SHAPES OF ATOMIC ORBITALS

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An orbital is the region of space around the nucleus within which the probability of finding an electron of given energy is maximum (about 90%). The probability at any point around the nucleus is calculated using Schrödinger wave equation and is represented by the density of the points. The shape of electron cloud thus obtained gives the shape of the orbital.
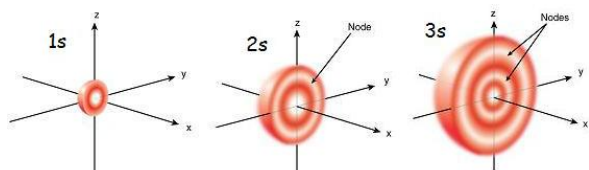
Shapes of s-orbital:- The probability of finding an electron belonging to s-orbital of any main shell is found to be identical in all directions at a given distance from the nucleus. Hence, s-orbital is spherical in shape which is symmetrical around the nucleus.

For s-orbital, azimuthal quantum number l=0. Hence, magnetic quantum number 'm' =0 i.e., it has only one value. Thus s-orbital has only one orientation. The intermediate region (a spherical shell) where the probability of finding the electron is zero is called a nodal surface or node. Thus, 2s orbital has one node within it. 3s orbital has two nodes. In general, any ns orbital has (n-1) nodes.

1s=no node, 1-1=0

2s=one node, 2-1=1

3s=two nodes, 3-1=2   1s,2s and 3s-orbital differ in their size and energy. These increase with increase in principal quantum number 'n' 1s<2s<3s


Shapes of p-orbitals:- On the basis of probability calculation, it is found that the probability of finding the p-electron is maximum in two lobes on the opposite sides of the nucleus. This gives rise to a dumb-bell shape for the p-orbital.
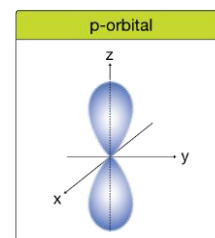

However, it may be noted that the probability of finding a particular p-electron is equal in both the lobes. Further, there is a plane passing through the nucleus on which the probability of finding the electron is almost zero. This is called a nodal plane. For p-orbital, l=1 hence, m=-1, 0, +1. Thus, p-orbital has three different orientations. These are designated as p_x, p_y, p_z depending upon whether the electron density is maximum along the x-axis, y-axis and z-axis respectively.
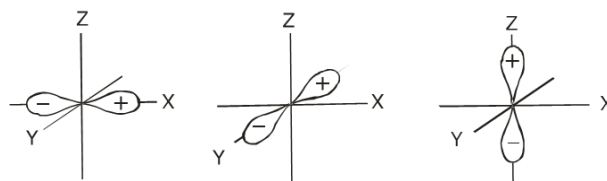
p-orbitals have directional characteristics and hence are helpful in predicting the shapes of molecules. Further, it may be mentioned that every energy level with principal quantum number greater than 1 has three p-orbitals. As principal quantum number increases, these p-orbitals become larger in size and have higher energies. However, the three p-orbitals belonging to a particular energy shell have equal energies and are called degenerate orbitals. Further, 2p has no node, 3p has one node, 4p has two nodes and so on.

Shapes of d-orbitals- For d-orbital, l=2. Hence, m= -2, -1, 0, +1, +2. There are five d-orbitals

in each of the energy levels from n=3 onwards. On the basis of probability calculations, their shapes are shown in fig.
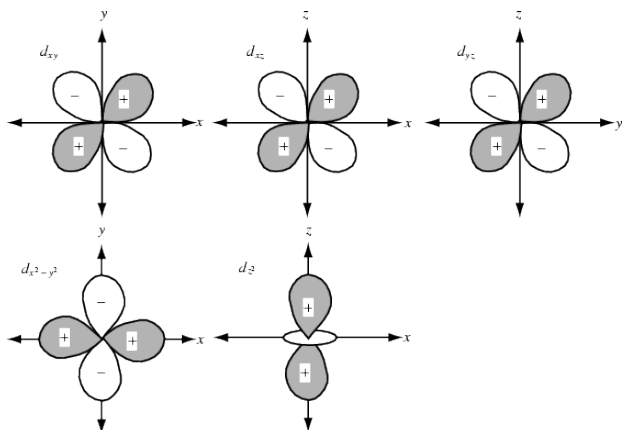
These are known as d_{xy}, d_{xz}, d_{yz}, d_{x2-y2}, d_{z2}. The five d-orbitals possess equal energies and differ only in their orientation. The three of the d-orbitals (d_{xy}, d_{xz}, d_{yz}) have four lobes of high electron density lying in xy, xz, yz planes. These lobes project in between the coordinate axes. Fourth d-orbital (d_{x2-y2}) has four lobes of high electron density in xy plane along x- and y- axis. The fifth d-orbital (d_{z2}) has only two lobes lying along the z-axis with a ring of high electron density around the nucleus in xy plane. 3d-orbital has no node while 4d and 5d have one and two nodes. Number of node in any orbital = n-l-1

REMEMBER- **1.** The formula (n-l-1) is for finding the number of spherical/radial nodes only. It is interesting to point out that whereas s-orbitals have spherical nodes only, p and d-orbitals have spherical as well as planar nodes. For example, 2p orbital has one nodal plane passing through the nucleus at the origin. Similarly, d-orbitals have two nodal planes. The number of spherical nodes depends upon the value of 'n'.

Thus, the above results may be generalized as follows:

Number of spherical/radial nodes in any orbital = n-l-1

Number of planar nodes in any orbital=l

$\therefore$ Total number of nodes in any orbital=n-l. Note that all d-orbital have two nodal planes expect d_{z2} which has no nodal plane.

2. Positive and negative signs shown inside the lobes of p and d-orbitals are for the wave function ψ and have nothing to do with the positive or negative charge. However, the probability density, ψ^2, is always positive.

3. The opposite lobes of p-orbitals have different signs (one +ve, the other −ve) but opposite lobes of d-orbitals have the same sign (two opposite lobes have +ve sign while the other two opposite lobes have −ve sign).

ELECTRONIC CONFIGURATION OF ELEMENTS – The distribution of electrons into different shells, subshells and orbitals of an atom is called its electronic configuration. Electronic configuration of any orbital can be simply represented by the notation, nl^x where n= number of the main or principal shell, l= symbol of the subshell or orbital (s, p, d, f) x= number of electrons present in that orbital. Thus, $4p^1$ means that the p-orbital of the 4th main shell contains one electron. The filling of electrons into various orbitals in the ground state is determined by the following rules.

1. **Aufbau Principle** – The word 'aufbau 'in German means 'building up'. The building up of orbitals means the filling up of orbitals with electrons. The principle states as follow : In the ground state of the atoms, the orbitals are filled in order of their increasing energies. In other words, electrons first occupy the lowest- energy orbital available to them and enter into higher energy orbitals only when the lower energy orbitals are filled. The order in which the orbital are filled is as follow:

   1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s, 4d, 5p, 6s, 4f, 5d, 6p, 7s, 5f, 6d, 7p, ………
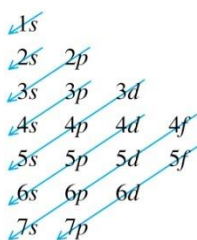
This order may be remembered by using method given in fig. starting from the top, the direction of the arrows gives the order of filling of orbitals. The order of increasing energies of the various orbitals can be calculated on the basis of Bohr Bury's rule (n+l), sum of the values of principal quantum number (n) and the azimuthal quantum number (l). According to this rule- In neutral isolated atom, the lower the value of (n + l) for an orbital, lower is its energy. However, if the two different types of orbitals have the same value of (n + l), the orbital with lower value of n has lower energy.

To illustrate the (n + l) rule, different example are given in the table

TPYE OF ORBITAL	VALUE OF n	VALUE OF l	VALUE OF n + l	RELATIVE ENERGY
1s	1	0	1+0 =1	Lowest energy
2s	2	0	2 + 0=2	Higher energy than 1s orbital
2p	2	1	2+1=3	
3s	3	0	3+0=3	2p orbitals (n=2) have lower energy than 3s (n=3) orbital
3p	3	1	3+1=4	
4s	4	0	4+0=4	3p orbitals (n=3) have lower energy than 4s (n=4) orbital
3d	3	2	3+2=5	
4p	4	1	4+1=5	3d orbital (n=3) have lower energy than 4p (n=4) orbital

2. **Pauli Exclusion Principle-** An orbital can accommodate maximum of two electrons and these two must have opposite spins. This means that an orbital can have 0,1 and 2 electrons. For example, two electrons in an orbital can be represented by (i) and not by (ii).
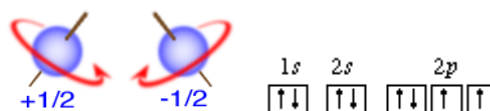
Correct-electrons have opposite spins ------ (i)
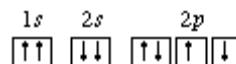
Incorrect- electrons must spin in opposite directions ----- (ii)

3. **Hund's Rule of maximum multiplicity** – this rule deals with the filling of electrons into degenerate (equal energy) orbitals of the same sub-shell (p, d ,f). According to this rule: ''Electron pairing in p, d, and f orbitals cannot occur until each orbital of a given sub-shell contains one electron each or is simply occupied with parallel spin''. This is due to the fact that electron being identical in charge , repel each other when present in the same orbital. This repulsion can be minimized if two electrons move as far apart as possible by occupying different degenerate orbitals. Further, all the singly occupied orbitals will have parallel spins i.e., in same direction (either clockwise or
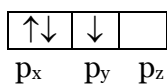
anticlockwise). This is due to the fact that two electrons with parallel spin (in different orbitals) will encounter less inter-electronic repulsions in space than when they have opposite spins (while saying in different orbitals).

↑	↓	↑

p_x $\quad$ p_y $\quad$ p_z
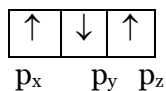
(a) Total spin of unpaired electrons = 1/2- 1/2 + 1/2
$\quad$ = 1/2

↑	↑	↑

p_x $\quad$ p_y $\quad$ p_z
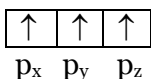
(b) Total spin of unpaired electrons =1/2 +1/2 + 1/2
$\quad$ =$1\frac{1}{2}$

↑↓	↓	

p_x $\quad$ p_y $\quad$ p_z

(c) Total spin = 1/2

In accordance with the Hund's rule, the configuration (a) in which the unpaired electrons do not have parallel spins is incorrect. The configuration (b) in which the three unpaired electrons occupying p_x, p_y, and p_z orbitals have parallel spins (either all clockwise or anticlockwise) is correct while the configuration (c) in which the pairing of the electrons has been shown in p_x orbital without putting the third electron in p_z orbital is also not consistent with the Hund's rule of maximum multiplicity. By the term maximum multiplicity, the total spin of unpaired electrons is maximum. For example, the total spin of the unpaired electron in configuration (a), (b) and (c) are 1/2, $1\frac{1}{2}$ and 1/2 . According to Hund's rule, configuration (b) with maximum multiplicity of $1\frac{1}{2}$ is correct.

Some examples

Electronic configuration of elements with atomic numbers 11 to 20

Element	Atomic number	Electronic configuration	Electronic configuration using noble gas core
Sodium (Na)	11	$1s^2$ $2s^2$ $2p^6$ $3s^1$	[Ne] $3s^1$
Magnesium (Mg)	12	$1s^2$ $2s^2$ $2p^6$ $3s^2$	[Ne] $3s^2$
Aluminium (Al)	13	$1s^2$ $2s^2$ $2p^6$ $3s^2$ $3p^1_x$	[Ne] $3s^2$ $3p^1_x$
Silicon (Si)	14	$1s^2$ $2s^2$ $2p^6$ $3s^2$ $3p^1_x$ $3p^1_y$	[Ne] $3s^2$ $3p^1_x$ $3p^1_y$
Phosphorus	15	$1s^2$ $2s^2$ $2p^6$ $3s^2$ $3p^1_x$ $3p^1_y3p^1_z$	[Ne] $3s^2$ $3p^1_x$ $3p^1_y$ $3p^1_z$
Sulphur (S)	16	$1s^2$ $2s^22p^6$ $3s^2$ $3p^2_x3p^1_y3p^1_z$	[Ne] $3s^2$ $3p^2_x$ $3p^1_y3p^1_z$
Chlorine (Cl)	17	$1s^2$ $2s^2$ $2p^2$ $3s^2$ $3p^2_x$ $3p^2_y$ $3p^1_z$	[Ne] $3s^2$ $3p^2_x$ $3p^2_y$ $3p^1_z$
Argon (Ar)	18	$1s^2$ $2s^2$ $2p^6$ $3s^2$ $3p^2_x$ $3p^2_y$ $3p^2_z$	
Potassium	19	$1s^2$ $2s^2$ $2p^6$	[Ar] $4s^1$

		3s² 3p⁶ 4s¹	
Calcium (Ca)	20	1s² 2s² 2p⁶ 3s² 3p⁶ 4s²	[Ar] 4s²

The electron added in going from one element to the next is called the differentiating electron. It makes the configuration of the atom different from that of atom that precedes it. The differentiating electron is added in each step to the orbital of lowest energy available to it.

**Exceptional Configurations- Stability of Completely filled and Exactly Half-filled Orbitals:**

In certain elements when the two subshells differ slightly in their energies, an electron may shift from a subshell of lower energy to a subshell of higher energy only if such a shift results in the symmetrical distribution (either completely filled or exactly half-filled) of the electron in the various orbitals of the subshell of high energy. This is due to the following two reasons:-

1. **Symmetrical distribution**. It is well known fact symmetry leads to stability. Thus, the electronic configuration in which all the orbital of the same subshell are either completely filled or are exactly half-filled are more stable because of symmetrical distribution of electrons. For example, the expected electronic configuration of chromium (Z=24) is as follow:

$[Cr]_{24}$ - $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^4$
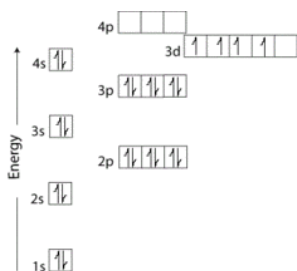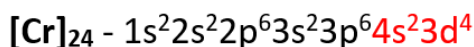
But if one of the 4s electrons shifts to vacant 3d-orbital, the distribution of the electrons will become more symmetrical and this will impart extra stability. Therefore, the electronic

configuration of Cr, as given above, is worng and the actual configuration is as follow :
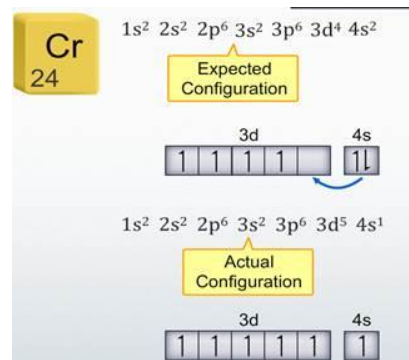
Similarly, the expected electronic configuration of Cu(Z=29) is $1s^2 2s^2 2p^6 3s^2 3p^6 3d^9 4s^2$ is
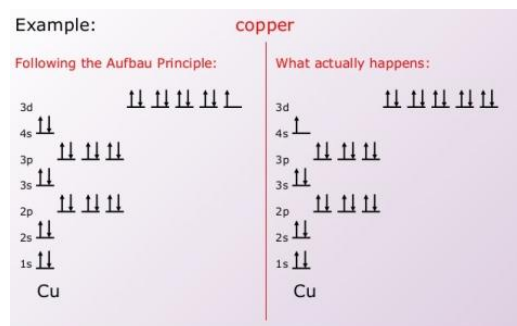

But in this configuration, the distribution of electrons in the five 3d-orbital is not symmetrical. A shift of one electron from the lower energy 4s-orbital to higher energy 3d-orbital will make the distribution of electrons symmetrical and hence will impart more stability. Thus ,the actual electronic configuration of Cu is: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^1$

2. **Exchange energy.** The half-filled and completely filled electronic configuration are also stable due to large exchange of energy of stabilization. The exchange means the shifting of electrons from one orbital to another in the same sub-shell. The electrons with parallel spins present in the degenerate orbitals tend to exchange their position. The energy released during this exchange is called exchange energy. The number of exchanges that can take place is maximum when the degenerate orbitals are exactly half-filled or completely filled. As a result,

the exchange energy is mximum and so is the stability.

The number of exchange that can take place in d^4 configuration are as follow:-

Total exchanges = 3 + 2 + 1 = 6
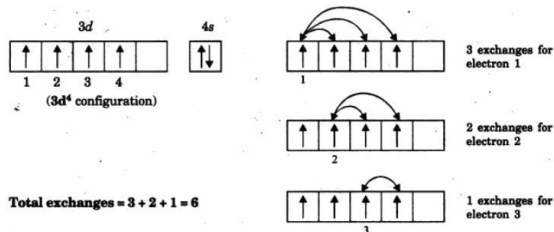
Thus, in **3d^4** arrangement electron exchanges are **six** which implies that there are six possible arrangements with parallel spin in 3d^4 configuration.

The number of exchange that can take place in d^5 configuration are as follows:-

Total exchanges = 4 + 3 + 2 + 1 = 10
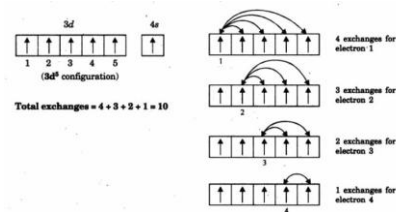
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