

# Development of Electronic Configurations

## INTRODUCTION -

There are more than 220 subatomic particles discovered so far as components of atoms. Three of these electron, neutron and proton, are of much interest to the chemists. The number of electrons which is the same as the number of protons in an atom determines the atomic number, whereas the sum of the number of protons and neutrons determine the mass number.

It could be said that the number of electrons and their arrangement in an atom determines the reactivity of the atom. This is the singular reason why elements in the same group in the periodic table have the same electron architecture. Elements with similar electron arrangement react in the same way. The number of electrons could determine how slow or fast they will react.

The arrangement of electrons in an atom of an element is called the electron configuration. For any atom, the four quantum numbers, principal, subsidiary, magnetic and spin quantum number, describe the position of each electron in terms of the shell, subshell, orbital or spin. The principal quantum number,  $n$ , describes the energy, the subsidiary quantum number,  $l$ , describes the shape while the magnetic quantum number,  $m$ , describes the orientation of the volume the electron occupies in an atom. This volume is called an orbital. The fourth quantum number, called the electron spin quantum number,  $s$ , describes the spin orientation of the electron in an orbital. It assumes only two values,  $+1/2$  or  $-1/2$ .

The orbitals occur in definite energy levels in the atoms. Therefore, it is possible to describe each electron based on its orbital occupation and the energy level.

The process of arranging the electrons is based on Aufbau's process.

## 1.1 The Aufbau process (German: "building up" process)

The Aufbau process discussed how that electrons fill the lowest energy orbital first, and then move up to higher energy orbitals only after the lower energy orbitals are full. However, there is a problem with this rule. Certainly, 1s orbital should be filled before 2s orbitals, because the 1s orbital have a lower value of  $n$ , and thus a lower energy. What about the three different 2p orbitals? In what order should they be filled? The answer to this question involves Hund's rule.

The Aufbau principle employs a shorthand notation for writing electronic configuration. The formulae  $n\ell^x$  where  $n$  is the principal quantum number,  $\ell$  is the subshell (orbital) and  $x$  is the number of electrons in the subshell is adopted. For example,  $2p^2$  implies that the energy level is 2, subshell (orbital) is p and number of electron in the orbital is 2.

This arrangement is based on three concepts (CnD) Rule, Hund's Rule and Pauli Exclusion Principle.

### 2 (CnD) Rule - Energy of Orbitals

2 This rule states that the electron will enter the subshell (orbital) of lowest energy first. What this implies is that in the building of atoms, electrons are fed into atomic orbitals and orbitals of lowest energy are filled first.

The orbitals of lowest energy is the one with lowest (n+l) values (n = principal quantum number and  $\ell$  = subshell quantum number).

if two orbitals have the same (n+l) value, the one of lower energy will be orbital of lower  $n$  value. The relative energies of the orbital will be in the order:  $1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s, 4d,$   
 $5p, 6s, 4f, 5d, 6p, 7s$  etc.

(2)

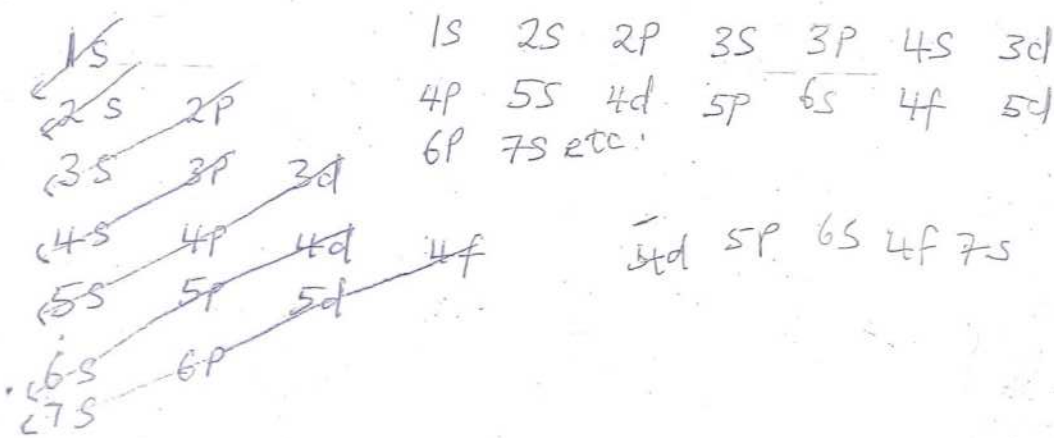
The (n+l) values of some of these orbitals is given in Table I: (n+l) values of some orbitals.

orbitals	n	l	(n+l)
3s	3	0	3
3p	3	1	4
4s	4	0	4
4p	4	1	5
5s	5	0	5
3d	3	2	5
4d	4	2	6
5p	5	1	6
6s	6	0	6

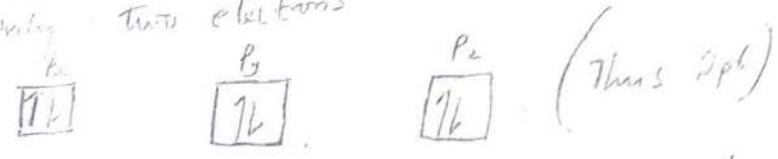
Note that l values are 0, 1, 2, 3 for s, p, d and f orbitals respectively, we can see from table I that 6s, 5p and 4d have the same (n+l) values. However, in determining which orbitals will be filled first (lowest energy) to use rule (3) by taking the combination with lowest n value. That means that energy gradation and sequence of filling will be  $4d < 5p < 6s$ .

Generally, the sequence of constructing the electron configuration will be as in Fig I.

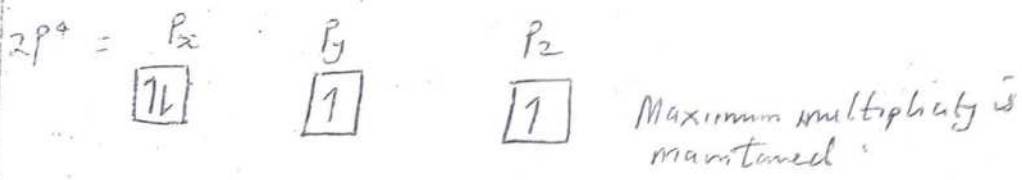
Fig I: Sequence of filling energy levels



For example, when  $n$  is equal to 2, there are two available orbitals ( $2s$  and  $2p$ ). The  $p$ -orbital has three sub-orbitals ( $p_x, p_y, p_z$ ) showing the orientation of the lobes of the orbitals in an atom. Each of these orbitals can accommodate only two electrons.



However for a  $2p^3$  configuration, Hund's rule gives that the filling will be:



Rather than  $\begin{array}{|c|} \hline \uparrow\downarrow \\ \hline \end{array}$   $\begin{array}{|c|} \hline \uparrow \\ \hline \end{array}$   $\begin{array}{|c|} \hline \downarrow \\ \hline \end{array}$  (Incorrect) or

or  $\begin{array}{|c|} \hline \uparrow\downarrow \\ \hline \end{array}$   $\begin{array}{|c|} \hline \uparrow\downarrow \\ \hline \end{array}$   $\begin{array}{|c|} \hline \\ \hline \end{array}$  (Incorrect)

As a result of Hund's rule, constraints are placed on the way atomic orbitals are filled in the ground state using the Aufbau principle. Before any two electrons occupy an orbital in a subshell, other orbitals in the same subshell must first each contain one electron. Also, the electrons filling a subshell will have parallel spin before the shell starts filling up with the opposite spin electrons (after the first orbital gains a second electron). As a result, when filling up atomic orbitals, the maximum number of unpaired electrons (and hence maximum total spin state) is assumed.

In general, atoms acquire extra stability when degenerate orbitals are either half filled (all parallel spins) or completely filled (spin paired).

## HUND'S RULE OF MAXIMUM MULTIPLICITY

The rule was discovered by Friedrich Hund in 1925, is of important use in atomic chemistry, spectroscopy, and quantum chemistry. The rule is based on observations of atomic spectra, which is used to predict the ground state of an atom or molecule with one or more open electronic shells. The rule states that for a given electron configuration, the lowest energy term is the one with the greatest value of spin multiplicity. This implies that if two or more orbitals of equal energy are available, electrons will occupy them singly before filling them in pairs.

In atoms with more than one electron, the electrons repel each other. The effective nuclear charge varies with the atomic number as the inner shell electrons screen the outer ones. The net result is only determined approximately. This approximation gives rise to similar orbital properties but different energies. As a result, the orbital energies are shifted as shown in Fig 2:

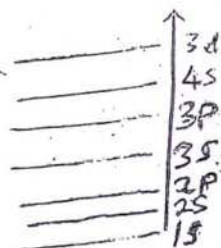


Fig 2: Relative orbital energies

In line with these developments, Hund developed a rule to account for the fact that electrons are distributed as far as possible.

The rule states that in a set of orbitals (subshells) of equal energy (degenerate), no two electrons will pair up until all the degenerate orbitals are single filled. In other words, when suborbitals of identical energy are available, an atom tends to have as many unpaired electrons as possible. The electrons are arranged so as to give optimal number of unpaired electrons.

In determining the electronic configuration of ions, the  $(n+l)$  rule will still be followed. In filling the electrons, it should be noted that electrons are <sup>first</sup> ~~last~~ <sup>last</sup> from the orbital with the highest  $n$  value.

Where many orbitals have the same  $n$  value, electron is first from the one with higher  $l$  value.

I Arrange the following orbitals in the order of increasing stability:  $6s, 5p, 4f, 7s, 4d$ .

Solution: the  $(n+l)$  rule is used to determine the relative energy of the orbitals.

Orbital	$n$	$l$	$(n+l)$
$6s$	6	0	6
$5p$	5	1	6
$4f$	4	3	7
$7s$	7	0	7
$4d$	4	2	6

\* The orbital of lowest  $(n+l)$  value is the orbital of lowest energy and therefore the most stable.

\* Where two orbitals have the same  $(n+l)$  value, the more stable orbital is the orbital with the lower  $n$  value.

② What is the maximum number of electrons orbitals with the following set of quantum numbers will possess and why?

- $n=2, l=1$
- $n=3, l=2$
- $n=3, l=3$
- $n=4, l=3$

Solution

(i) When  $l=1, m=1 = -1, 0, +1$  (three values of  $m$ )  
 For each value of  $m$  there are two values of  $s$  ( $+\frac{1}{2}$  and  $-\frac{1}{2}$ )

This is the case of noble gases, ions with half-filled configurations ( $p^3, d^5, f^7$ ) or completely filled configurations ( $p^6, d^{10}, f^{14}$ ) also show some degree of enhanced stability.

For example, nitrogen ( $Z=7$ )  $1s^2 2s^2 2p^3$ ,  
 Chromium ( $Z=24$ )  $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1 3d^5$ ,  
 Oxygen ( $Z=8$ )  $1s^2 2s^2 2p^4$ .

Keep in mind that elemental Oxygen and Nitrogen are found in nature typically as dioxygen and dinitrogen respectively.

Summarily according to Hund's rule of maximum multiplicity,

- (1) The electrons tend to avoid being in the same orbital. Thus as the electrons are successively added, a maximum number of electrons will try to occupy orbitals singly.
- (2) When all the orbitals are singly occupied, only then the pairing of electrons commences.
- (3) In the ground state, the electrons occupying the orbitals singly will have their spins parallel.

Hund's rule indicates that electronic arrangement  $\uparrow \uparrow$  is more stable than  $\uparrow \downarrow$   $\square$   $\square$   
 $N (Z=7)$   
 $1s^2, 2s^2, 2p_x^1, 2p_y^1, 2p_z^1$  = Correct  
 $1s^2, 2s^2, 2p_x^2, 2p_y^1, 2p_z^0$  = Incorrect

1.5. ELECTRONIC CONFIGURATION OF IONS

The only difference between writing a normal electron configuration and writing the electron configuration for an ion is that when writing an electron configuration for an ion, you have to remember to add or subtract electrons from your total. And, if the element is an anion (negative charge), you must add electrons to your total. Example are below:

$Al \rightarrow Al^{3+} + 3e^-$   $1s^2 2s^2 2p^6 = 10$  electrons instead of 13 electrons  
 $S \cdot + 2e^- \rightarrow S^{2-}$   $1s^2 2s^2 2p^6 3s^2 3p^6$  instead of 16 electrons

In determining the electronic configuration of an atom (or ion), the rule will still be followed by filling the orbitals. It should be noted that electrons are first <sup>lost</sup> from the orbital with the highest  $n$  value.

where many orbitals have the same  $n$  value, electrons are first lost from the one with higher  $l$  value.

Arrange the following orbitals in the order of increasing stability:  $6s, 4f, 5d, 7s, 4d$

Solution: The  $(n+l)$  rule is used to determine the relative energy of the orbitals.

Orbital	$n$	$l$	$(n+l)$
$6s$	6	0	6
$4f$	4	3	7
$5d$	5	2	7
$7s$	7	0	7
$4d$	4	2	6

- The orbital of lowest  $(n+l)$  value is the most stable (lowest energy) and therefore the one filled first.
- Where two orbitals have the same  $(n+l)$  value, the more stable orbital is the orbital with the lower  $n$  value.

Q. What is the maximum number of electron orbitals in the following set of quantum numbers will possess and why?

- (i)  $n=2, l=1$
- (ii)  $n=3, l=2$
- (iii)  $n=3, l=3$
- (iv)  $n=4, l=3$

Solution

(i) when  $l=1, m=1, 0, -1$  (three values of  $m$ )  
 for each value of  $m$  there are two values of  $m_s$  ( $+\frac{1}{2}$  and  $-\frac{1}{2}$ )



Therefore this orbital will occupy a maximum of  $2 \times 2$  electrons = 4 (one electron for  $4z$  and another for  $4x$ ).

(ii) where  $l=2$  the values of  $m = -2, -1, 0, 1, 2$ . Each value represents an orbital which can accommodate a maximum of two electrons. Therefore where  $l=2$ , the orbital can accommodate a maximum of 10 electrons.

(iii)  $n=3, l=3$ . This case is not possible since the value of  $l$  cannot be greater than  $n-1$ . This implies that  $l$  cannot be equal to  $n$ .

(iv) where  $n=4$  and  $l=3$ , the values of  $m$  will be  $-3, -2, -1, 0, 1, 2, 3$ . Seven values of  $m$ . The seven values implies 14 electrons.

3. Determine the maximum number of electrons in an orbital described by the following quantum numbers and write the appropriate orbital filling.

(i)  $n=2, l=0$ .

(ii)  $n=4, l=3$ .

(iii)  $n=3, l=2$ .

### Solution

(i)  $n=2, l=0$ : The value of  $m$  is only one. This implies maximum of two electrons. Where  $l=0$ , it represents an  $s$  orbital. Since  $n=2$ , the orbital occupation is  $2s^2$ .

(ii)  $n=4, l=3$ . <sup>This means</sup> where  $l=3, m = -3, -2, -1, 0, 1, 2, 3$  (seven values) <sup>Maximum of ten electrons</sup>. Since  $n=4$ , orbital filling will be  $4d^{10}$ .

(iii)  $n=3, l=2$ . where  $l=2, m = -2, -1, 0, 1, 2$  (five values). This implies a maximum of ten electrons. Since  $n=3$ , orbital filling will be  $3d^{10}$ .

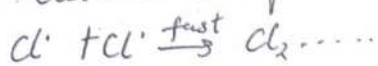
## 1.6 CONSEQUENCES OF ELECTRONIC CONFIGURATION

Electron Configuration of an atom of an element could be pointer to

- (i) Its reactivity
- (ii) Nature of bond it forms with other elements
- (iii) The magnetic properties
- (iv) Enhanced stability of the atom or ion
- (v) Colour of ions and compounds

### Reactivity:

Free radicals that have unpaired electrons are known to be <sup>very</sup> reactive. This is as a result of instability in that state. When it reacts it becomes stable when the electrons are paired up in orbital.

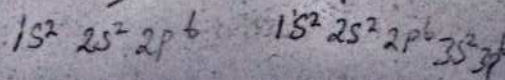
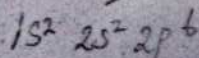
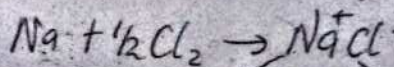
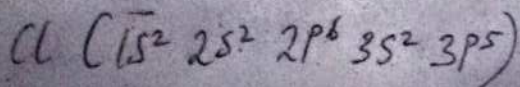
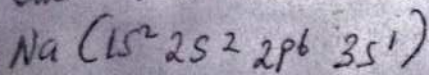


Group I elements have  $s^1$  electron configuration in their outermost shell. They will easily transfer this single electron to another atom during reaction in order to attain outer  $p^6$  which is more stable. Example  
Na ( $Z=11$ )  $1s^2, 2s^2, 2p^6, \underline{3s^1}$  will lose  $s^1$  to maintain more stable  $p^6$ .

### TYPES OF BONDING

Highly electropositive elements have such electron configuration that allows them to lose electrons in order to achieve a measure of stability.

When they lose electrons, they become positively charged. In this state, they can form ionic bonds with other atoms that accepted the electrons.



salt  
(ionic bond)

(11)  
The reaction (2) shows that Cl with electronic configuration  $3s^2 3p^5$  will easily accept electrons to become  $Cl^-$  were to react, the most likely pathway is to share the electrons in order to have  $3s^2 3p^6$  (Octet) this also ensures stability.

If two atoms of Cl were to react, the most likely pathway is to share the electrons in order to have  $3s^2 3p^6$  (Octet) configuration.

### MAGNETIC PROPERTIES

Any substance can exhibit any of three forms of magnetism, paramagnetism, diamagnetism and ferromagnetism, presence of unpaired electrons in the electronic configuration of an element leads to paramagnetism. This implies that it is attracted strongly in a magnetic field.

However, where paired electrons feature in the electronic configuration of an element, it results in diamagnetism, this is a feature indicating that the substance is weakly repelled in a magnetic field. Paramagnetism overshadows diamagnetism when both occur in an element.

All compounds exhibit diamagnetism properties because of presence of paired electrons in them. This is because the process of compounds formation results from bonding between atoms. Bonding is either by electron transfer or electron sharing.

Both processes lead to electron sharing (having paired electrons in all orbitals). However, ions and atoms could have unpaired electrons.

The extent of paramagnetism is given by the magnetic moment ( $M$ ):  $M = \sqrt{n(n+2)} B.M$

$n =$  Number of unpaired electrons

BM = Bohr magneton (Unit of magnetic moment)

for <sup>example</sup>  $Cu(I), Cu^{2+}$

It has one unpaired electron ( $n=1$ )

$$\mu = \sqrt{1(1+2)} = \sqrt{3} = 1.73 \text{ BM (paramagnetic)}$$

for  $Be = 1s^2, 2s^2$   $n=0$  (unpaired e<sup>-</sup>)

$$\mu = \sqrt{0(0+2)} = 0 \text{ B.M (Diamagnetic)}$$

Cooperative interactions of unpaired electrons of individual paramagnetic atoms with one another gives rise to very strong attraction of some substances to a magnetic field.

This phenomenon is known as ferromagnetism.

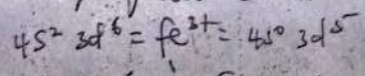
Fe, Ni, and Co exhibit ferromagnetism. Their magnetic susceptibility is greatly enhanced compared with what it would be if all the moments behaved independently.

Ferromagnetism features in many of the transition metals and their compounds; Fe, Ni, and Co can form permanent magnets.

Antiferromagnetism results when the moments in adjacent atoms are paired so that they point in opposite directions. This is some sense sort of destructive interaction of unpaired electrons of paramagnetic atoms. In this case, the substance is not attracted to a magnetic field as expected.

### ENHANCED STABILITY OF ATOM OR ION

Certain configurations result in enhanced stability of the atom or ion. It had earlier been stated that electron configurations bearing half-filled or completely filled shell result in enhanced stability.



For example,  $Fe^{3+}$  has  $d^5$  configuration (1/2 filled) but  $Fe^{2+}(d^6)$  is not half filled. Therefore  $Fe(III)$  is more stable than  $Fe(II)$ .

Why can  $Fe(II)$  is readily oxidized to  $Fe(III)$ ,  $Fe(III)$  is not readily reduced to  $Fe(II)$

$Zn(II)$  is  $d^{10}$  configuration (completely filled and very stable) it is difficult to oxidize it to  $Zn(III)$  ( $d^9$ )

The first ionization energies of the noble gases He, Ne, Ar, Xe and Kr are the highest in their respective periods. This is because they have completely filled shells that give them enhanced stability but it is difficult to remove the electrons

### COLOUR OF SUBSTANCE

Certain substances show different colours. For instance, transition metals and their compounds are coloured. Colours arise from absorption of visible light by substances. The colours that are seen are the complementary colours (wavelengths) absorbed. The colours seen are the emitted radiations. Absorption of light leads to promotion of electrons from a ground state to an excited state. When this absorbed radiation is emitted, the electrons return to the ground state.

Most substances that have unpaired electrons show colours because orbitals are available for electron transition.

Examples :-

#### Colours of Transition metal ions

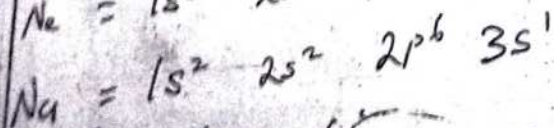
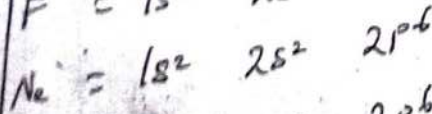
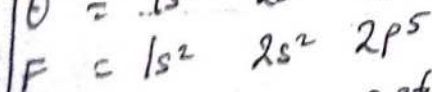
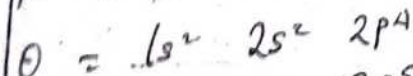
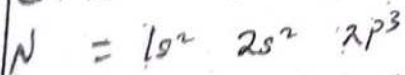
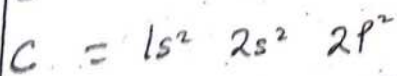
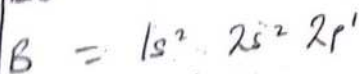
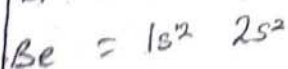
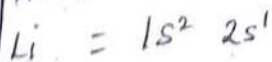
$Fe(II)$	$d^6$	Light blue
$Fe(III)$	$d^5$	brown
$Cu(II)$	$d^9$	blue
$Co(II)$	$d^7$	pink
$Zn(II)$	$d^{10}$	Colourless
$Cd(II)$	$d^{10}$	Colourless
$Mn(II)$	$d^5$	pink

## HUNDS'S RULES CONTD

When atoms are in their ground state, the electrons occupy the lowest possible energy levels.

The simplest element, hydrogen, has one electron, which occupies the 1s level; this level has the principal quantum number  $n=1$ , and the subsidiary quantum number  $l=0$ .

Helium has two electrons. The second electron also occupies the 1s level. This is possible because the two electrons have opposite spins. This level is now full. The next atom, Lithium, has three electrons - The third electron occupies the next lowest level. This is 2s level, which has the principal quantum number  $n=2$  and subsidiary quantum number  $l=0$ . The electronic structures of the first few atoms in the periodic table may be written

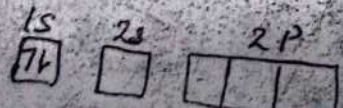


An alternative way of showing the electronic structure of an atom is to draw boxes for orbitals, and arrows for electrons.

Electronic structure of H atom in ground state



Electronic structure of He atom in ground state

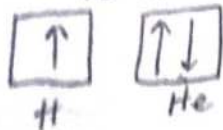


## 1.3 PAULI EXCLUSION PRINCIPLE

(4)

Wolfgang Pauli extensively studied atomic spectra. The Pauli Exclusion Principle states that, in an atom or molecule, no two electrons can have the same four quantum numbers. As an orbital can contain a maximum of only two electrons, the two electrons must have opposing spins. This means that if one is assigned an up-spin ( $+\frac{1}{2}$ ), the other must be down spin ( $-\frac{1}{2}$ ) and they are said to be paired.

Electrons in the same orbital have the same first three quantum numbers, e.g.  $n=1, l=0, m=0$  for 1s subshell. Only two electrons can have these numbers, so that their spin moments must either  $M_S = +\frac{1}{2}$  or  $M_S = -\frac{1}{2}$ . If 1s orbital contain only one electron, we have one  $M_S$  value and the electronic configuration written as  $1s^1$  (corresponding to hydrogen). If  $1s^2$  (corresponding to helium), it is fully occupied we have two electrons. For He,  $n=1$  for both e's,  $l=0$  and  $m_l=0$  for both electrons but  $M_S = +\frac{1}{2}$  and  $-\frac{1}{2}$ . As you can see, 1s subshell can hold two electrons and when filled, the electrons have opposite spins!



In any given shell, the total number of electrons is given by  $2n^2$  ( $n = \text{principal quantum number}$ ). All orbitals in each energy level have the same energy and are called degenerate.

Since three quantum numbers,  $n, l$  and  $m$ , are needed to define an orbital, each orbital may hold up to two electrons, provided they have opposite spins.

An extra quantum number is required to define the spin of an electron in an orbital. Thus four quantum numbers are needed to define the energy of an electron in an atom.

The Pauli exclusion principle states that no two electrons in one atom can have all four quantum numbers the same.

There are some things that you can't predict  
electron number and position is much interest to the  
chemist. The number of electrons in the atom is  
the number of protons in the atom. The atom  
number means the sum of the number of protons and  
neutrons. It is the same for all atoms.  
It could be said that the number of electrons and  
their arrangement in an atom determine the reactivity  
of the atom. This is the reason why elements  
in the same group in the periodic table have the same  
electron configuration. Elements with similar electron  
configuration react in the same way. The number of  
electrons could determine how slow or fast they will react.

The arrangement of electrons in an atom of an element  
is called the electron configuration. For any atom, the  
four quantum numbers, principal, subsidiary, magnetic and  
spin quantum number, describe the position of each  
electron in terms of the shell, subshell, orbital or spin.  
The principal quantum number,  $n$ , describes the energy,  
the subsidiary quantum number,  $l$ , describes the shape while  
the magnetic quantum number,  $m$ , describes the orientation  
of the volume the electron occupies in an atom. This  
volume is called an orbital. The fourth quantum number,  
called the electron spin quantum number,  $s$ , describes  
the spin orientation of the electron in an orbital.  
It assumes only two values,  $+\frac{1}{2}$  or  $-\frac{1}{2}$ .

The orbitals occur in definite energy levels in the atoms.  
Therefore, it is possible to describe each electron based on  
its orbital occupation and the energy level.

The process of arranging the electrons is based on Aufbau  
principle.