1. Details of Module and its structure

Module Detail	
Subject Name	Chemistry
Course Name	Chemistry 01 (Class XI, Semester 01)
Module Name/Title	Structure of Atom: Part 4
Module Id	kech_10204
Pre-requisites	Knowledge of Bohr‘s model of atom, spectra of hydrogen atom
Objectives	After going through this module you will be able to: 1. Understand the quantum mechanical model of atom 2. Correlate the hydrogen atom and the Schrodinger equation 3. Describe orbitals and quantum numbers 4. Draw shapes of various atomic orbitals
Keywords	Quantum Mechanics, Shell, Subshell, Azimuthal Quantum Number, Magnetic Orbital Quantum Number, Electron Spin, Quantum Number, Atomic Orbitals, Nodes

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1. INTRODUCTION

In the previous module you have learned about the Bohr’s model of atom which could explain the line spectrum of hydrogen atom or hydrogen like species but it could not explain the spectrum of multielectron species. It can be explained by the quantum mechanical model of atom, about which you will study in this module.

2. QUANTUM MECHANICAL MODEL OF ATOM

Classical mechanics, based on Newton’s laws of motion, successfully describes the motion of all macroscopic objects such as a falling stone and orbiting planets, which have essentially a particle-like behaviour. However it fails when applied to microscopic objects like electrons, atoms and molecules. This is mainly because of the fact that classical mechanics ignores the concept of dual behaviour of matter especially for sub-atomic particles and the uncertainty principle. The branch of science that is based on this dual behaviour of matter is called **quantum mechanics**.

Quantum mechanics is a theoretical science that deals with the study of the motions of the microscopic objects that have both wave like and particle like properties. It specifies the laws of motion that are obeyed by these objects. When quantum mechanics is applied to macroscopic objects (for which wave like properties are insignificant) the results are the same as those from the classical mechanics.

Quantum mechanics was developed independently in 1926 by Werner Heisenberg and Erwin Schrödinger. Here, however, we shall be discussing the quantum mechanics which is based on the ideas of wave motion developed by Schrödinger. This won him the Nobel Prize in Physics in 1933. This equation which incorporates wave-particle duality of matter as proposed by de Broglie is quite complex and knowledge of higher mathematics is needed to solve it. You will learn its solutions for different systems in higher classes.

For a system (such as an atom or a molecule whose energy does not change with time) the Schrödinger equation is written as $\hat{H}\psi = E\psi$ where $\hat{H}$ is a mathematical operator called Hamiltonian. Schrödinger gave a method of constructing this operator from the expression for the total energy of the system. The total energy of the system takes into account the kinetic energies of all the sub-atomic particles (electrons, nuclei), potential energy due to attraction between the electrons and nuclei and potential energy due to repusion among the electrons and nuclei individually. Solution of this equation gives E and ψ.

3. HYDROGEN ATOM AND THE SCHRÖDINGER EQUATION

When Schrödinger equation is solved for hydrogen atom, the solution gives the possible energy levels that the electron can occupy and the 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 Schrödinger equation. When an electron is in any energy state, the wave function corresponding to that energy state contains all the information about the electron. The wave function is a mathematical function which 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** of one-electron systems. The probability of finding an electron at a point within an atom is proportional to the $|\psi|^2$ at that point. The quantum mechanical results of the hydrogen atom successfully predict all aspects of the hydrogen atom spectrum including some phenomena that could not be explained by the Bohr model.

Application of Schrödinger 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 in atoms other than hydrogen do not differ in any radical way from the hydrogen orbitals discussed above. The principal difference lies in the consequence of increased nuclear charge. Because of this all the orbitals are somewhat contracted. Further, as you shall see later, unlike orbitals of hydrogen or hydrogen like species, whose energies depend only on the quantum number n, the energies of the orbitals in multi-electron atoms depend on quantum numbers *n* and *l*.

Important Features of the Quantum Mechanical Model of Atom

Quantum mechanical model of an atom is the picture of the structure of the atom, which emerges from the application of the Schrödinger equation to the atom. The following are the important features of the quantum-mechanical model of atom:

1. The energy of electrons in atoms is quantized (i.e., energy of electron can only have certain specific values), when electrons are bound to the nucleus in the atom.

2. The existence of quantized electronic energy levels is a direct result of the wave like properties of electrons and are allowed solutions of Schrödinger wave equation.

3. Both the exact position and exact velocity of an electron in an atom cannot be determined simultaneously (Heisenberg uncertainty principle). The path of an electron in an atom, therefore, can never be determined or known accurately. That is why, as you shall see later on, one talks of only probability of finding the electron at different points in an atom.

4. An atomic orbital is the wave function ψ for an electron in an atom. Whenever an electron is

described by a wave function, we say that the electron occupies that orbital. Since many such wave functions are possible for an electron, there are many atomic orbitals in an atom. These "one electron orbital wave functions" or orbitals form the basis of the electronic structure of atoms. In each orbital, the electron has a definite energy. An orbital cannot contain more than two electrons. In a multi-electron atom, the electrons are filled in various orbitals in the order of increasing energy. For each electron of a multi-electron atom, there shall, therefore, be an orbital wave function characteristic of the orbital it occupies. All the information about the electron in an atom is stored in its orbital wave function ψ and quantum mechanics makes it possible to extract this information out of ψ.

5. The probability of finding an electron at a point within an atom is proportional to the square of the orbital wave function i.e., $|\psi|^2$ at that point. $|\psi|^2$ is known as probability density and is always positive. **From the value of $|\psi|^2$ at different points within an atom, it is possible to predict the region around the nucleus where electron will most probably be found.**

4. ORBITALS AND QUANTUM NUMBERS

A large number of orbitals are possible in an atom. Qualitatively these orbitals can be distinguished by their size, shape and orientation. An orbital of smaller size means there is more chance of finding the electron near the nucleus. Similarly shape and orientation mean that there is more probability of finding the electron along certain directions than along others. Atomic orbitals are precisely distinguished by what are known as quantum numbers. Each orbital is designated by three quantum numbers labelled as n, l and m_l.

4.1 Principal quantum number '*n*'

It is a positive integer with value of n = 1,2,3....... . The principal quantum number determines the size and to large extent the energy of the orbital. For hydrogen atom and hydrogen like species (He^+, Li^{2+}, ... etc.) energy and size of the orbital depends only on 'n'.

The principal quantum number also identifies the **shell**. With the increase in the value of 'n', the number of allowed orbital increases and **are given by 'n^2' All the orbitals of a given value of '*n*' constitute a single shell of atom** and are represented by the following letters

n =	1	2	3	4	……
Shell =	K	L	M	N	……

Size of an orbital increases with increase of principal quantum number 'n'. In other words the electron will be located away from the nucleus. Since energy is required in shifting away the negatively charged electron from the positively charged nucleus, the energy of the orbital will increase with increase of n.

4.2 Azimuthal quantum number '*l*'

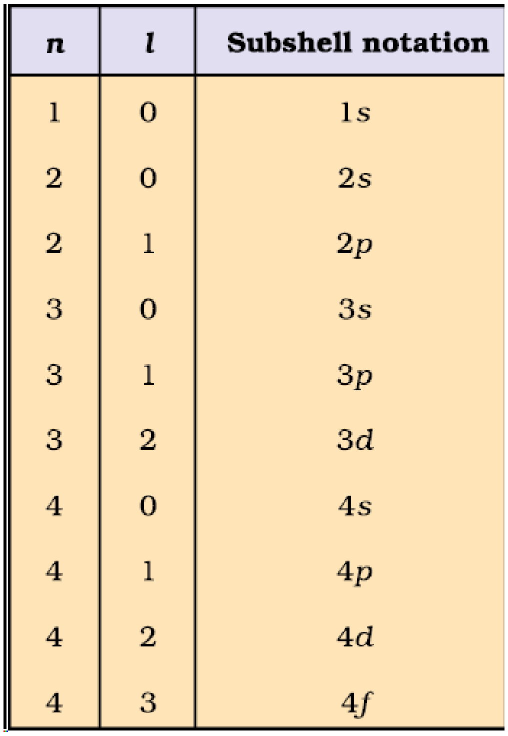
It is also known as **orbital angular momentum or subsidiary quantum number.** It defines the three dimensional shape of the orbital. For a given value of n, l can have n values ranging from 0 to $n - 1$. That is, for a given value of n, the possible value of l are : l = 0, 1, 2, ..., (n–1).

For example, when $n = 1$, the only possible value of l is 0. For $n = 2$, the possible value of l can be 0 and 1. For $n = 3$, the possible l values are 0, 1 and 2. This implies that, each shell consists of one or more **sub-shells** or **sub-levels**. The number of sub-shells in a principal shell is equal to the value of n. For example, in the first shell ($n = 1$), there is only one sub-shell which corresponds to $l = 0$. There are two sub-shells ($l = 0, 1$) in the second shell ($n = 2$), three ($l = 0, 1, 2$) in third shell ($n = 3$) and so on. Each sub-shell is assigned an azimuthal quantum number (l). Sub-shells corresponding to different values of l are represented by the following symbols.

Value for l:	0	1	2	3	4	5	……
notation for sub-shell	s	p	d	f	g	h	…….

Table 1 shows the permissible values of ‘l’ for a given principal quantum number and the corresponding sub-shell notation.

Table 1 Subshell Notations



n	l	Subshell notation
1	0	1*s*
2	0	2*s*
2	1	2*p*
3	0	3*s*
3	1	3*p*
3	2	3*d*
4	0	4*s*
4	1	4*p*
4	2	4*d*
4	3	4*f*

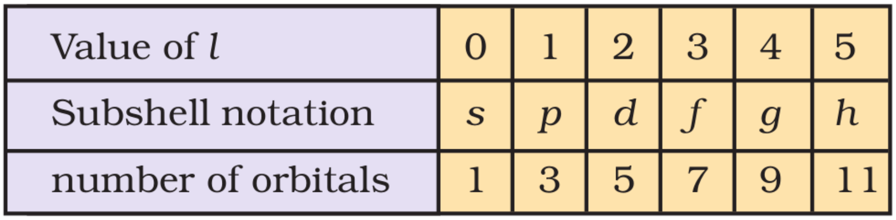
4.3 Magnetic orbital quantum number ‘m_l’

‘m_l’ gives information about **the spatial orientation of the orbital with respect to standard set of co-ordinate axis.** For any **sub-shell (defined by ‘l’ value)** $2l+1$ values of m_l are possible and these values are given by :

$m_l = – l, – (l–1), – (l–2)... 0,1... (l–2), (l–1), l$

Thus for $l = 0$, the only permitted value of $m_l = 0$, [2(0)+1 = 1, one s orbital]. For $l = 1$, m_l can be –1, 0 and +1 [2(1)+1 = 3, three p orbitals]. For $l = 2$, $m_l = –2, –1, 0, +1$ and +2, [2(2)+1 = 5, five d orbitals]. It should be noted that the values of m_l are derived from l and that the value of l are derived from n.

Each orbital in an atom, therefore, is defined by a set of values for n, l and m_l. An orbital described by the quantum numbers $n = 2$, $l = 1$, $m_l = 0$ is an orbital in the p sub-shell of the second shell. The following chart gives the relation between the sub-shell and the number of orbitals associated with it.



Value of l	0	1	2	3	4	5
Subshell notation	*s*	*p*	*d*	*f*	*g*	*h*
number of orbitals	1	3	5	7	9	11

4.4 Electron spin ‘s’

The three quantum numbers labelling an atomic orbital can be used equally well to define its energy, shape and orientation. But all these quantum numbers are not enough to explain the line spectra observed in the case of multi-electron atoms, that is, some of the lines actually occur in doublets (two lines closely spaced), triplets (three lines, closely spaced) etc. This suggests the presence of a few more energy levels than predicted by the three quantum numbers.

In 1925, George Uhlenbeck and Samuel Goudsmit proposed the presence of the fourth quantum number known as the **electron spin quantum number (m_s).** An electron spins around its own axis, much in a similar way as earth spins around its own axis while revolving around the sun. In other words, an electron has, besides charge and mass, intrinsic spin angular quantum number. Spin angular momentum of the electron — a vector quantity, can have two orientations relative to the chosen axis. These two orientations are distinguished by the spin quantum numbers m_s which can take the values of +½ or –½. These are called the **two spin states of the electron** and are normally represented by two arrows, ↑ (spin up) and ↓ (spin down). Two electrons that have different m_s values (one +½ and the other –½) are said to have opposite spins. An orbital cannot hold more than two electrons and these two electrons should have opposite spins.

To sum up, the four quantum numbers provide the following information :

i) ***n*** defines the shell, determines the size of the orbital and also to a large extent the energy of the orbital.

ii) There are n subshells in the nth shell. ***L*** identifies the subshell and determines the shape of the orbital. There are $(2l+1)$ orbitals of each type in a subshell. For example, when $n= 2$, there is one s orbital ($l = 0$), three p orbitals ($l = 1$) and five d orbitals ($l = 2$) per subshell. In a multi-electron atom l also determines the energy of the orbital along with n.

Iii) $\boldsymbol{m_l}$ designates the orientation of the orbital. For a given value of l, m_l has $(2l+1)$ values, the same as the number of orbitals per subshell. It means that the number of orbitals is equal to the number of ways in which they are oriented.

iv) $\boldsymbol{m_s}$ refers to orientation of the spin of the electron.

Orbit, orbital and its importance

Orbit and orbital are not synonymous. An orbit, as proposed by Bohr, is a circular path around the nucleus in which an electron moves. A precise description of this path of the electron is impossible according to Heisenberg uncertainty principle. Bohr orbits, therefore, have no real meaning and their existence can never be demonstrated experimentally. An atomic orbital, on the other hand, is a quantum mechanical concept and refers to the one electron wave function ψ in an atom. It is characterized by three quantum numbers (n, l and m_l) and its value depends upon the coordinates of the electron. Ψ has, by itself, no physical meaning. It is the square of the wave function i.e., $|\psi|^2$ which has a physical meaning. $|\psi|^2$ at any point in an atom gives the value of probability density at that point. Probability density ($|\psi|^2$) is the probability per unit volume and the product of $|\psi|^2$ and a small volume (called a volume element) yields the probability of finding the electron in that volume (the reason for specifying a small volume element is that $|\psi|^2$ varies from one region to another in space but its value can be assumed to be constant within a small volume element). The total probability of finding the electron in a given volume can then be calculated by the sum of all the products of $|\psi|^2$ and the corresponding volume elements. It is thus possible to get the probable distribution of an electron in an orbital.

Problem 1

What is the total number of orbitals associated with the principal quantum number $n = 3$?

Solution

For $n = 3$, the possible values of l are 0, 1 and 2. Thus there is one 3s orbital ($n = 3$, $l = 0$ and $m_l = 0$); there are three 3p orbitals ($n = 3$, $l = 1$ and $m_l = -1, 0, +1$); there are five 3d orbitals ($n = 3$, $l = 2$ and $m_l = -2, -1, 0, +1+, +2$).

Therefore, the total number of orbitals is $1+3+5 = 9$

The same value can also be obtained by using the relation; number of orbitals $= n^2$, i.e. $3^2 = 9$.

Problem 2

Using s, p, d, f notations, describe the orbital with the following quantum numbers

(a) n = 2, l = 1, (b) n = 4, l = 0, (c) n = 5, l = 3, (d) n = 3, l = 2

Solution

	n	*l*	orbital
a)	1	2	2p
b)	0	4	4s

c)	3	5	5f
d)	2	3	3d

4.5 Shapes of Atomic Orbitals

The orbital wave function or ψ for an electron in an atom has no physical meaning. It is simply a mathematical function of the coordinates of the electron. However, for different orbitals the plots of corresponding wave functions as a function of r (the distance from the nucleus) are different. Fig. 1(a), gives such plots for 1s (*n* = 1, *l* = 0) and 2s (*n* = 2, *l* = 0) orbitals.

According to the German physicist, Max Born, the square of the wave function (i.e.,ψ^2) at a point gives the probability density of the electron at that point. The variation of ψ^2 as a function of r for 1s and 2s orbitals is given in Fig. 1 (b). Here again, you may note that the curves for 1s and 2s orbitals are different.

It may be noted that for 1s orbital the probability density is maximum at the nucleus and it decreases sharply as we move away from it. On the other hand, for 2s orbital the probability density first decreases sharply to zero and again starts increasing. After reaching a small maxima it decreases again and approaches zero as the value of r increases further. The region where this probability density function reduces to zero is called **nodal surfaces** or simply **nodes**. In general, it has been found that ns-orbital has (n – 1) nodes, that is, number of nodes increases with increase of principal quantum number n. In other words, number of nodes for 2s orbital is one and two for 3s.

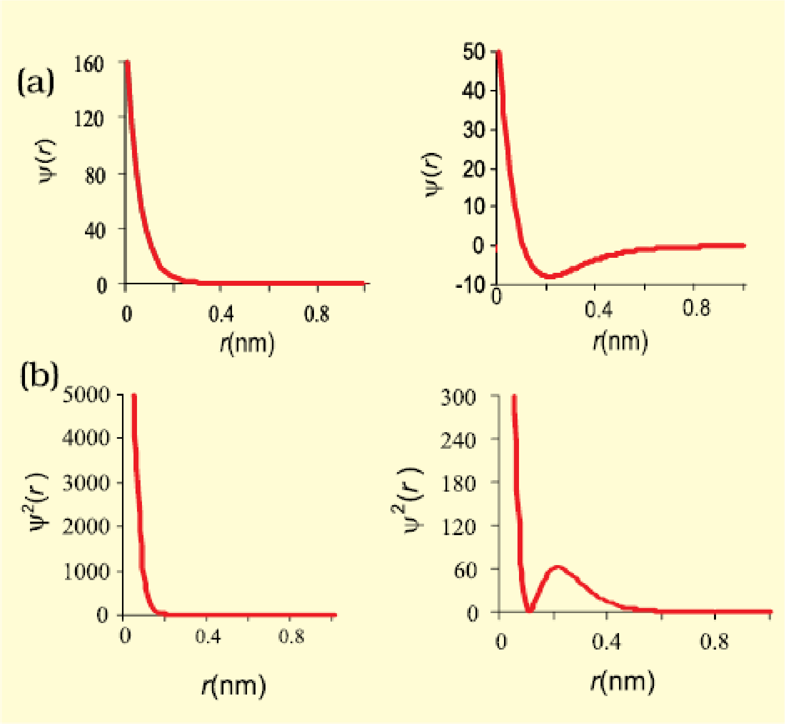


Fig. 1 The plots of (a) the orbital wave function ψ(r); (b) the variation of probability density ψ2(r) as a function of distance r of the electron from the nucleus for 1s and 2s orbitals.

These probability density variations can be visualized in terms of charge cloud diagrams Fig. 2(a). In these diagrams, the density of the dots in a region represents electron probability density in that region.

Boundary surface diagrams of constant probability density for different orbitals give a fairly good representation of the shapes of the orbitals. In this representation, a boundary surface or contour surface is drawn in space for an orbital on which the value of probability density $|\psi|^2$ is constant. In principle many such boundary surfaces may be possible. However, for a given orbital, only that boundary surface diagram of constant probability density is taken to be good representation of the shape of the orbital which encloses a region or volume in which the probability of finding the electron is very high, say, 90%. The boundary surface diagram for 1s and 2s orbitals are given in Fig. 2(b).If probability density $|\psi|^2$ is constant on a given surface, $|\psi|$ is also constant over the surface. The boundary surface for $|\psi|^2$ and $|\psi|$ are identical.

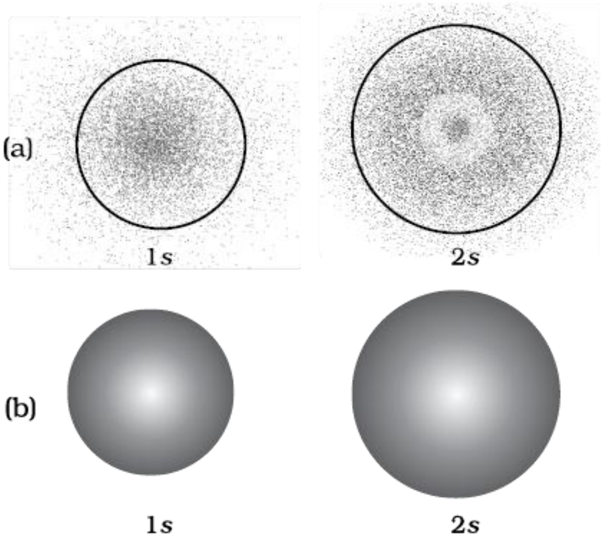


***Fig. 2** (a) Probability density plots of 1s and 2s atomic orbitals. The density of the dots represents the probability density of finding the electron in that region. (b) Boundary surface diagram for 1s and 2s orbitals.*

One may ask a question : Why do we not draw a boundary surface diagram, which bounds a region in which the probability of finding the electron is, 100 %? The answer to this question is that the probability density $|\psi|^2$ has always some value, howsoever small it may be, at any finite distance from the nucleus. It is therefore, not possible to draw a boundary surface diagram of a rigid size in which the probability of finding the electron is 100%. Boundary surface diagram for s orbital is actually a sphere centred on the nucleus. In two dimensions, this sphere looks like a circle. It encloses a region in which probability of finding the electron is about 90%.

Thus we see that 1s and 2s orbitals are spherical in shape. In reality all the s-orbitals are spherically symmetric, that is, the probability of finding the electron at a given distance is equal in all the directions. It is also observed that the size of the s orbital increases with increase in *n*, that is, 4s > 3s > 2s> 1s and the electron is located further away from the nucleus as the principal quantum number increases

Boundary surface diagrams for three 2p orbitals ($l = 1$) are shown in Fig. 3. In these diagrams, the nucleus is at the origin. Here, unlike s-orbitals, the boundary surface diagrams are not spherical. Instead each p orbital consists of two sections called lobes that are on either side of the plane that passes through the nucleus. The probability density function is zero on the plane where the two lobes touch each other. The size, shape and energy of the three orbitals are identical. They differ however, in the way the lobes are oriented. Since the lobes may be considered to lie along the x, y or z axis, they are given the designations $2p_x$, $2p_y$, and $2p_z$. It should be understood, however, that there is no simple relation between the values of m_l (–1, 0 and +1) and the x, y and z directions. For our purpose, it is sufficient to remember that, because there are three possible values of m_l, there are, therefore, three p orbitals whose axes are mutually perpendicular. Like s orbitals, p orbitals increase in size and energy with increase in the principal quantum number and hence the order of the energy and size of various p orbitals is 4p > 3p > 2p. Further, like s orbitals, the probability density functions for p-orbital also pass through value zero, besides at zero and infinite distance, as the distance from the nucleus increases. The number of nodes are given by the $n - 2$, that is number of radial node is 1 for 3p orbital, two for 4p orbital and so on.

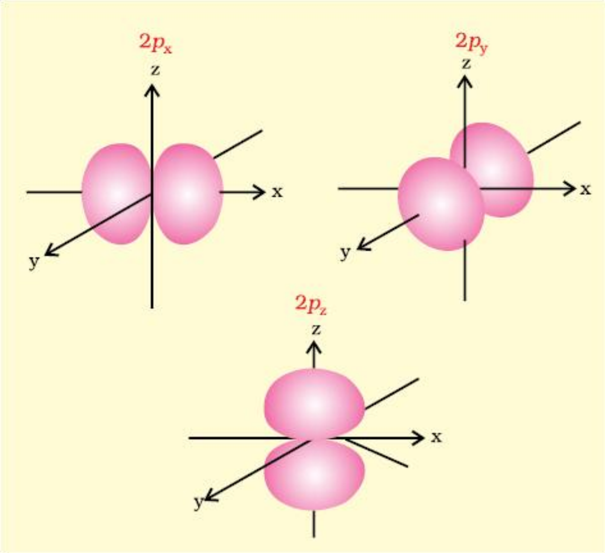


Fig. 3 Boundary surface diagrams of the three 2p orbitals.

For l = 2, the orbital is known as d-orbital and the minimum value of principal quantum number (n) has to be 3. as the value of l cannot be greater than n–1. There are five m_l values (–2, –1, 0, +1 and +2) for l = 2 and thus there are five d orbitals. The boundary surface diagram of d orbitals are shown in Fig. 4.

The five d-orbitals are designated as d_{xy} , d_{yz} , d_{xz}, $d_{x^2-y^2}$ and d_{z^2}. The shapes of the first four d-orbitals are similar to each other, where as that of the fifth one, d_{z^2}, is different from others, but all five 3d orbitals are equivalent in energy. The d orbitals for which n is greater than 3 (4d, 5d...) also have shapes similar to 3d orbital, but differ in energy and size.

Besides the radial nodes (i.e., where probability density function is zero), the probability density functions for the *np* and *nd* orbitals are zero at the plane (s), passing through the nucleus (origin). For example, in case of p_z orbital, xy-plane is a nodal plane, in case of d_{xy} orbital, there are two nodal planes passing through the origin and bisecting the xy plane containing z-axis. These are called angular nodes and number of angular nodes are given by '*l*', i.e., one angular node for p orbitals, two angular nodes for 'd' orbitals and so on. **The total number of nodes are given by (n–1), i.e., sum of *l* angular nodes and (n – *l* – 1) radial nodes.**

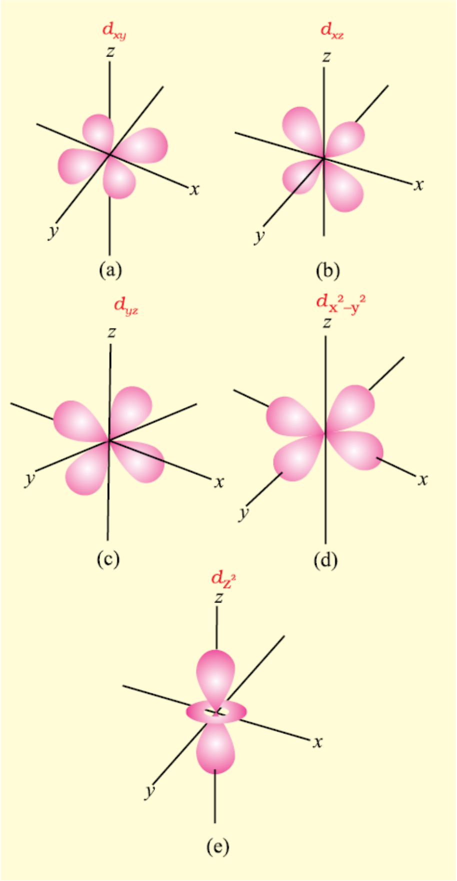


Fig. 4: The boundary surface diagram of d orbitals

5. SUMMARY

- Schrodinger equation describes the electron distribution in space and the allowed energy levels in atom.
- The quantized energy states of electrons and corresponding wave functions are characterized by a set of three quantum numbers.

- The principal quantum number *(n)* determines the size and to a large extent the energy of an orbital.
- Azimuthal quantum number *(l)* is also known as orbital angular momentum and defines the three dimensional shape of the orbital.
- Magnetic quantum number (m_l) gives information about the spatial orientation of the orbital.
- Electron spin quantum number *(s)* represents the spin of an electron and can have a value of +1/2 or -1/2.
- The region where the probability density function is zero, is called nodal surface or simply a node.