CHAPTER 3

THE QUANTUM MECHANICAL MODEL
The wave mechanical model (also called the wave mechanical model) involves the use of mathematical equation to describe the arrangement and motion of electrons in atoms.

According to Albert Einstein, light has both wave and particle like character. That is, matter has a dual nature. A French physicist took up the idea that very small particles such as electrons might also display wave properties.

In 1926, the Austrian Physicist – Erwin Schrodinger formulated wave-equation to describe the location and energy of electrons. He incorporated the Bohr, Louis de Broglie and the Heisenberg uncertainty principle concept and developed the wave mechanical model (Quantum mechanical model). Unlike the Bohr model, the wave mechanical model does not propose that electrons are localized in fixed orbits. In fact it does not define the exact location (orbit) of an electron around a nucleus. It describes the probability of finding can electron in a certain position at any time. If we assume a cloud of electron round the nucleus, the cloud would be most dense where we have a greater probability of finding an electron. Such regions where we could find an electron is called an "orbital". The electron cloud defines the shape of the orbital.

3.1 ENERGY LEVELS OF AN ATOM
Electrons are arranged in energy level. As we have already known, electrons do not move in fixed path, the Bohr orbit should not be confused with orbitals.

Electrons with the lowest energy level are found nearer the nucleus while electrons with higher energy are successively found further away from the nucleus depending on the energy level of the electron. Each energy level referred to as orbitals have a maximum number of electrons they can hold, the first energy level which is closest to the nucleus can hold not more than two electrons. Let us consider the illustration below.

Figure 3.1: Energy level of an atom
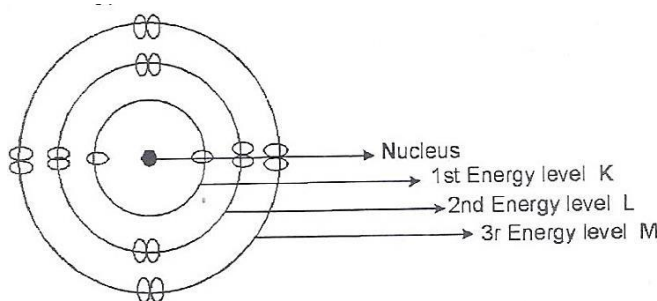
3.2 QUANTUM NUMBERS
Quantum numbers are numbers used to completely describe the properties of the electronsaround a nucleus. These properties can be described in terms of four quantum numbers. There are:

Principal quantum number: (n)
This describes the distance of an electron from the nucleus. The number is the same with that given by Bohr. It describes the size and energy of the orbital. Principal quantum number (n) is assigned values of integral numbers ranging from n = l, 2, 3, 4 and so on to∞. The number of electrons that can occupy a given energy level is given by $2n^2$. Orbitals with the same n-value aresaid to belong to the same energy level or the same shell.

**Azimuthal or subsidiary or angular momentum quantum number: ( ).**
This number determines the shape of the subshells. The principal quantum energy shell isdivided into sub energy shells. Each sub shell corresponds to several electron cloud space. The energy of the subshells increases as the value of increases. Azimuthal quantum number has integral values ranging from = 0, 1 2, 3 to n-1. The subshells are designated as s, p, d, f and so on. The subshells all have different energies. The energy of the subshells are in this order s<p<d<f.

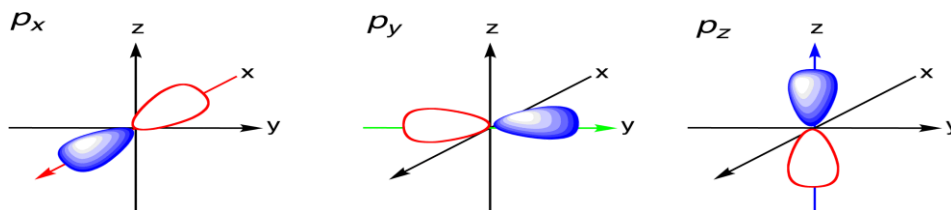**Table 3.1Summary of subshells, number of orbitals, shape of orbitals and their maximum number of electrons**

Subshell	Number of Orbitals	Shape of Orbitals	Maximum No. of Electrons
S	1	Spherical	2
P	3	Dumbbell	6
D	5	Double Dumbbell	10
F	7	Complex	14

Figure 3.2: **Shape of Orbitals**

(a) The one s-orbitals
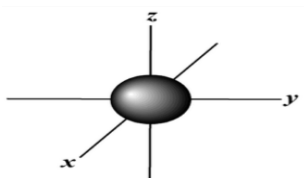
(b) The three p-orbitals

(c) The five d-orbitals

d_{XY} d_{zx} d_{yz} $d_{x^2} - d_{y^2}$ d_{z^2}
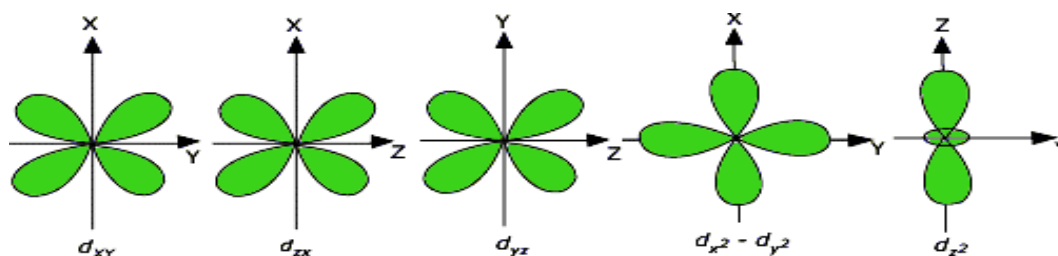
Magnetic Quantum Number (m): Magnetic Quantum Number (m): This specifies the permitted orientation in space for an electron cloud. It gives the number of orbital types in an energy level. And it has integral values of m = • --- 0 --- + . That is, the number of orbital in a sub shell is given by 2 + l.

When = 0, m = 0, which means that there is only one orientation, which is a spherical distribution (s-sub level or s-orbital).When = I, then m = -l, 0, + 1, that is there are three permitted orientation. The axes of these dumb-bells shaped orbital lie at 90° to each other. They are designated as P_x, P_y and P_z as shown in Fig. 3.2b, corresponding to major charge concentration along each of the three Cartesian coordinates.

Table 3.2: Relationship between Quantum Numbers and Atomic orbital

Principal Quantum No. (n)	Subsidiary Quantum No. (n)	Number of Sublevels	Number of Orbital m = 2 +1	Atomic Orbital	Number of Electron
1	0	1	1	1s	2
2	0	2	1	2s	8
	1		3	2p	
3	0	3	1	3s	18
	1		3	3p	
	2		5	3d	
4	0	4	1	4s	32
	1		3	4p	
	2		5	4d	
	3		7	4f	

Table 3.2 shows the first four energy levels in the quantum mechanical model of the atom.

Spin quantum number(s): This does not arise from Schrodinger equation but comes from other consideration. It gives the direction of electron spin on its axis. It has two values: $+\frac{1}{2}$ and $-\frac{1}{2}$. This means that an electron in a particular orbital has two permitted orientation of spin on its own axis, opposite to one another s = $+\frac{1}{2}$ (for electron spinning in clockwise direction) and s = $-\frac{1}{2}$ (for anticlockwise direction).

All the orbitals in a particular sub-shell are of equal energy. As seen in Figure 5.3. The energy gap between successive shells gets smaller as the principal quantum number increases. This explains why the 3d orbital which is an orbital in an inner shell is at a higher energy level thanthe 4s orbital in the next shell further away from the nucleus but lower than the 4p orbitals.

Example 3.1: How many orbitals do we have in the second principal level n = 2?

Solution: The second principal energy level has 2 sub-shells: 2s and 2p orbitals. The 2s sub-shell has one orbital, and the 2p sub-shell has 3 orbita1"s so in all, we have four orbitals in the second principal level.

Can you write the number of orbitals in:
   (i)   The fourth energy level n = 4
   (ii) The 4s orbital

3.3 ELECTRONIC CONFIGURATION OF ELEMENTS
Electron configuration of an element is the arrangement of electrons in its atomic orbital when it is at the ground state. In order to understand how electrons are arranged in orbitals. It isnecessary to understand some basic principles. These principles are discussed below;

3.3.1 HEISENBERG UNCERTAINTY PRINCIPLE
This principle states that it is impossible to know simultaneously at the same time the exact position and momentum of small particles like electrons.

3.3.2 PAULI'S EXCLUSION PRINCIPLE
This principle states that in an atom of many electrons, no two electrons in that atom can behave identically or have the same set of all the four quantum numbers. That is, even if the principal quantum number, subsidiary quantum number and the magnetic quantum number, are identical. The spin quantum number must have opposite spin on its axis. That is the spin must be clockwise and anticlockwise.

This is used to represent an electron and its direction of spin

$$\boxed{t}$$

While an orbital containing an electron pair is represented as

$$\boxed{t\downarrow}$$

3.3.3 HUND'S RULE
This states that electrons will singly occupy orbitals of equal energy (degenerate orbitals) until all the orbitals contain one electron each with parallel spins before pairing with opposite spin.

$$\boxed{t\downarrow} \quad \boxed{t\downarrow} \quad \boxed{t} \; \boxed{t} \; \boxed{t}$$

1s   2s   2px 2py 2pz
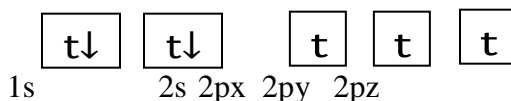
3.3.4 AUFBAU'S PRINCIPLE OR BUILDING - UP PRINCIPLE
The Aufbau"s principle is:

  1. Electrons go into orbital with the lowest energy before occupying higher energy level.

2. The Pauli"s exclusion principle (two versions).
   (a) It is impossible for two electrons in the same orbital to have the same or identical spin quantum number.
   (b) An orbital can contain a maximum of two electrons.

3. Electrons will fill a set of degenerate orbital singly with parallel spin before pairing with opposite spin.

Finally, electron structures are shown by writing down the list of orbitals, with number of electrons in each orbital shown as a superscript e.g. the 9 electrons in a fluorine atom can be arranged in the order $1s^2\ 2s^2\ 2p^5$. This order is referred to as electronic configuration of F.

By following the arrows in figure 3.4 below, it will help you work out the correct order of orbitals in the electron structures and thus write the electronic configuration of elements onceyou know the atomic number

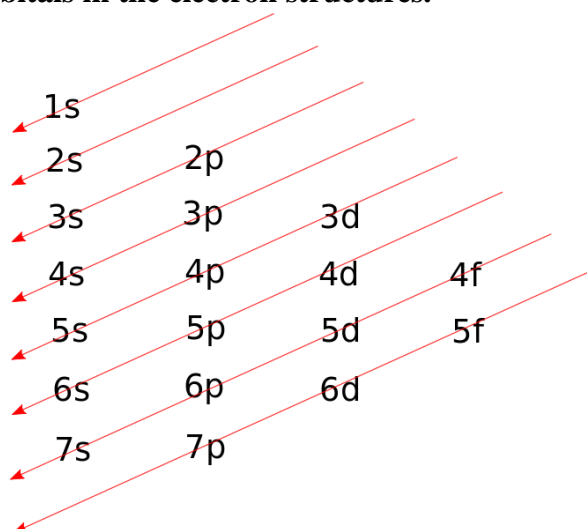**Figure 3.4: Order of orbitals in the electron structures.**

Table 3.3: The electronic configuration of the first 10 elements of the periodic table

Atomic	Element	Electronic configuration
1	H	$1s^1$
2	He	$1s^2$
3	Li	$1s^2\ 2s^1$
4	Be	$1s^2\ 2s^2$
5	B	$1s^2\ 2s^2\ 2p^1$

6	C	$1s^2\ 2s^2\ 2p^2$
7	N	$1s^2\ 2s^2\ 2p^3$
8	O	$1s^2\ 2s^2\ 2p^4$
9	F	$1s^2\ 2s^2\ 2p^5$
10	Ne	$1s^2\ 2s^2\ 2p^6$

From the table above, Helium and Neon both have their outermost *s* orbital and *p* orbital filled. This makes them very stable and they are referred to as noble gases. The next element sodium begins the filling of the next energy level n = 3.

The electronic configuration of Neon $1s^2\ 2s^2 2p^6$ can also be represented in a box diagram as:
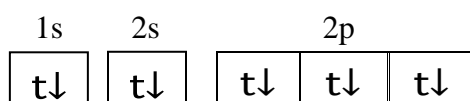
In Neon all the orbitals are filled.

Sodium has atomic number of 11, so the electronic configuration is written as $ls^2\ 2s^3\ 2p^6\ 3s^1$ The 3s orbital has one unpaired electron.

Magnesium has atomic number of 12, its electronic configuration is written as $ls^2\ 2s^2\ 2p^6\ 3s^2$

Aluminum has atomic number of 13, its electronic configuration is written as $ls^2\ 2s^2\ 2p^6\ 3s^2\ 3p^1$

Silicon is the next with atomic number of 14, its electronic configuration is written as $ls^2\ 2s^2\ 2p^6\ 3s^2 3p^2$

One electron is added to the 3p orbitals as atomic number of the elements increases until the 3p orbitals of Argon with atomic number 18 is completely filled. The next element is potassium, the electrons do not enter the 3d orbital instead it goes into the 4s orbital because the energy of the 3d orbital is slightly higher than that of the 4s orbital but lower than the 4p orbital. It then follows that the 4s orbital has to be completely filled before the 3d orbitals are filled. It then follows that the electronic configuration of K is written as $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^1\ 3d^5$

Perfectly half-filled or completely filled orbitals confer stability on atoms. Since atoms strive towards stability, an atom like Cr would prefer to have a half filled 3d orbital and the electronic configuration which is supposed to be $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^4$ then becomes $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^1\ 3d^5$

3.5 HYBRIDIZATION OF ATOMIC ORBITAL
Some atoms form covalent bonds that are different from what their electronic configuration

Suggests. When these bonds are formed between atoms, there is a change in the nature of the Atomic Orbitals in each atom. This peculiar bonding character can be explained with the concept called **hybridization**. It involves combining a number of orbitals to create a set of an equal number of new orbitals, where each of the new hybrid orbitals has properties which are an average of those of the orbitals from which they were created.

Thus, hybridization is a process whereby the orbitals of an atom (usually a central atom) interact to get a set of equivalent orbital called the HYBRID ORBITAL. Hybridization can also be defined as the mixing or overlapping of orbital of an atom to give a set of equivalent orbitals known as hybrid orbital. The hybrid orbital shows characteristics of both atomic orbitals.

A number of different types of hybrid orbitals are known for elements. These hybrid orbitals and the shape of the resulting molecules are given in table 3.4 below. However, only a few of the hybrid orbitals will be discussed here.

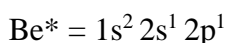**Table 3.4**: hybrid orbitals types in coordination compounds

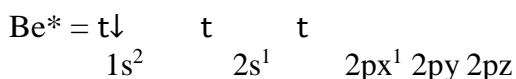| Atomic Orbitals	Hybrid Type	Numbers of Orbitals	Structure
Sp	sp	2	Linear
Sd	sd	2	Linear
spp	sp^2	3	Trigonal planar
sppp	sp^3	4	Tetrahedral
dspp	dsp^2	4	Square planar
dsppp	dsp^3	5	Trigonal bipyramid
sppdd	sp^2d^2	5	Square-base bipyramid
ddsppp	d^2sp^3	6	Octahedral
spppdd	sp^3d^2	6	Octahedral

3.5.1 sp-HYBRIDISATION
In considering the shape of a hybridized orbital, the electronic configuration of the central atom must be known. Let''s Consider $BeCl_2$; the central atom is Be, and its ground state electronic configuration is;

$$Be = 1s^2\, 2s^2$$
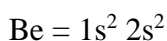
Beryllium has to be excited to generate orbitals to accommodate the two chlorine atoms. Thus if energy is supplied to raise one of the 2s electrons to a higher energy level the excited state electronic configuration of Be will be;

$$Be^* = 1s^2\, 2s^1\, 2p^1$$

More specifically, the electronic configuration of the excited beryllium atom can be written as;

$$Be^* = t\downarrow \qquad t \qquad t$$
$$1s^2 \qquad 2s^1 \qquad 2px^1\ 2py\ 2pz$$

And the excited state valence shell electronic configuration is;
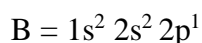
Be* = t   t

　　　$2s^1$ $2px^1$ $2py$ $2pz$
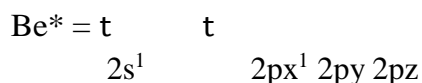
The two chlorine atoms will be accommodated in the 2s and 2px orbitals created as a result of the excitation. One would expect that one chlorine atom would occupy the $2s^1$ orbital while the other would occupy $2px^1$ orbital, making two non-equivalent $BeCl_2$ hybrids. However, the two $BeCl_2$ bonds formed are identical in every respect, indicating that the 2s and 2p orbitals mixed (hybridized) to form two equivalent sp hybrids orbital.

Also, because one s and one p orbital are used in the hybridization, the shape of the molecule will be a linear geometry.
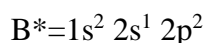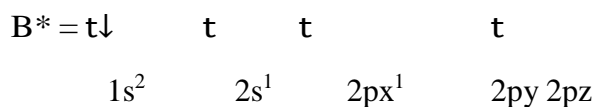

180°
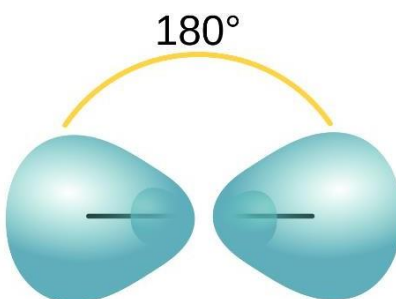
3.5.2 sp2-HYBRIDISATION

For this, we are going to consider boron trifloride (BF_3). Here the central atom is boron (B) and its ground state (i.e. the lowest energy state) electronic configuration of boron is;

　　　$B = 1s^2\ 2s^2\ 2p^1$

Boron has to be excited to generate orbitals to accommodate all the three fluorine atoms. Thus if energy is supplied to raise one of the 2s electrons to a higher energy level the excited state electronic configuration of Be will be;

　　　$B^* = 1s^2\ 2s^1\ 2p^2$

But more specifically, the electronic configuration of the excited beryllium atom can be written as;

B* = t↓   t   t   t

　　　$1s^2$ $2s^1$ $2px^1$ $2py$ $2pz$

And the excited state valence shell electronic configuration is:

B* =   t   t   t

　　　$2s^1$ $2px^1$ $2py$ $2pz$
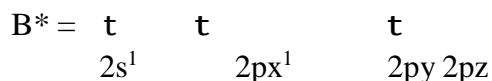
The three fluorine atoms will be accommodated in the $2s^1$, $2px^1$ and $2py^1$ orbital created as a result of the excitation. One would expected three non- equivalent BF_3 hybrids. However, the

three BF_3 bonds formed are identical in every respect, indicating that the 2s, 2px and 2py orbitals mixed (hybridized) to form three equivalent sp^2 hybrids orbital.

Also, because one s and two p (sp^2) orbitals were used in the hybridization the shape of the molecule will be a triangular planar. The three sp^2 orbitals lie in a plane with an angle 120° between any two.
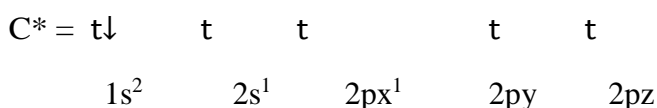
3.5.3 Sp^3-HYBRIDISATION

Here, we will be considering methane (CH_4). The central atom is carbon (C) and its ground state (i.e. the lowest energy state) electronic configuration is:

$$C = 1s^2\ 2s^2\ 2p^2$$
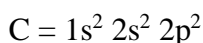
Carbon has to be excited to generate orbitals to accommodate the four hydrogen atoms. Thus if energy is supplied to raise one of the 2s electrons and one of the 2p electrons to a higher energy level, the excited state electronic configuration of C will be;

$$C^* = 1s^2\ 2s^1\ 2p^3$$
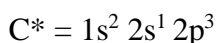
But more specifically, the electronic configuration of the excited carbon atom can be written as;

$$C^* = t\downarrow \qquad t \qquad t \qquad\qquad t \qquad t$$
$$\qquad\quad 1s^2 \qquad 2s^1 \qquad 2px^1 \qquad 2py \qquad 2pz$$

And the excited state valence shell electronic configuration is;

$$C^* = t \qquad t \qquad\qquad t \qquad t$$
$$\qquad 2s^1 \qquad 2px^1 \qquad 2py \qquad 2pz$$
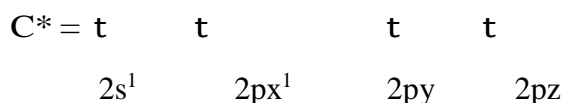
The four hydrogen atoms will be accommodated in the $2s^1$, $2px^1$, $2py^1$ and $2pz$ orbitals created as a result of the excitation. Four CH_4 bonds are formed which are identical in every respect, indicating that the 2s, 2px, 2py and 2pz orbitals mixed (hybridized) to form the four equivalent sp^3 hybrids orbital.

Also, because one s and three p (sp^3) orbitals were used in the hybridization, the shape of the molecule will be a tetrahedral. All the hydrogen carbon hydrogen angles are 109.5°
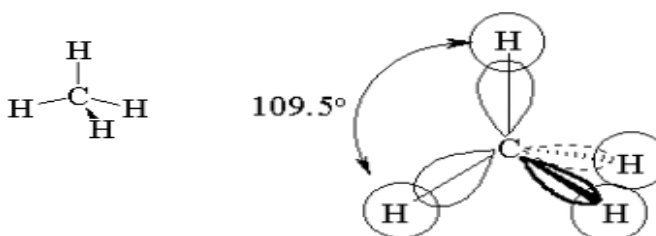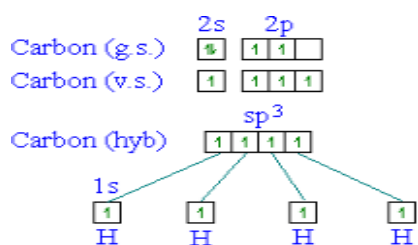
It is interesting to note that hybrid formed by only using the *s* and the *p* (i.e. sp^1, sp^2 and sp^3) orbitals in molecule complies with the octet rule. This is because regardless of the type of hybridization in an atom involving one *s* and three *p* orbitals will be four orbitals which is enough to accommodate a total of eight electrons in a compound. However the octet rule does not hold in some molecules where the atom may use the d orbital in addition to the *s* and *p* orbitals to form hybrid orbitals.

3.5.4: s, p and d ORBITALS-HYBRIDISATION

Atoms of elements in the second period of the periodic accommodate a maximum of eight electrons in their valence shell and also the s and p orbitals for their hybrid. This explains why they usually obey the octet rule. However, elements of the third period on, with more than eight electrons in their valence shell cannot always form hybrid molecules by using only the s and p orbitals. That is the formation of these hybrids must include the d orbitals.

As an illustration, PF_5 will be considered. Here the central atom is phosphorus (P) and the ground state (i.e. the lowest energy state) electronic configuration of phosphorus is;
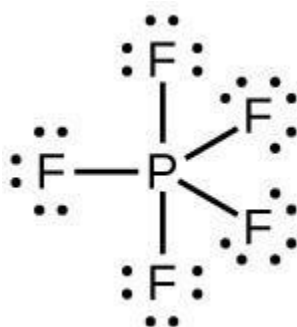
$$P = 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^3$$

Phosphorus has to be excited to generate orbitals to accommodate all the five chlorine atoms. Thus if energy is supplied to raise one of the 3s /3p electrons to a higher energy level the excited state electronic configuration of P will be:

$$P^* = 1s^2\ 2s^2\ 2p^6\ 3s^1\ 3p^3\ 3d^1$$

But more specifically, the excited state valence shell electronic configuration is;
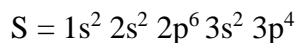
$P^* =$ tt t   t   t

    $3s^1$ $3px^1$ $3py^1$ $3pz^1$ 3d   3d   3d   3d   3d
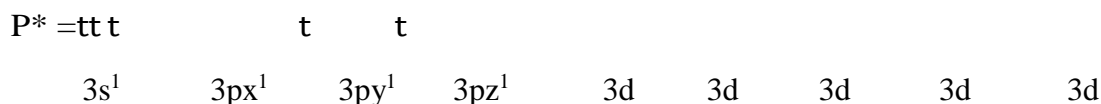
The five fluorine atoms will be accommodated in the 3s, 3px, 3py, 3pz and 3d orbitals created as a result of the excitation. Also, because one s, three p and one d (sp^3d) orbitals were used in the hybridization, the shape of the molecule will be a trigonal bipyramid.
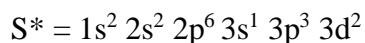

Here, there are ten electrons around the phosphorus atom, which means that the octet rule has been exceeded. Thus the use of the d orbital in addition to the *s* and *p* orbitals to form covalent bonds is an example of valence - shell expansion (expansion to the octet rule).

As another illustration, let"s consider SF_6. Here the central atom is sulphur (S) and the ground state (i.e. the lowest energy state) electronic configuration of sulphur is;
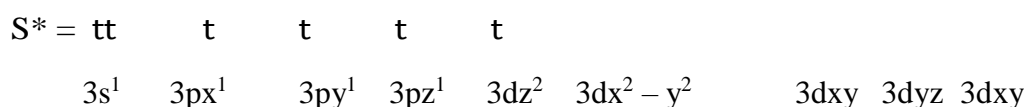
$$S = 1s^2\, 2s^2\, 2p^6\, 3s^2\, 3p^4$$

Sulphur has to be excited to generate orbitals to accommodate all the six fluorine atoms. Thus if energy is supplied to raise one of the $\frac{3s}{3p}$ electrons to a higher energy level the excited state electronic configuration of S will be:
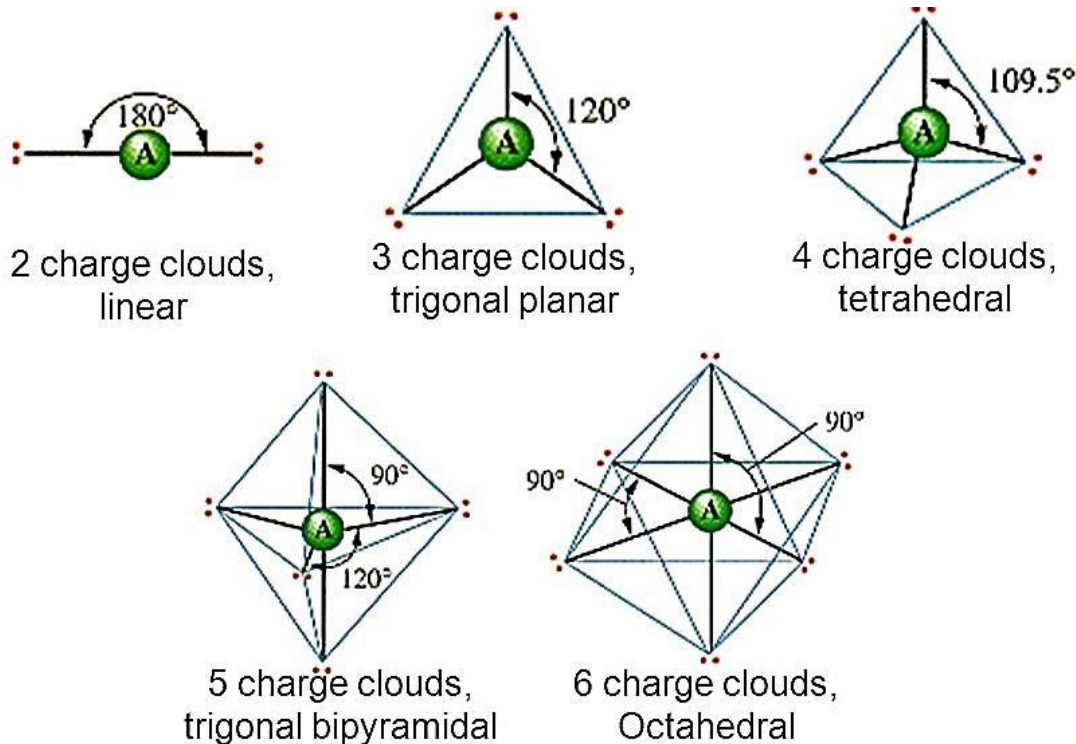
$$S* = 1s^2\, 2s^2\, 2p^6\, 3s^1\, 3p^3\, 3d^2$$

But more specifically, the excited state valence shell electronic configuration is;

$$S* = tt \quad\quad t \quad\quad t \quad\quad t \quad\quad t$$

$$3s^1 \quad 3px^1 \quad 3py^1 \quad 3pz^1 \quad 3dz^2 \quad 3dx^2 - y^2 \quad\quad 3dxy \;\; 3dyz \;\; 3dxy$$

The six fluorine atoms will be accommodated in the 3s, 3px, 3py, 3pz, $3dz^2$ and $3dx^2 - y^2$ orbitals created as a result of the excitation. Also, because one s, three p and two d (sp^3d^2) orbitals were used in the hybridization, the shape of the molecule will be an octahedral. Here also, there are twelve electrons around the sulphur atom; which means that the octet rule has also been exceeded. Thus the use of the d orbital in addition to the s and p orbitals to form covalent bonds is an example of valence – shell expansion (expansion to the octet rule).

2 charge clouds,
linear

3 charge clouds,
trigonal planar

4 charge clouds,
tetrahedral

5 charge clouds,
trigonal bipyramidal

6 charge clouds,
Octahedral

PRACTICE QUESTIONS

1. (a) How many orbitals are in the following:
    (i) The 3p orbitals
    (ii) The 2s orbitals
    (iii) The third energy level corresponding to n = 3.
    (b) Write the maximum number of electrons that each orbital and each energy level can take.

2. Give reasons for the following:
    (i) Electrons will fill the 4s orbital before other electrons will fill in the 3d orbitals.
    (ii) An unpaired electron will enter into an} of the vacant 3p orbital during the filling of orbitals
    (iii) No two (2) electrons have the same four quantum numbers.

3. Write the electronic configuration of the following elements K, S, P, and Ar

4. Deduce the shape of the following molecules.
    (a) PCI_5 (b) PF_3 (c) SP_6 (d) XeF_4 (e) CH_4 (f) NH_3
    (Xe = 54, S = 16, P = 15, C = 6, N = 7, Al = 13, B = 5, Be = 4)