CONCEPT OF QUANTUM NUMBERS SECTION - 6

Introduction to Quantum Mechanics

Macroscopic Objects :

Motion of these objects *can be* described/calculated using classical mechanics (based on Newton's law of motion).

Microsopic Objects

Motion of these objects *can not be* described/calculated using classical mechanics (based on Newton's law of motion).

(i) Dual nature of matter is not considered in classical mechanics, so there is a need for Quantum Mechanics (takes into consideration the dual nature of matter).

(ii) Quatum mechanics can also be applied on macroscopic objects (we can ignore their wave like properties) and still get the same results as Classical Mechanics.

Equation of Quantum Mechanics :

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

It defines the laws of motion that microscopic objects must obey.

Schrödinger equation is the governing equation of Quantum Mechanics. It is a complex equation and difficult to understand and solve with the knowledge of mathematics in classes XI and XII.

For a system whose energy doesn't vary with time, Schrödinger equation can be represented as :

$$\hat{H}\,\psi = E\,\psi$$

where $\hat{H}$ = Hamiltonian operator (a mathematical operator).

ψ = Wave function.

E = Energy.

Schrödinger equation is relatively easier to construct. For a H-atom, when this equation is solved, it gives the energy levels for the electrons and corresponding wave function (ψ) of the electron associated with each energy level.

What is a wave function (ψ) ?

- It is a mathematical function whose value depends upon the coordinates of the electron in the atom.
- It doesn't have any physical significance.
- It is characterized (represented) by set of three quantum numbers (n : Principal quantum number, ℓ : Azimuthal quantum number and m_ℓ : Magnetic quantum number).

Basically, it contains all the information about the electron.

Note :
- Schrödinger equation can not be solved exactly for multi-electron atom (but can be solved approximately).
- In case of single electron atom, energy of the orbital depends only on the principal quantum number (n) but in case of multi-electron atom, it depends on 'n' as well as ℓ.

Designation of An Electron in an Orbital

An orbital is basically designated by three quantum numbers n, ℓ and m_ℓ as defined below :

(i) Principal Quantum Number (n) :

It is a positive integer with values of n = 1, 2, 3, ... In other way, it can also be designated with letters as K (n = 1), L (n = 2), M (n = 3), ...

Significance :

(a) It determines the size and energy of the orbital.

Note : For H and H-like species, orbital size and energy depends only on 'n' but for multi electron species, orbital energy depends on both 'n' and 'ℓ'.

(b) It is also used to calculate the number of orbitals given by 'n^2'. Thus, the maximum number of electrons in a shell (i.e. energy level as designated with letters as K, L, M etc.) are given by '$2n^2$', since one orbital can at the maximum contains two electrons.

- As we have learnt in Bohr Model, increasing 'n' increases the energy of the electron, thus, energy of the orbital increases.
- Also, we have learnt that size of the energy shells increases with increasing 'n'. Thus, we can expect the orbital size to increase with 'n'.

(ii) Azimuthal Quantum Number (ℓ) : It is an integer having all values between 0 and n – 1. It is also also known as orbital angular momentum quantum number or subsidiary quantum number.

Significance :

(a) It is used to define the shape of an orbital.

(b) It is used to represent a subshell (Each shell has subshells equal to shell number). A subshell can be thought of as sub-energy level inside an energy level.

For example **:** n = 1 (K shell) has only one subshell ($\ell = 0$)
n = 2 (L shell) has two subshells ($\ell = 0, 1$)
And so on . . . . .

Each value of 'ℓ' can be designated with letters as s ($\ell = 0$), p ($\ell = 1$), d ($\ell = 2$), f ($\ell = 3$), g ($\ell = 4$) and so on . . . . .

We can create the following notation :

$n = 1, \quad \ell = 0 \quad \Rightarrow \quad$ 1s
$n = 2, \quad \ell = 0, 1 \quad \Rightarrow \quad$ 2s, 2p
$n = 3, \quad \ell = 0, 1, 2 \quad \Rightarrow \quad$ 3s, 3p, 3d and so on . . . . .

(iii) Magnetic Quantum Number (m_ℓ) :

It is an integer having values between $-\ell$ to $+\ell$ including zero.

Significance :

(a) It gives information about the orientation of an orbital with respect to coordinate axis.

➤ ***For example*** : 's' orbital is spherical in shape. So, it can be oriented only in one way in space, hence only one orbital is possible.

Note : Number of orbitals in a sub-shell ≡ Number of possible orientations of an orbital.

➤ 'p' orbital has lobes above and below the plane as shown on page 29.

'p' subshell can be oriented in three ways (lobes can be along X, Y and Z axes).

Thus, three orbitals are possible in a p-subshell.
In general, number of orbitals in a sub-shell = $2\ell + 1$

Thus, 's' – subshell ($\ell = 0$) has $2(0) + 1 = 1$ orbital
'p' – subshell ($\ell = 1$) has $2(1) + 1 = 3$ orbital

Subshell	ℓ	No. of orbitals	Max. e's per subshell	Possible values of m_ℓ
s	0	1	2	0
p	1	3	6	–1, 0, 1
d	2	5	10	–2, –1, 0, 2
f	3	7	14	–3, –2, –1, 0, 1, 2, 3

Note the conventions :

's' – subshell

$m_\ell = 0$

'p' – subshell

Orbitals	m_ℓ
p_x	+1 or –1
p_y	+1 or –1
p_z	0

'd' – subshell

Orbitals	m_ℓ
d_{xy}	± 2
d_{yz}	± 1
d_{zx}	± 1
$d_{x^2-y^2}$	± 2
d_{z^2}	0

Note : n, ℓ, m_ℓ are the solutions of Schrödinger equation. There is another quantum number known as spin quantum number (m_s) which has been obtained experimentally.

There is an orbital angular momentum associated with an electron in subshell as given below.
It depends on both Azimuthal and Magnetic quantum numbers.

$$L = \sqrt{\ell(\ell+1)}\,\frac{h}{2\pi} \equiv \sqrt{\ell(\ell+1)}\,\hbar \quad \left(\text{where } \hbar = \frac{h}{2\pi} = \text{reduced Planck's constant}\right)$$

Spin Quantum number (m_s) : This quantum number accounts for the spin of electron about its axis similar to earth's motion about the sun as well as about its own axis.

An orbital can have a maximum of two electrons spinning in opposite directions leading to a spin angular momentum (vector quantity).

Thus, for two electron in an orbital, $m_s = +\frac{1}{2}$ (spin anticlockwise) $\equiv \uparrow$; $m_s = -\frac{1}{2}$ (spin clockwise) $\equiv \downarrow$

Magnitude of spin angular momentum is given by :

$$\sqrt{s(s+1)}\,\frac{h}{2\pi} \equiv \frac{\sqrt{3}}{2}\,\frac{h}{2\pi}\left(s=\frac{1}{2}\ \text{for an electron}\right) \equiv \frac{\sqrt{3}}{2}\,\hbar\left(\hbar=\frac{h}{2\pi}=\text{reduced planck's constant}\right)$$

Note :
- $m_s = \frac{1}{2}$ for any electron. In an orbital, $m_s = \pm\frac{1}{2}$ has been taken so as to distinguish the two electrons in it.
- spin quantum number has no classical analogue.

Difference between Orbit and Orbital :

Orbit	Orbital
1. It is circular path around the nucleus in which an electron moves.	**1.** It is a quantum mechanical concept and refers to one electron wave.
2. It is characterized by n.	**2.** It is characterized by n, ℓ, m_ℓ.
3. It has no real meaning.	**3.** It represents the probability of finding an electron at any point (through $\lvert\psi\rvert^2$).

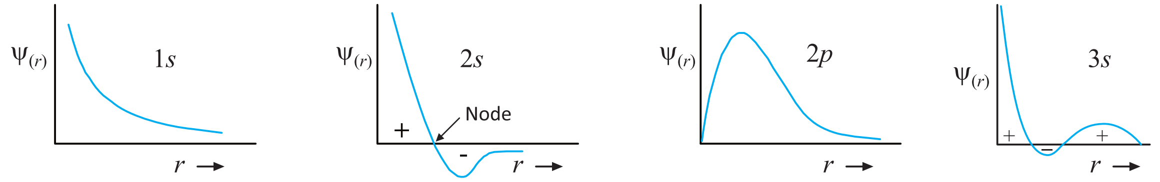
Hydrogen Atom and the Schrodinger Equation:

When Schrodinger equation is solved for hydrogen atom, the solution gives the possible energy levels the electrons can occupy and the corresponding wave function(s) (ψ) of the electron associated with each energy level. These quantized energy states and corresponding wave functions which are characterized by a set of three quantum numbers (principal quantum number n, azimuthal quantum number l and magnetic quantum number m_l) arise as a natural consequence in the solution of the Schrodinger equation. when an electron is in any energy state, the wave function corresponding to that energy state contains all information about the electron. The wave function is a mathematical function whose value depends upon the coordinates of the electron in the atom and does not carry any physical meaning. Such wave functions of hydrogen or hydrogen like species with one electron are called atomic orbitals. Such wave functions pertaining to one-electron species are called one-electron systems. The probability of finding an electron at a point within an atom is proportional to the $|\psi|^2$ at that point.

Application of Schrodinger equation to multi-electron atoms presents a difficulty: the Schrodinger equation cannot be solved exactly for a multi-electron atom. This difficulty can be overcome by using approximate methods. Such calculations with the aid of modern computers show that orbitals discussed above. The principal difference lies in the consecuence of increased nuclear charge. Because of this all the orbitals are somewhat contracted. Further, as you shall see later (in subsections 2.6.3 and 2.6.4), unlike orbitals of hydrogen or hydrogen only on the quantum number n, the energies of the orbitals in multi-electron atoms depend on quantum numbers n and l.

Plots of Radial Wave Function R(r), Radial Probability Density R²(r) and Radial Probability Function $[4\pi r^2 R^2]$ Vs 'r': The probability of finding the electron in a spherical shell of thickness *dr* at a distance r from the nucleus is equal to the product of the volume of shell of thickness dr at distance r from the nucleus $(4\pi r^2 dr)$ and the radial probability density $R^2(r)$ per unit volume i.e., equal to $4\pi r^2 R^2(r)dr = P\,dr$ where $P = 4\pi r^2 R^2(r)$ is called Radial Probability Function.

(a)



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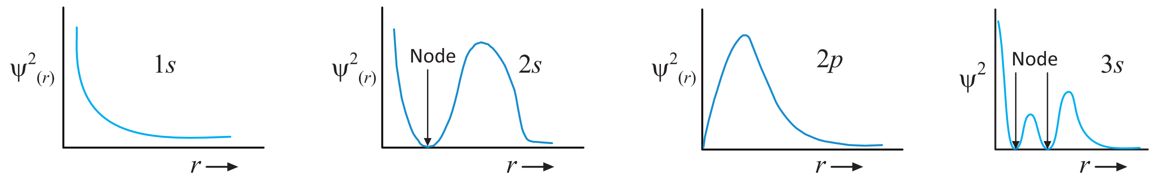

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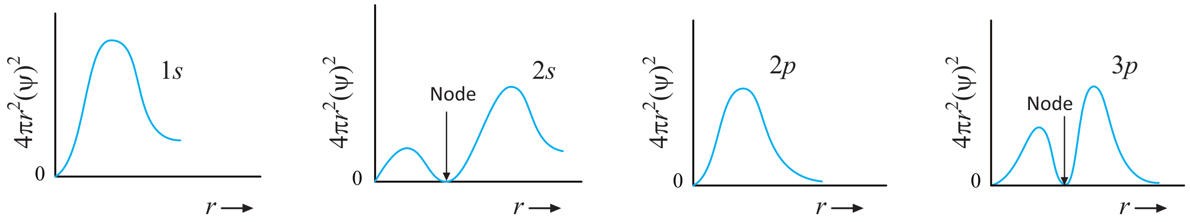


- In the plots of radial probability versus distance from the nucleus, number of peaks i.e. region of maximum probability = n – l for instance, 2s has two peaks 3s will have 3 peaks, 2p has one peak, 3p has two peaks and so on.

As we see from the above graph, ψ^2 decreases and approaches to zero as r increases. Region where ψ^2 reduces to zero is called nodal surface (nodes). A node is a region of space where probability of finding the electron is zero. There are also angular nodes (nodal plane) which represents plane passing through nucleus and having probability density function as zero.

For a hydrogen like atom wave function, of principal quantum number *n*, there are

(i) $(n - \ell - 1)$ radial nodes

(ii) ℓ angular nodes

(iii) $(n - 1)$ total nodes.

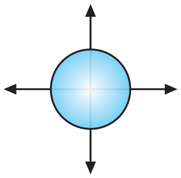
Thus :

- 2s has one node. 3s has two nodes and so on.
- 1*s* ($n = 1, \ell = 0$) subshell is without any node.
- 2*s* ($n = 2, \ell = 0$) subshell will have only one radial node, while 2*p* ($n = 2, \ell = 1$) subshell will have only one angular node.
- 3*s* ($n = 3, \ell = 0$) subshell will have two radial nodes, 3*p* ($n = 3, \ell = 1$) subshell will have one radial and one angular node while 3*d* ($n = 3, \ell = 2$) will have two angular nodes.

Boundary surface diagram : It is surface (contour) which represents a constant $|\psi|^2$. In general, it is the region where the probability of finding the electron is 90%.

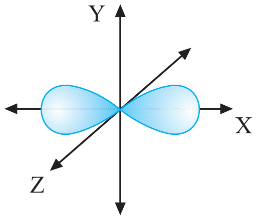
As mentioned earlier, the 's' orbitals are spherical in shape which means that the probability of finding the electron at a given distance is equal in all the direction.

Also, the size of these orbitals increases as 'n' increases.

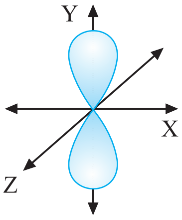


s-orbital

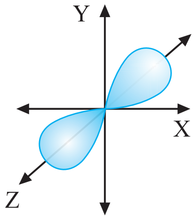
Boundary Surface Diagrams of p-orbitals are not spherical as shown :



p_x orbital



p_y orbital



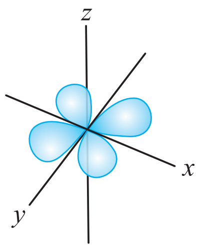
p_z orbital

As we can see, there are two lobes on either side of the plane passing through the nucleus having probability of finding the electron as zero on it.

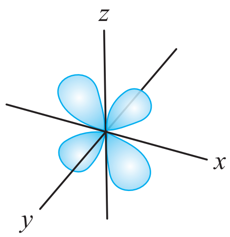
- All three orbital have same shapes and energy.
- Here also, energy of these orbitals increases with increasing 'n'.
- No. of radial nodes (for p-orbitals) are given by n – 2

Boundary Surface Diagrams of d-orbitals are shown below. For d-subshells, there are 5 values of m_ℓ. Thus, d has 5 orbitals.

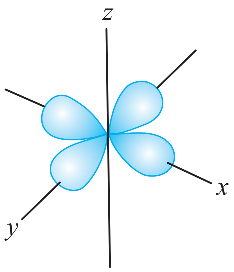
d_{xy}



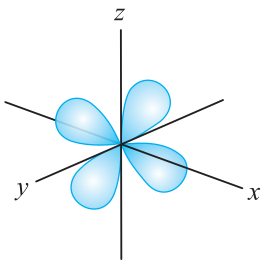
d_{xz}



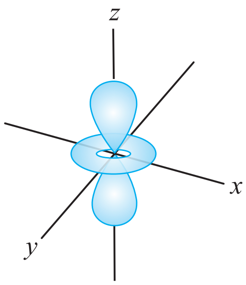
$d_{x^2-y^2}$



d_{yz}



d_{z^2}



Energy of orbitals :

- For H-atom, energy of an orbital can be solely calculated by using 'n'

  Thus, $1s < 2s = 2p < 3s = 3p = 3d < 4s = 4p = 4d = 4f < \ldots\ldots$

  Orbitals having same energy are called degenerate orbitals.

- For an atom containing multi electrons, energy of an electron depends on 'n' as well as 'ℓ'.

In this case, each e^- is attracted by the nucleus but is repelled by every other electron. The electrons in the outer shell experiences less attractive force as there is a partial screening of positive change known as shielding of the outer shell electrons from the nucleus.

- 's' orbitals are more tightly bound to nucleus than p orbitals, p orbitals are more tightly bound to nucleus than d orbitals and so on. Thus, energy of 's' orbitals is more negative than p-orbitals.

Illustration - 15 *In all, how many nodal planes are there in the atomic orbitals for the principal quantum number* $n = 3$.

SOLUTION :

Shell with n = 3 has 1 ‘s’ (3s), 3 ‘p’ (p_x, p_y, p_z) and 5 ‘d’ (d_{xy}, d_{xz}, d_{yz}, $d_{(x^2-y^2)}$ and d_{z^2}) orbitals.

- ‘s’ has no nodal plane.
- Each of p_x, p_y, p_z has one nodal plane, which means a total of 3 nodal planes.
- d_{z^2} has no nodal plane.

Each of d_{xy}, d_{xz}, d_{yz}, $d_{(x^2-y^2)}$ has 2 nodal planes, which means a total of 8 nodal planes.

Hence for n = 3, a total of 11 nodal planes are there.

Illustration - 16 *The wave function* (ψ) *of 2s-orbital is given by :* $\psi_{2s} = \frac{1}{\sqrt{32\pi}}\left[\frac{1}{a_0}\right]^{3/2}\left[2-\frac{1}{a_0}\right]e^{-r/2a_0}$

At $r = r_0$, *radial node is formed. Calculate* r_0 *in terms of* a_0.

SOLUTION :

For radial node at $r = r_0$, $\psi_{2s}^2 = 0$. This is possible only when $\left[2-\frac{r_0}{a_0}\right] = 0$ $\quad\therefore\quad r_0 = 2a_0$