

1.2 PAULI'S EXCLUSION PRINCIPLE

Electrons with the same spin repel each other and occupy different orbitals and if they have to occupy the same orbital, they must have opposite spins. This is the result of Pauli's exclusion principle put forward by Pauli in 1925. It states:

No two electrons in an atom can have identical set of four quantum numbers.

Another way of stating Pauli principle is as follows:

In an atom, a maximum of two electrons can occupy the same orbital.

The two electrons in the same orbital will have identical n , l and m but must have different spins ($+ 1/2$ and $- 1/2$).



Wolfgang Pauli

Pauli exclusion principle has no mathematical explanation but is an experimental fact. Although no proof of the exclusion principle exists, there has been no contradiction to this.

1.3 HUND'S RULE OF MAXIMUM MULTIPLICITY

It can be stated in two parts as given below:

(a) In an atom, no electron pairing takes place in the p and d or f orbitals respectively until each orbital of the given subshell contains one electron.

(b) The unpaired electrons present in the various orbitals of the same subshell should have parallel spins.

For example, each of three p -orbitals of the $2p$ -subshell gets one electron of parallel spin before any one of them receives a second electron of opposite spin.

This is because presence of the electron each in two orbitals of the same subshell involves lesser inter-electronic repulsion as compared to the electrons in the same orbital. Therefore, it leads to lower energy state.

Moreover, electrons in half-filled orbitals of the same subshell experience less inter-electronic repulsion in space when they have parallel spins than when their spins are opposite.

1.4 ORDER OF FILLING OF VARIOUS ORBITALS

The energy state of an orbital depends not only upon the principal quantum number, n , but also, to some extent, on the angular momentum quantum numbers, l . In other words, the orbitals having the same principal quantum number can have different energy values.

This happens because

- (i) The increased nuclear charge leads to somewhat contraction of all the inner orbitals.
- (ii) The shielding of nucleus by the intervening core of electrons affects the energy of the outer electrons.

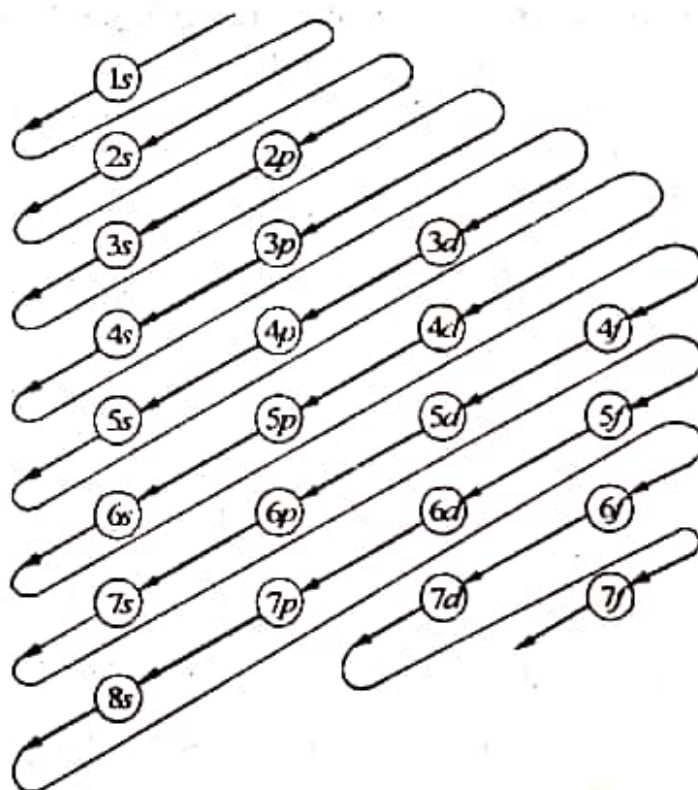
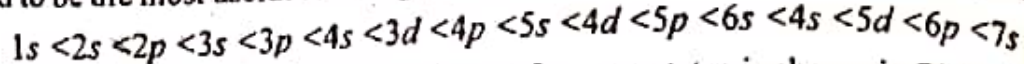


Fig. 1.21. An aid to memory for order of filling orbitals.

It has been found that within a given main energy level (n), the energy states do not degenerate but increase in the order $s < p < d < f$. Since the energy of a given orbital depends on nuclear charge (z) different types of orbitals are affected to different extents. The following sequence is considered to be the most useful for assigning outermost or valence electrons for all the elements:



An easy way to remember the order of filling of energy states is shown in Fig. 1.19. Represent a given orbital by a circle. Then draw orbitals of each principal quantum number on the same horizontal level. Draw parallel arrows and follow these as shown in Fig. 1.26, starting from $1s, 2s, 2p, 3p \rightarrow 4s$ and so on.

Example 9. Arrange the following orbitals in order of increasing energy for a multielectron atom $1s, 3s, 5s, 2p, 4p, 3d, 4d,$ and $4f$.

Solution. Follow Fig. 1.21. The order comes out to be: $1s, 2p, 3s, 3d, 4p, 5s, 4d, 4f$

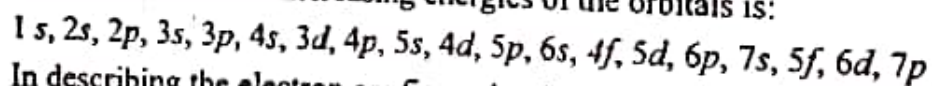
1.5 AUFBAU PRINCIPLE ($n + l$) RULE

According to Aufbau principle: "In the ground state of an atom the electrons occupy the lowest energy orbitals available to them". This means that the electrons enter the orbitals in order of increasing energies. The lowest energy available orbitals being filled up first.

Since the energy of orbitals is determined by the quantum numbers n and l , the sequence of filling the orbitals proceeds according to the following rules:

- Orbitals are filled in order of increasing value of $n + l$. For instance, $4s$ ($n + l = 4 + 0 = 4$) is filled before $3d$ ($n + l = 3 + 2 = 5$).
- For the orbitals having the same value of $n + l$ the orbital having lower value of n is filled up first. For example, $2p$ ($n + l = 2 + 1 = 3$) is filled before $3s$ ($n + l = 3 + 0 = 3$) because $2p$ has lower value of n .

The general order of increasing energies of the orbitals is:



In describing the electron configuration by s, p, d and f notations, one must remember that there is one orbital in an s -subshell, three degenerate (of equal energy) orbitals in a p -subshell, five degenerate orbitals in a d -subshell and seven degenerate orbitals in an f -subshell. Each orbital accommodates two electrons and a given subshell is filled before electrons are added to the next subshell. Each subshell can accommodate a maximum of $4l + 2$ electrons. As for example, s -subshell ($l = 0$) has a maximum of 2 electrons, p -subshell ($l = 1$) 6 electrons, d -subshell ($l = 2$) 10 electrons, f -subshell ($l = 3$) 14 electrons.

The ground state electronic configuration of hydrogen atom is obtained by placing the electron in the lowest energy subshell. It is represented as $1s^1$. The four quantum numbers n, l, m and m_s for hydrogen atom have values 1, 0, 0 and $1/2$ (there is no preference for $1/2$ and it may be any orientation $1/2$ or $-1/2$) respectively. The electronic configuration for He is $1s^2$ with n, l, m and m_s values 1, 0, 0 and $1/2$ and $1, 0, 0, -1/2$ respectively for the two electrons. The first energy level gets completely filled at He because the maximum number of electrons it can have is two ($2n^2 = 2 \times 1^2 = 2$). The electronic configurations for Li ($z = 3$), Be ($z = 4$), B ($z = 5$) are $1s^2, 2s^1, 1s^2, 2s^2$ and $1s^2, 2s^2, 2p^1$ respectively.

Electronic configuration of carbon ($z = 6$) is $1s^2, 2s^2, 2p_x^1, 2p_y^1$, and not $1s^2, 2s^2, 2p_z^2$ as per Hund's rule of maximum multiplicity.

Thus, the electronic configuration of nitrogen ($z = 7$) would be $1s^2, 2s^2, 2p_x^1, 2p_y^1, 2p_z^1$ and not $1s^1, 2s^2, 2p_x^2, 2p_y^1$ and $2p_z^0$. Once all the three p -orbitals in the subshell are half-filled, pairing will start at oxygen ($z = 8$) to give $1s^2, 2s^2, 2p_x^2, 2p_y^1, 2p_z^1$. The pattern continues and nothing unusual is observed up to Argon ($z = 18$), $1s^2, 2s^2, 2p^6, 3s^2, 3p^6$ as given in Table 1.3.

Although $3d$ -orbitals are vacant, yet the ground state configurations of potassium ($z = 19$) and calcium ($z = 20$) are $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^1$ and $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2$ respectively because $4s$ subshell is lower in energy than the $3d$ subshell. Because of greater penetration, $4s$ electron faces higher nuclear charge and this effect is so pronounced that in spite of higher principal quantum number, the energy of the $4s$ subshell is lower than that of $3d$ subshell. At the next element scandium ($z = 21$), the $3d$ orbitals start filling up and this continues till $3d$ subshell is completely filled at zinc ($z = 30$).

Electronic configuration of the elements are given in Table 1.3.

Table 1.3. Ground state electronic configurations of gaseous atoms.

Z	Symbol	Configuration as [Core] plus "Outermost" Orbitals	Z	Symbol	Configuration as [Core] plus "Outermost" Orbitals
1	H	$1s^1$	21	Sc	$[\text{Ar}] 3d^1 4s^2$
2	He	$1s^2$, or [He]	22	Ti	$[\text{Ar}] 3d^2 4s^2$
3	Li	[He] $2s^1$	23	V	$[\text{Ar}] 3d^3 4s^2$
4	Be	[He] $2s^2$	24	Cr	$[\text{Ar}] 3d^5 4s^1$
5	B	[He] $2s^2 2p^1$	25	Mn	$[\text{Ar}] 3d^5 4s^2$
6	C	[He] $2s^2 2p^2$	26	Fe	$[\text{Ar}] 3d^6 4s^2$
7	N	[He] $2s^2 2p^3$	27	Co	$[\text{Ar}] 3d^7 4s^2$
8	O	[He] $2s^2 2p^4$	28	Ni	$[\text{Ar}] 3d^8 4s^2$
9	F	[He] $2s^2 2p^5$	29	Cu	$[\text{Ar}] 3d^{10} 4s^1$
10	Ne	[He] $2s^2 2p^6$ or [Ne]	30	Zn	$[\text{Ar}] 3d^{10} 4s^2$
11	Na	[He] $3s^1$	31	Ga	$[\text{Ar}] 3d^{10} 4s^2 4p^1$
12	Mg	[Ne] $3s^2$	32	Ge	$[\text{Ar}] 3d^{10} 4s^2 4p^2$
13	Al	[Ne] $3s^2 3p^1$	33	As	$[\text{Ar}] 3d^{10} 4s^2 4p^3$
14	Si	[Ne] $3s^2 3p^2$	34	Se	$[\text{Ar}] 3d^{10} 4s^2 4p^4$
15	P	[Ne] $3s^2 3p^3$	35	Br	$[\text{Ar}] 3d^{10} 4s^2 4p^5$
16	S	[Ne] $3s^2 3p^4$	36	Kr	$[\text{Ar}] 3d^{10} 4s^2 4p^6$ or [Kr]
17	Cl	[Ne] $3s^2 3p^5$	37	Rb	[Kr] $5s^1$
18	Ar	[Ne] $3s^2 3p^5$ or [Ar]	38	Sr	[Kr] $5s^2$
19	K	[Ar] $4s^1$	39	Y	[Kr] $4d^1 5s^2$
20	Ca	[Ar] $4s^2$	40	Zr	[Kr] $4d^2 5s^2$

(Contd.)