Electronic configuration principles.

The distribution of electrons in different orbitals of atom is known as electronic configuration of the atoms.

Filling up of orbitals in the ground state of atom is governed by the following rules:

(1) Aufbau principle

(I) Auf bau is a German word, meaning 'building up'.

(ii) According to this principle, "In the ground state, the atomic orbitals are filled in order of increasing energies i.e. in the ground state the electrons first occupy the lowest energy orbitals available".

(iii) In fact the energy of an orbital is determined by the quantum number n and l with the help of (n+l) rule or Bohr Bury rule.

(iv) According to this rule

(a) Lower the value of n + l, lower is the energy of the orbital and such an orbital will be filled up first.

(b) When two orbitals have same value of (n+l) the orbital having lower value of "n" has lower energy and such an orbital will be filled up first.

Thus, order of filling up of orbitals is as follows:

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

(2) Pauli's exclusion principle

(I) According to this principle, "No two electrons in an atom can have same set of all the four quantum numbers n, l, m and s .

(ii) In an atom any two electrons may have three quantum numbers identical but fourth quantum number must be different.

(iii) Since this principle excludes certain possible combinations of quantum numbers for any two electrons in an atom, it was given the name exclusion principle. Its results are as follows:

(a) The maximum capacity of a main energy shell is equal to $2n^2$ electron.

(b) The maximum capacity of a subshell is equal to 2(2l+1) electron.

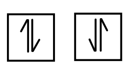
(c) Number of sub-shells in a main energy shell is equal to the value of n.

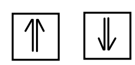
(d) Number of orbitals in a main energy shell is equal to n^2.

(e) One orbital cannot have more than two electrons.

(iv) According to this principle an orbital can accommodate at the most two electrons with spins opposite to each other. It means that an orbital can have 0, 1, or 2 electron.

(v) If an orbital has two electrons they must be of opposite spin.


Correct


Incorrect

(3) Hund's Rule of maximum multiplicity

(I) This rule provides the basis for filling up of degenerate orbitals of the same sub-shell.

(ii) According to this rule "Electron filling will not take place in orbitals of same energy until all the available orbitals of a given subshell contain one electron each with parallel spin".

(iii) This implies that electron pairing begins with fourth, sixth and eighth electron in p, d and f orbitals of the same subshell respectively.

(iv) The reason behind this rule is related to repulsion between identical charged electrons present in the same orbital.

(v) They can minimize the repulsive force between them serves by occupying different orbitals.

(vi) Moreover, according to this principle, the electron entering the different orbitals of subshell have parallel spins. This keep them farther apart and lowers the energy through electron exchange or resonance.

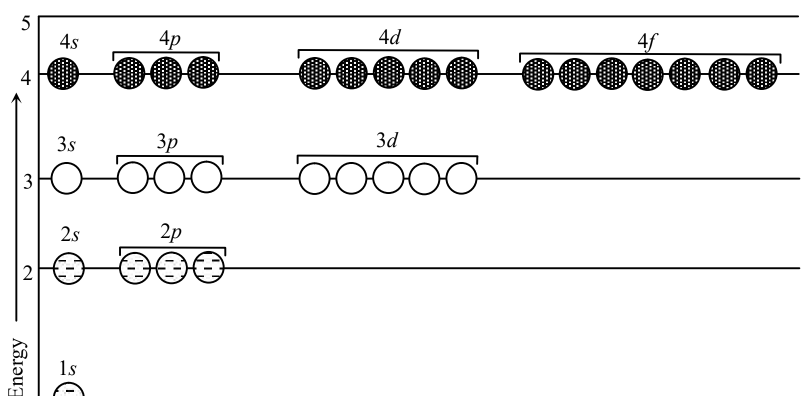
(vii) The term maximum multiplicity means that the total spin of unpaired e^- is maximum in case of correct filling of orbitals as per this rule.

Energy level diagram

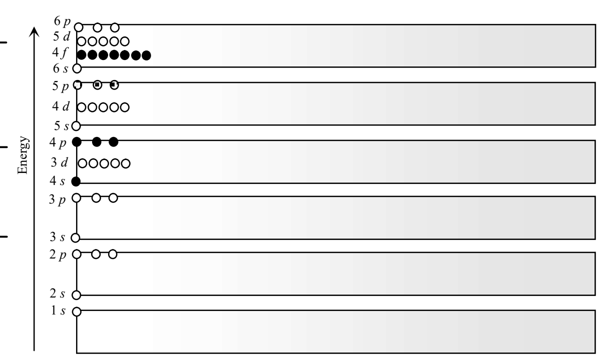
The representation of relative energy levels of various atomic orbital is made in the terms of energy level diagrams.

One electron system: In this system $1s^2$ level and all orbital of same principal quantum number have same energy, which is independent of (l). In this system l only determines the shape of the orbital.

Multiple electron system: The energy levels of such system not only depend upon the nuclear charge but also upon the electron present in them.



Energy level diagram of one electron system



Energy level diagram of multiple electron system

Diagram of multi-electron atoms reveals the following points:

(i) As the distance of the shell increases from the nucleus, the energy level increases. For example energy level of 2 > 1.

(ii) The different sub shells have different energy levels which possess definite energy. For a definite shell, the subshell having higher value of l possesses higher energy level. For example in 4th shell.

Energy level order	4f	>	4d	>	4p	>	4s
	l= 3		l = 2		l = 1		l= 0

(iii) The relative energy of sub shells of different energy shell can be explained in the terms of the (n+l) rule.

(a) The sub-shell with lower values of (n + l) possess lower energy.

For	3d	n = 3	l= 2	∴ n + l = 5
For	4s	n = 4	l = 0	n + l = 4

(b) If the value of (n + l) for two orbitals is same, one with lower values of 'n' possess lower energy level.

Extra stability of half-filled and completely filled orbitals

Half-filled and completely filled sub-shell have extra stability due to the following reasons:

(I) Symmetry of orbitals

(a) It is a well-known fact that symmetry leads to stability.

(b) Thus, if the shift of an electron from one orbital to another orbital differing slightly in energy results in the symmetrical electronic configuration. It becomes more stable.

(c) For example p^3, d^5, f^7 configurations are more stable than their near ones.

(ii) Exchange energy

(a) The electron in various subshells can exchange their positions, since electron in the same subshell have equal energies.

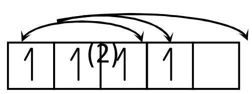
(b) The energy is released during the exchange process with in the same subshell.

(c) In case of half-filled and completely filled orbitals, the exchange energy is maximum and is greater than the loss of orbital energy due to the transfer of electron from a higher to a lower sublevel e.g. from 4s to 3d orbitals in case of Cu and Cr .

(d) The greater the number of possible exchanges between the electrons of parallel spins present in the degenerate orbitals, the higher would be the amount of energy released and more will be the stability.

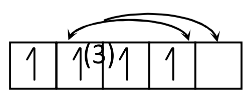
(e) Let us count the number of exchange that are possible in d^4 and d^5 configuration among electrons with parallel spins.

d^4(1)



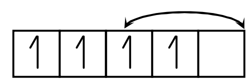
3 exchanges by 1st e^-

(2)



2 exchanges by 2nd e^-

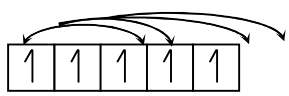
(3)



Only 1 exchange by 3rd e^-

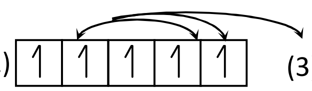
To number of possible exchanges = 3 + 2 + 1 =6

d^5(1)



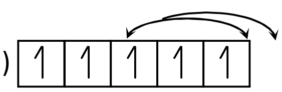
4 exchanges by 1st e^-

(2)



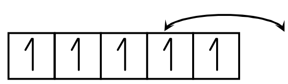
3 exchanges by 2nd e^-

(3)



2 exchange by 3rd e^-

(4)



1 exchange by 4th e^-

To number of possible exchanges = 4 + 3 + 2 +1 = 10