to another. the difference ($E_2 - E_1$) may be expressed in terms of energy of photon as***

$$\Delta E = E_2 - E_1 = h\nu$$

Successes of Bohr's Model

- 1. Bohr's atomic model explained the stability of an atom.
- 2. Bohr's concept of atom explained successfully the atomic spectrum of hydrogen atom (Lyman, Balmer, Paschen, Brackett, Pfund series).
- 3. Bohr's theory helped in calculating the energy of the electron in a particular orbit of hydrogen atom.



Limitations of Bohr's Atomic Theory

- **1.** ***Bohr's model of an atom could not account for the finer details (doublet, two closely spaced lines) of the hydrogen spectrum observed using sophisticated spectroscopic techniques.***
- **2.** ***Bohr's model of an atom could not explain the line spectra of atoms containing more than one electron called multielectron atoms.***
- **3.** ***It failed to explain the effect of magnetic field on the spectra of atoms or ions (known as*** **Zeeman effect).**
- **4.** ***Bohr's theory also could not explain the effect of electric field (known as Stark effect) on the spectra of atoms.***
- **5.** ***Bohr's theory does not provide any clue to explain the shapes of molecules arising out of the directional bonding between atoms.***
- **6. The new principles namely *dual nature of matter* and *uncertainty principle states that the* path of the motion of the electron cannot be well-defined. Thus, these principles overruled the Bohr's idea of well defined circular paths.**

Radius of H-atom & velocity of an electron

- **Bohr radius**

We can also calculate the radius of each circular orbit. According to Bohr's model, radius of n^{th} orbit is

$$r_n = n^2h^2/(4\pi^2 me^2 Z)$$

$r_n = a_0 n^2$ [For H atom (Z = 1)], where a_0 = 52.9 pm (or **0.0529 nm** or **0.529 Å**). * **{in cgs unit}**

Similarly, **for H like ions**, $r_n = a_0 (n^2/Z)$ **[in SI unit, $r_n = n^2h^2/(4\pi^2 me^2 kZ)$; $k = 1/4\pi\varepsilon_0$]**

- **Velocity of electron in any orbit**

The velocity of electron in any orbit is given by the expression $v = 2\pi e^2 Z/nh$

or, $v = (2.19 \times 10^6) Z/n \quad mS^{-1}$

- The velocities of the electrons in different orbits may be given as :

$$v_n = v_0 \times (Z/n)$$

- where v_0 is the velocity of the electron in the first orbit of hydrogen atom and $v_0 = 2.19 \times 10^6\ ms^{-1}$.

No. of revolutions $=(2\pi mvZe^2/n^2h^2)$ (*velocity/ circumference of orbit*)

Energy of an electron in nth orbit

- Energy of an electron is given by

$$E_n = -(2\pi^2 m Z^2 e^4/n^2 h^2)$$

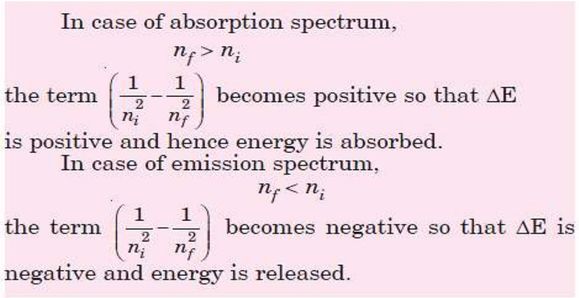
$$or,\ E_n = -(2\pi^2 m e^4/ n^2 h^2) \text{ x } (Z^2) \qquad [Z= 1]$$

$$Now,\ E_{n_2} - E_{n_1} = -(2\pi^2 m e^4/n_2^2 h^2) - \{-(2\pi^2 m e^4/n_1^2 h^2)\} \qquad [\Delta E= h\nu = hc/\lambda\ ]$$

$$\Delta E= h\nu = hc/\lambda = (2\pi^2 m e^4/h^2)\ (\ 1/n_1^2 - 1/n_2^2) \qquad \leftarrow[\text{ I.P. of H atom} = 13.54 \text{ eV; by this equation}]$$

$$1/\lambda = (2\pi^2 m e^4/ch^3)\ (\ 1/n_1^2 - 1/n_2^2) \qquad [\ 1 \text{ erg} = 6.24 \text{ x } 10^{11} \text{ eV}];(1 \text{ eV} = 1.6022 \times 10^{-19}\text{J})$$

$$1/\lambda = R(\ 1/n_1^2 - 1/n_2^2) \qquad \text{where, Rydberg constant, } R = 109677 \text{ cm}^{-1} \text{ (in cgs)}$$



In case of absorption spectrum,

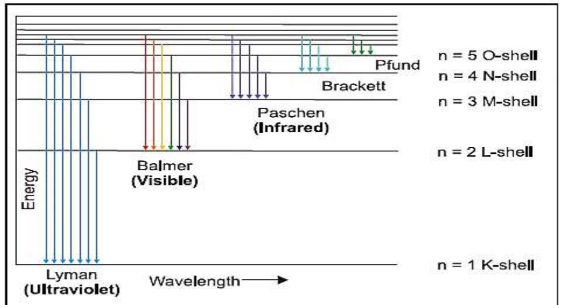
$$n_f > n_i$$

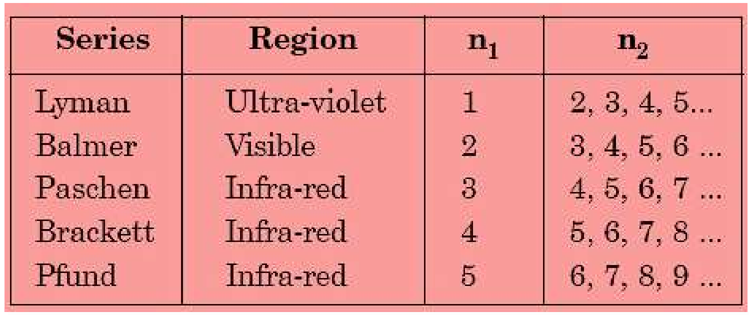
the term $\left(\frac{1}{n_i^2} - \frac{1}{n_f^2}\right)$ becomes positive so that ΔE is positive and hence energy is absorbed.

In case of emission spectrum,

$$n_f < n_i$$

the term $\left(\frac{1}{n_i^2} - \frac{1}{n_f^2}\right)$ becomes negative so that ΔE is negative and energy is released.





Series	Region	n_1	n_2
Lyman	Ultra-violet	1	2, 3, 4, 5...
Balmer	Visible	2	3, 4, 5, 6 ...
Paschen	Infra-red	3	4, 5, 6, 7 ...
Brackett	Infra-red	4	5, 6, 7, 8 ...
Pfund	Infra-red	5	6, 7, 8, 9 ...

Dual Nature of Matter

• de Broglie Wave Equation:

According to de Broglie, e or electron like particles have dual nature like light, one is particle nature and another is wave nature. So, the mass of e and wavelength of e-wave must be associated to each other.

The wavelength of e-wave is inversely proportional to its momentum.

$$\text{i.e., } \lambda \propto 1/mv \quad [\, E= mc^2;\ E= h\nu;\ \nu= c/\lambda]$$

$$\lambda = 1/mv \quad [\text{ note: } \lambda= 2\pi a_0;\ a_0 \text{ is Bohr radius}]$$

• Heisenberg’s Uncertainty Principle:

*The **position** and **momentum** of a moving particle like electron can not be simultaneously determine accurately. According to* Heisenberg’s,

$$\Delta x \times m(\Delta v) \geq h/4\pi \quad [\Delta p = m\Delta v]$$

$$\text{or } \Delta x \times \Delta v \geq h/4\pi m \quad [\text{note: } \Delta E \times \Delta T \geq h/4\pi \text{ ; T= time and E= energy}]$$

Schrödinger wave equation (elementary idea)

The **Schrödinger wave equation** is,

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

where ψ is the amplitude of the wave, x, y and z are the coordinates of the position of electron, E is the total energy of the electron, V is the potential energy, m is the mass of the electron and h is the Planck's constant. $\delta^2\psi/\delta x^2$ represents second differential derivative of ψ w.r.t. x.

- ***ψ Indicates the probability of finding electron around the nucleus in space. But ψ^2 indicates the maximum probability of finding electron around the nucleus in space.***
- ***Characteristics of ψ***

  a) ψ must be single valued. b) ψ must be continuous. c) ψ must be finite. d) ψ must be normalised.

Concept of atomic orbital

- The solution of Schrodinger wave equation led to the concept of ***most probable regions*** in place of well-defined circular paths proposed by Bohr.
- Definition: ***An orbital*** may be defined ***as a region in space around the nucleus where the probability of finding the electron is maximum.***

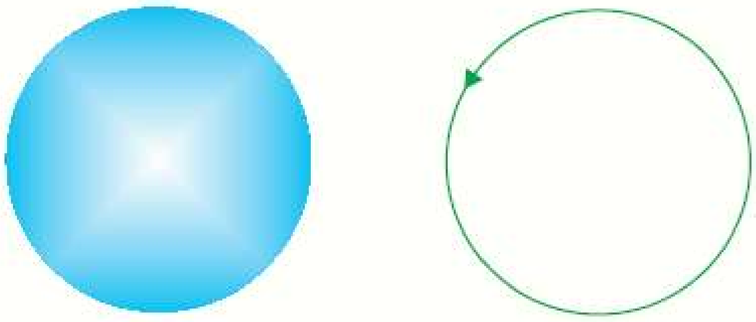
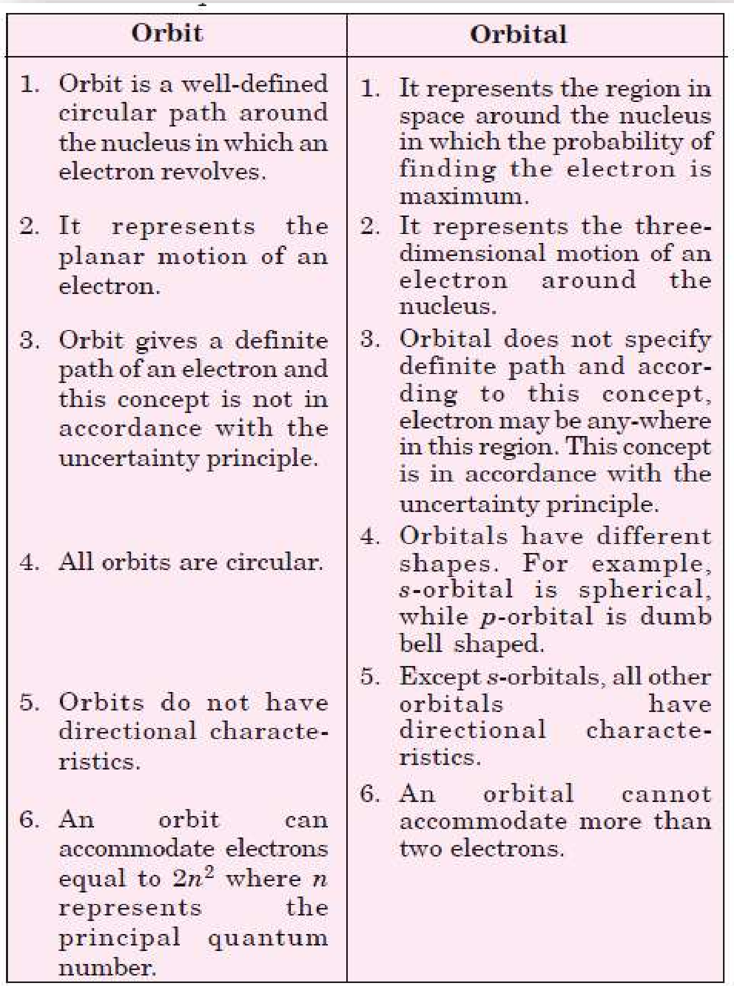

(a) Orbital (b) Orbit

Fig. 29. (*a*) Electron cloud representation of an orbital (*b*) Bohr's orbit.



Orbit	Orbital
1. Orbit is a well-defined circular path around the nucleus in which an electron revolves.	1. It represents the region in space around the nucleus in which the probability of finding the electron is maximum.
2. It represents the planar motion of an electron.	2. It represents the three-dimensional motion of an electron around the nucleus.
3. Orbit gives a definite path of an electron and this concept is not in accordance with the uncertainty principle.	3. Orbital does not specify definite path and according to this concept, electron may be any-where in this region. This concept is in accordance with the uncertainty principle.
4. All orbits are circular.	4. Orbitals have different shapes. For example, *s*-orbital is spherical, while *p*-orbital is dumb bell shaped.
5. Orbits do not have directional characteristics.	5. Except *s*-orbitals, all other orbitals have directional characteristics.
6. An orbit can accommodate electrons equal to $2n^2$ where n represents the principal quantum number.	6. An orbital cannot accommodate more than two electrons.

Quantum Numbers

- *To describe each electron in an atom in different orbitals, we need a set of four quantum numbers- n, l, m_l and m_s . These are discussed below*

- **1. Principal quantum number (n).** *This quantum number determines the main energy shell or level in which the electron is present. It is denoted by n. It can have whole number values starting from 1 such as*

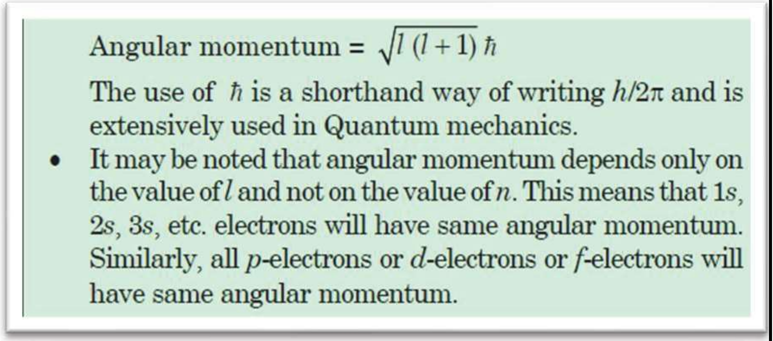
$$n = 1, 2, 3, 4 ....$$

- *This quantum number also identifies as* ***shell.*** *The shell with n = 1 is called the first shell. The shell with n = 2 is called the second shell and so on. The various shells are also called K, L, M, N.*

- **2. Azimuthal quantum number (l).** *This quantum number determines the angular momentum of the electron (and also known as* ***orbital angular momentum*** *or* ***subsidiary quantum number).***

- *The value of l gives the* ***subshell*** *or* ***sublevel*** *in a given principal energy shell to which an electron belongs. It can have positive integer values ranging from zero to (n –1) where n is the principal quantum number. That is,*

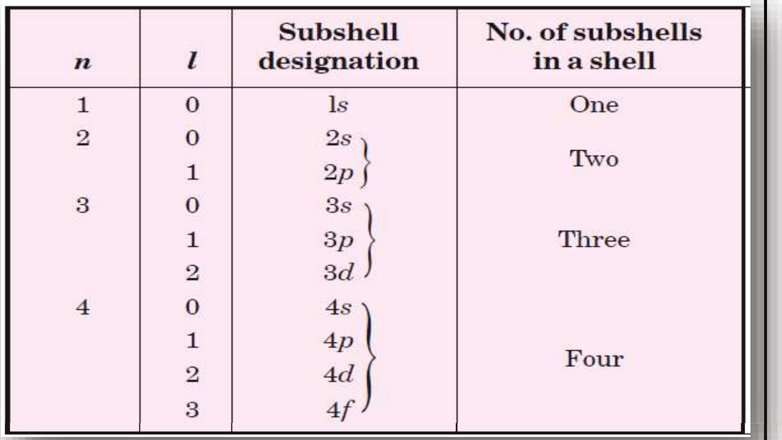
$$l = 0, 1, 2, 3 ... (n -1)$$



Angular momentum = $\sqrt{l\,(l+1)}\,\hbar$

The use of $\hbar$ is a shorthand way of writing $h/2\pi$ and is extensively used in Quantum mechanics.

- It may be noted that angular momentum depends only on the value of l and not on the value of n. This means that 1*s*, 2*s*, 3*s*, etc. electrons will have same angular momentum. Similarly, all *p*-electrons or *d*-electrons or *f*-electrons will have same angular momentum.



n	*l*	Subshell designation	No. of subshells in a shell
1	0	1s	One
2	0	2*s*	Two
	1	2*p*	
3	0	3*s*	Three
	1	3*p*	
	2	3*d*	
4	0	4*s*	Four
	1	4*p*	
	2	4*d*	
	3	4*f*	

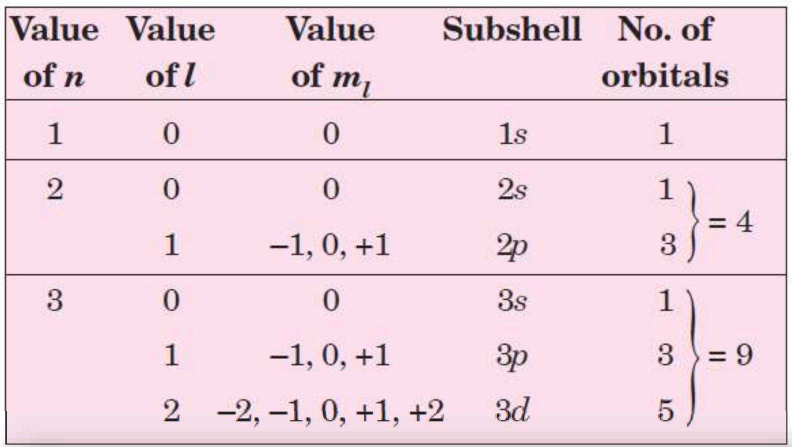
Subshell	*s*	*p*	*d*	*f*
No. of orbitals	1	3	5	7

- ***3. Magnetic quantum number (m_l).*** *We know that the movement of electrical charge is always associated with magnetic field. Since the revolving electron possesses angular momentum, it will give rise to a very small magnetic field which will interact with the external magnetic field of the earth. Under the influence of external magnetic field, the electrons in a given subshell orient themselves in certain preferred regions of space around the nucleus. These are called* ***orbitals.*** *Thus, this quantum number gives the number of orbitals in a given subshell. The allowed values of m_l depends upon the value of l. For a given value of l, m can have values – l through 0 to + l. That is*

$$m_l = -l \,.....0.....\, +l \;;\; [\, m = (2l + 1)\,]$$

- ***4. Spin quantum number(m_s).*** *It is observed that the electron in an atom is not only revolving around the nucleus but is also spinning around its own axis.* The *spin quantum number values are* ***:+ ½ or – ½.***

$$\text{Spin angular momentum} = \sqrt{s(s+1)}\,\frac{h}{2\pi}$$



Value of n	Value of l	Value of m_l	Subshell	No. of orbitals
1	0	0	1s	1
2	0	0	2s	1 } = 4
	1	−1, 0, +1	2p	3
3	0	0	3s	1
	1	−1, 0, +1	3p	3 } = 9
	2	−2, −1, 0, +1, +2	3d	5

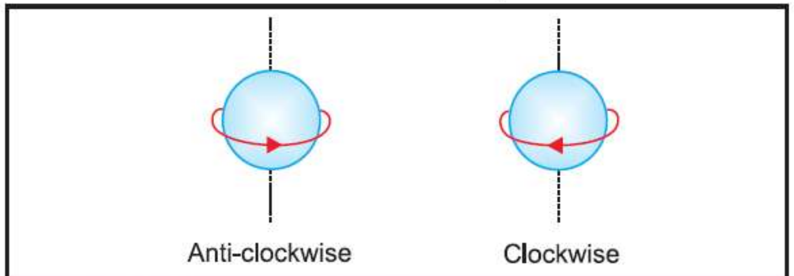
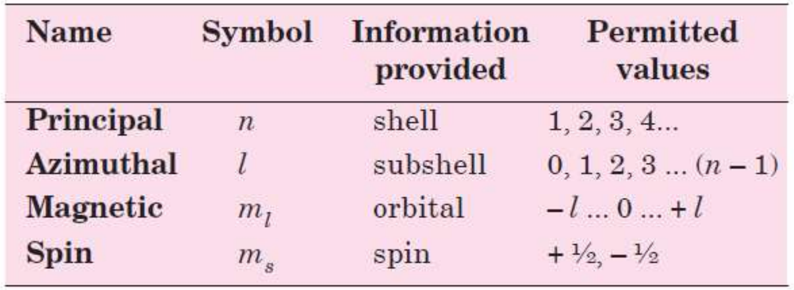


Fig. 30. Two possible orientations of the spin of an electron $m_s = +½$ and $m_s = −½$



Name	Symbol	Information provided	Permitted values
Principal	n	shell	1, 2, 3, 4...
Azimuthal	l	subshell	0, 1, 2, 3 ... $(n-1)$
Magnetic	m_l	orbital	$-l$ ... 0 ... $+l$
Spin	m_s	spin	+ ½, − ½

Shapes of atomic orbitals or boundary surface diagrams

- **Boundary surface diagrams or orbitals:** *The most **probable regions** where finding of electron is maximum (~ 90—95%) are called boundary surface diagrams or **orbitals.***

- **Radial Wave Functions:** *The shapes of orbitals are obtained from the variation of wave function* ***Ψ*** *as a function of* ***r*** *(distance from the nucleus). This is also called radial dependence or **radial wave function.***

- *It has been found that **ns orbitals have (n – 1) nodes**. Similarly, **np orbitals have (n – 2) nodes and so on.** For example, the radial wave function for 2p-orbital has no node as shown in Fig. 32.*

- **Probability Density (Ψ^2) Graphs:** *The plots of* ψ^2 *against r for 1s-, 2s- and 2p orbitals are shown in Figure ahead. These diagrams look similar to Fig.32 except that these become positive throughout. These graphs are called **probability density graphs.***

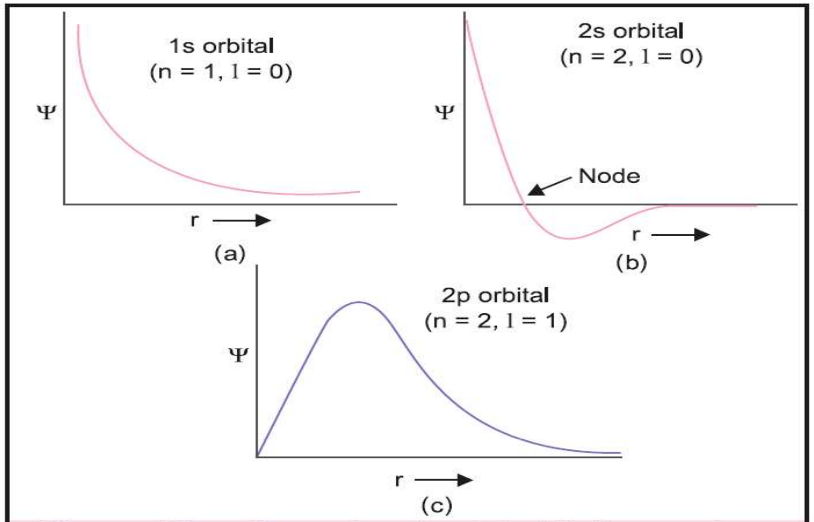
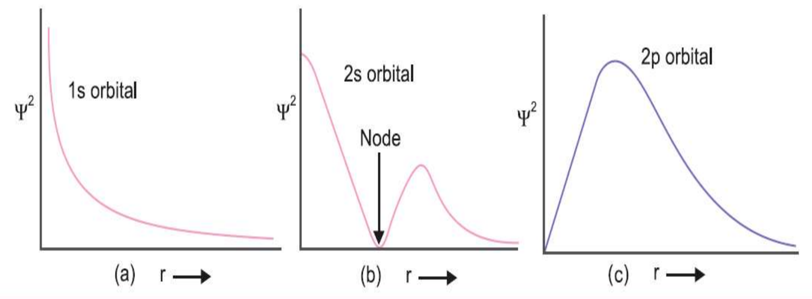


Fig. 32. Plots of wave function (Ψ) with distance from the nucleus for (*a*) 1*s*-orbital (*b*) 2*s*-orbital (*c*) 2*p*-orbital



Shapes of Orbitals

- **Shapes of *s*-orbitals:** *s-orbitals are non-directional and spherically symmetrical. This means that the probability of finding the electron is same in all directions at a particular distance from the nucleus.*

- **Shapes of *p*-orbitals:** *For p-orbitals (l = 1), there are three possible orientations corresponding to $m_l = -1, 0, +1$ values. This means that there are three p-orbitals in each p-subshell. These are designated as p_x, p_y and p_z for example,* ***$2p_x$, $2p_y$*** *and* ***$2p_z$****.*

- **Shapes of *d*-orbitals:** *For d-orbital (l = 2), there are five possible orientations corresponding to $m_l = -2, -1, 0, +1, +2$. This means that there are* ***five orbitals*** *in each d-subshell. For 3d-subshell, these are designated as* ***$3d_{xy}$, $3d_{yz}$, $3d_{zx}$, $3d_{x^2-y^2}$*** *and* ***$3d_{z^2}$****. These five orbitals are equal in energy but differ in their orientations.*