



General Chemistry

Part : 2

1. INTRODUCTION

Atoms are the building blocks of which all matter in the universe is made. In everyday life we are familiar with many kinds of structures made of building blocks that we can see. For example, the wall of your house is constructed of bricks bound together with mortar. If we stand at a distance, we do not see the individual bricks, only the total structure can be seen; but, if we approach more closely, we can see the shape and size of each individual brick together with the layer of mortar that binds each brick to its neighbors. By way of contrast, in observing structures made of atoms we are always standing at a distance, we are always so far away that we can not see the sizes and shapes of individual atoms. In fact, as we understand more about the fundamental laws that govern the behavior of matter, we believe that it will never be possible to construct any instrument that will enable us to see atoms distinctly in the same way that we can see bacteria through a microscope. But, through many decades of experiments in chemistry and physics, indirect evidence has been accumulating that proves beyond any doubt that atoms do exist, and that all matter is made of atoms and atoms their selves are constructed of many particles.

Many of the fundamental particles are now recognized to be the basic building blocks of all atoms. Under ordinary

conditions, three fundamental particles are of major importance in chemistry. These particles are: the **electron**, mass = 0.000555 amu (on the scale on which that of ^{12}C is 12.00000) and charge -1.6021×10^{-19} C or -1 (relative scale); the **proton**, mass = 1.00728 amu and charge equal but opposite to that of the electron and **neutron**, mass = 1.00867 amu and charge zero.

In addition to these three fundamental particles, many other particles, such as quarks, positrons, neutrinos, pions and muons, have also been discovered. It is not necessary to study their characteristics to learn the fundamentals of atomic structure that are important in chemical reactions.

Although this evidence does not give us directly a picture of atoms, it does enable us to deduce their shapes and structure. Now we are going to use our previous knowledge to construct a mental picture for the atom. For our immediate purpose, the important conclusion is that sometimes, as in the collision of gaseous atoms, we find that atoms behave as elastic spheres with diameters of the order of $1/100\ 000\ 000$ cm (10^{-8} cm). At other times the atoms behave as if they were made up of electrons moving in orbits like planets around the sun. At still other times, when taking part in chemical combination or chemical reaction, the behaviour of the atom suggests that its outer part is made up of an

electron cloud the shape of which is determined by what is called ***wave mechanics***. The evidence indicate that, at the center of the atom there is an extremely small subatomic particle called the ***nucleus*** which contains a positive charge equivalent to but opposite in sign to the negative charge of the electron cloud. The nucleus also contains nearly all the mass of the atom and its atomic energy. It is roughly one-billionth (10^{-12}) centimeter in diameter. This gives us an idea of the infinitesimally small size of the atomic nucleus.

4. MOLECULAR GEOMETRY AND BONDING

4.1. Lewis formulas for polyatomic molecules and ions

We can use the dot (or x) method to represent the valence electrons in covalent molecules or polyatomic ions. We can do this so simply by following some guiding rules. These rules may be formulated as;

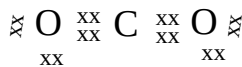
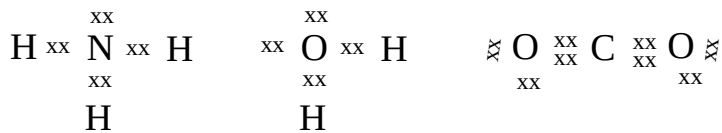
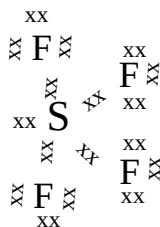
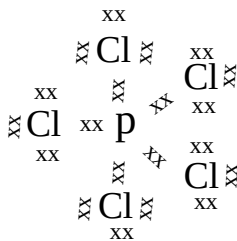
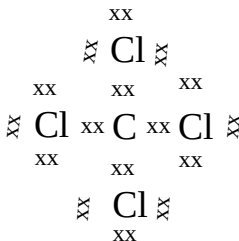
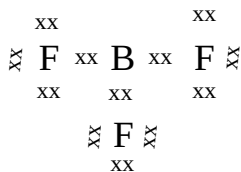
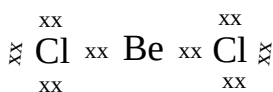
i) The number of valence electrons belong to a molecule can be obtained by summing the valence electrons of its constituting atoms.

ii) Determine the central atom and bind it with the terminal atoms, a pair of electrons is needed for each bond.

iii) Fill up the valence shells of the terminal atoms and if some electrons are still remaining put them on the central atom.

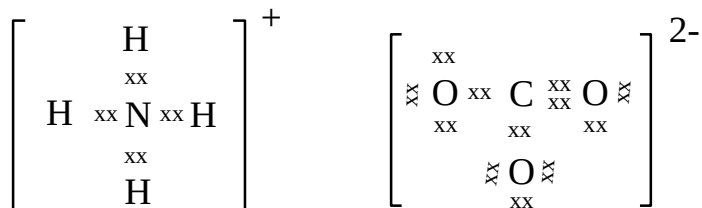
iv) The central atom valence shell must also be filled and this in some cases may come by moving one (or more) electron pair to be shared between the central and one (or more) of the terminal atoms.

Now we can go, using these rules to state the dot representations of some molecules such as BeCl_2 , BF_3 , CCl_4 , PCl_5 , SF_4 , NH_3 , H_2O , and CO_2 . The number of valence electrons according to rule (i) is 16, 24, 32, 40, 32, 8, 8, and 16, respectively. The dot formulas can then be stated as follows;



For ions, a number of electrons must be omitted (for positive ions) or added (for negative ions) depending on the number of positive or negative charges associated with ion, here

you are some examples; NH_4^+ and CO_3^{2-} ions with 8 and 32 valence electrons are stated as;



4.1.1. Resonance

The electron dot formulas of the bonding in many common and important molecules lead us to make various predictions that agree with the results of experiments. There are, however, many other compounds for which predictions based on electron dot pictures are not in accord with experiment. More than one reasonable electron dot formula can be drawn for most of these latter compounds. The theory of **resonance**, developed by Pauling and others, serves to modify our concept of the meaning of electron dot pictures of such molecules and brings expectations based on a mental image, or pencil picture, of bonding into accord with results of experiments.

Consider the bonding in SO_2 , sulfur dioxide. It is known from results of various experiments that SO_2 is a nonlinear molecule and that the sulfur atom is between the two oxygen atoms. The total number of electrons to be considered is 18. Two different electron dot formulas can be drawn;



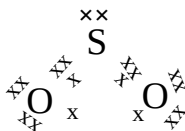
Both formulas are consistent with the information given above about SO_2 . These formulas indicate that both oxygen atoms and the sulfur atom have attained the noble gas electronic configuration with 8 electrons in the outer shell.

The difficulty of these pictures is their indication that the two oxygen atoms in SO_2 are not equivalent: one oxygen atom is bonded to the sulfur atom by a single bond while the other is bonded by a double bond. Experiments show, however, that the two oxygen atoms are equivalent. It is known that double bonds between two atoms are shorter than single bonds between the same atoms. Both sulfur-oxygen bonds in SO_2 have been found to be exactly the same length. Hence, we are forced to conclude that the electron dot formulas do not correspond closely to the way that

sulfur and oxygen atoms in SO_2 are really bonded. This same situation arises when we try to use electron dot pictures to explain bonding in many other molecules for which we can draw more than one apparently reasonable electron dot picture.

Pauling and others have found a quantum mechanical way out of this difficulty. According to their theory of resonance, the actual structure of SO_2 is best described as a mixture of the structures indicated by the two electron dot formulas drawn for SO_2 . It is sometimes said that the electronic structure of SO_2 is a resonance hybrid of the structures represented by these two electron dot formulas. Molecule of SO_2 has only one electronic structure, and that one electronic structure is intermediate between the two that we have drawn. This theory explains both the equivalence of the two sulfur-oxygen bonds and the identical bond lengths that are intermediate between expected lengths for $\text{S}-\text{O}$ and $\text{S}=\text{O}$ bonds.

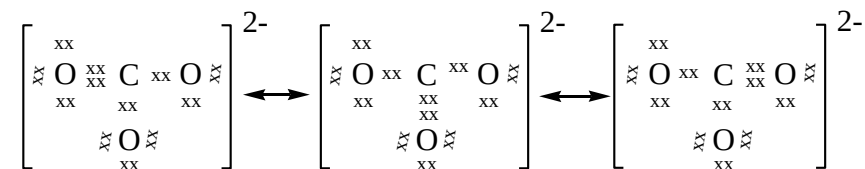
It is incorrect, however, to interpret this hybrid as

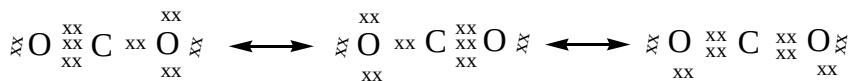
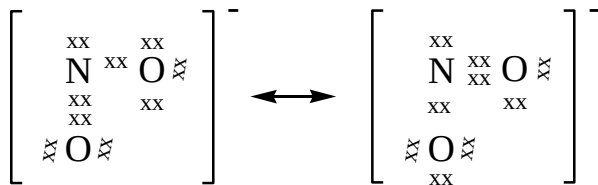
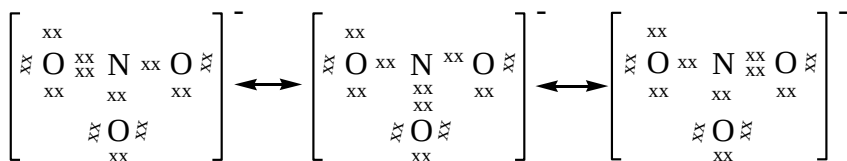


Because this picture indicates that there are unpaired electrons in SO_2 . Unpaired electrons seems unlikely on the basis of energy considerations and can definitely be ruled out because the observed magnetic properties of SO_2 are not consistent with the presence of unpaired electrons.

Paramagnetic substances are attracted by magnets, and diamagnetic substances are weakly repelled by magnets. Paramagnetic properties come about when the magnetic properties of spinning electrons are not cancelled out by the pairing of electron spins. Hence, substances with unpaired electrons are paramagnetic; and substances with no unpaired electrons are diamagnetic. Because SO_2 is diamagnetic, we know that it has no unpaired electrons.

We simply must admit that we are unable to draw an electron dot picture that correspond to the real structure of SO_2 and must, therefore, draw two electron pictures and make use of the concept of resonance. More examples are given below.





4.2. Valence Shell Electron Pair Repulsion (VSEPR)

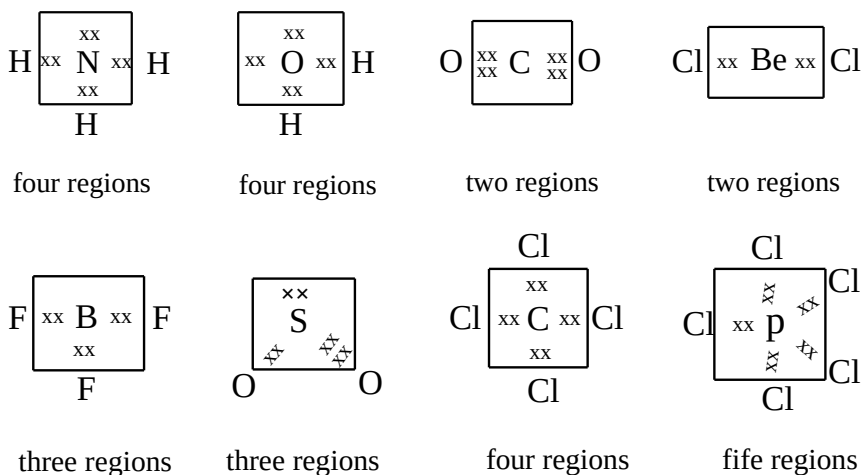
Theory

In 1940 Sidgwick and Powell pointed out that the shape of a molecule is related to number of electron pairs in the outer shell of the central atom. The basic ideas of valence shell electron pair repulsion theory can be summarized as follows;

*The electron pairs in the valence shell repel one another, therefore, they arranged about the central atom so that repulsion among them

are as small as possible. The result obtained is the maximum separation among regions of high electron density about the central atom.

*The number of regions of high electron density is easily counted by considering Lewis dot formulas. A region may be occupied by one, two or three electron pairs, as shown in the following scheme.



*The strength of the repulsion among electronic pairs can be arranged as ***lone pair – lone pair > lone pair – bond pair > bond pair – bond pair.***

According to the foregoing discussion two regions of high electron density are most stable when they are on opposite sides of

the central atom, i.e., linear. Three regions are most stable when an plane triangle. The following scheme shows the relationship between the common numbers of regions of high electronic density and the corresponding electronic geometry, together with the bond angles.

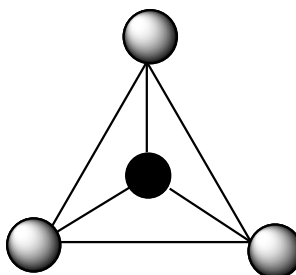
Two regions



linear

bond angle
 180°

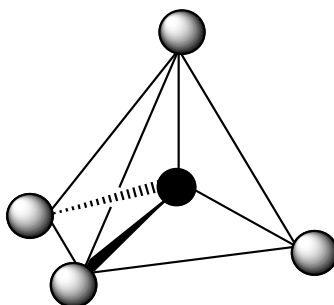
Three regions



Trigonal planar

bond angles
 120°

Four regions

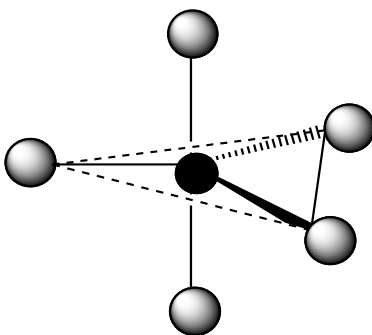


tetrahedron

bond angles

 $109^{\circ}28'$

Five regions

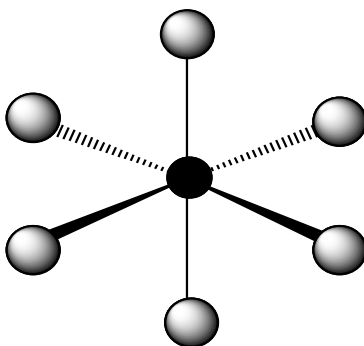


trigonal bipyramid

bond angles

 90° 120° 180°

Six regions



octahedron

bond angles

 90° 180°

The arrangement of the regions of high electron density around the central atom is referred to as the electronic geometry.

After we know the electronic geometry, we consider how many of these regions of high electronic density connect (bond) the central atom to other atoms (the terminal atoms). This let us deduce *the arrangement of terminal atoms around the central atom, i.e. molecular geometry.*

4.3. Valence bond (VB) theory

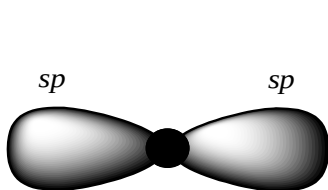
The basic idea of valence bond theory is that covalent bonding occurs when two orbitals of two different atoms are overlapped and share the electrons, it describe how bonding occurs. To explain the experimentally observed geometry we usually need to invoke the concept of hybrid orbital, which are formed by the combination or **hybridization** of the atom`s valence shell atomic orbitals.

The number of regions of high electron density about a central atom in a molecule or polyatomic ion suggests the kind of hybridization occurs for the valence orbitals of that atom. The label given to a set of hybrid orbitals reflects the number and kind of

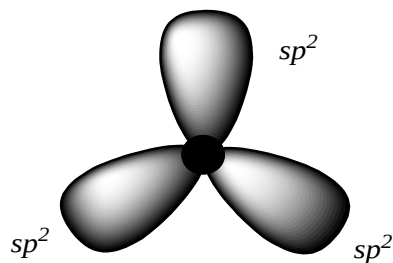
atomic orbitals hybridized to produce the set, as shown in Table (4.1), and Figure (4.1)

Table (4.1): The electronic geometry as a function of hybridization

Regions H. E. D.	Type of hybridization	At. Orbitals mixed	Electronic geometry
2	sp	one s + one p	Linear
3	sp^2	one s + two p`s	Plane triangle
4	sp^3	one s + three p`s	Tetrahedral
5	sp^3d	one s + three p`s + one d	Trigonal bip.
6	sp^3d^2	one s + three p`s + two d	octahedral



linear



plane triangle

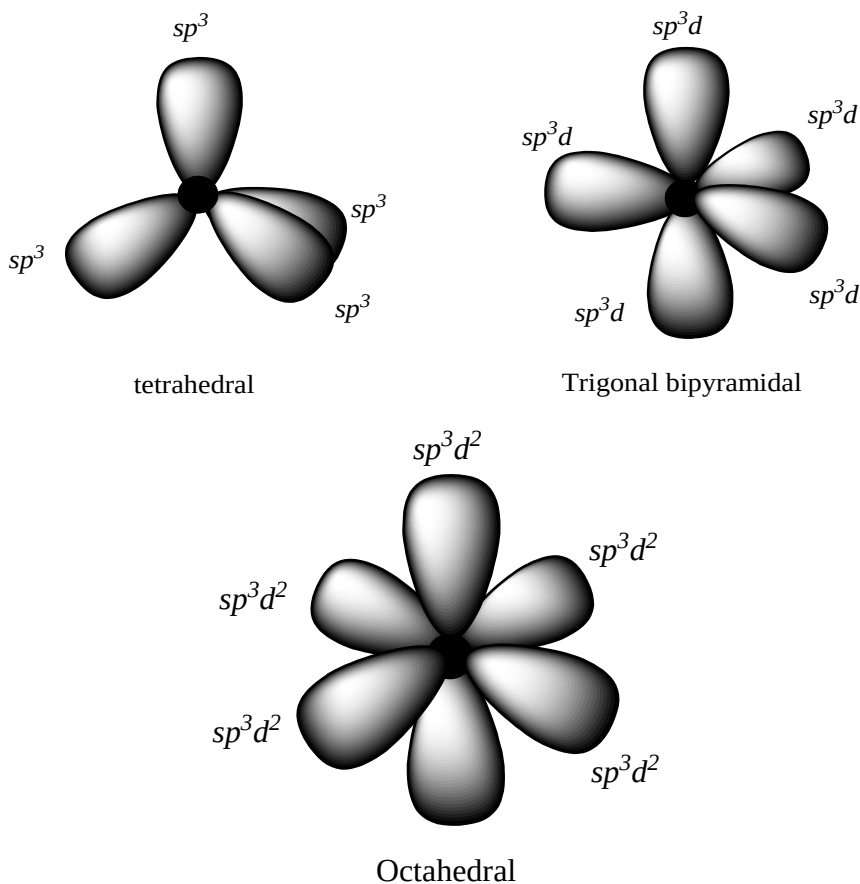


Figure (4.1): The shapes of hybrid orbitals

In many examples throughout this chapter, we shall first use the valence shell electron repulsion theory to describe the orientations of the regions of high electron density, (electronic geometry), molecular geometry and molecular polarity. Then we shall use the valence bond theory to describe the atomic orbitals that overlap to produce the bonding with that geometry. The two theories must work together to give a fuller description of the bonding.

4.4. Linear geometry

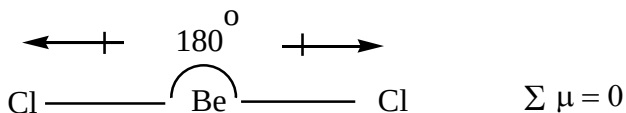
4.4.1. Beryllium chloride, BeCl_2

The difference in electronegativity between Be and Cl is so large that we might expect ionic bonding. However, the radius of Be is so small and its charge density (ratio of charge to density) is so high that it is able to attract and distort the electron cloud of halogens except fluoride and oxygen (Fajans' rules). Therefore, the bonds in BeCl_2 attain covalent character. Lewis dot representation for BeCl_2 , section (3.4) shows two regions of high electron density (two electron pairs) around the beryllium atom.

VSEPR Theory

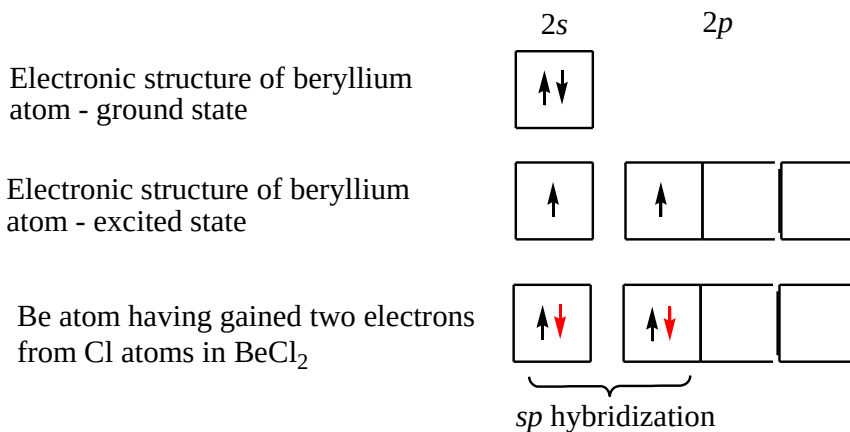
The theory places the two regions of high electron density on Be 180° apart; this means a linear electronic geometry. Both regions of high electron density are bonding pairs, so VSEPR theory predicts a linear molecular geometry for BeCl_2 , $\text{Cl}-\text{Be}-\text{Cl}$.

Because of the electronegativity difference between Be and Cl atoms, the two bonds are polar but in opposite directions, so they cancel each other, consequently, the molecule is nonpolar.



Valence bond theory

The beryllium atom in this molecule (the central atom) has the electronic structure $1s^2 2s^2$ (we are concerned only with the valence shell). The atom in its ground state has not any unpaired electrons, but in the excited state has two, so two bonds can be formed.



sp hybridization predicts a linear geometry and the two sp hybrid orbitals on beryllium atom overlap with orbitals from chlorine atoms (p orbitals) to form the bonds, as shown in Figure (4.2)

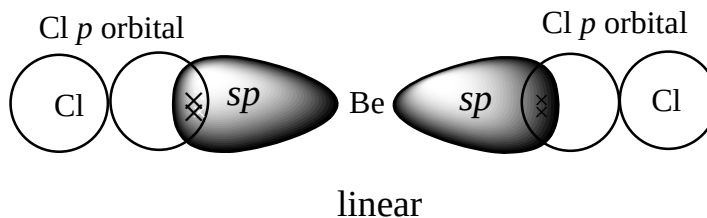


Figure (4.2): BeCl_2 molecule

The structures of BeX_2 , CdX_2 and HgX_2 where $\text{X} = \text{Cl}$, Br , or I are all the same, linear molecules.

4.5. Trigonal planar geometry

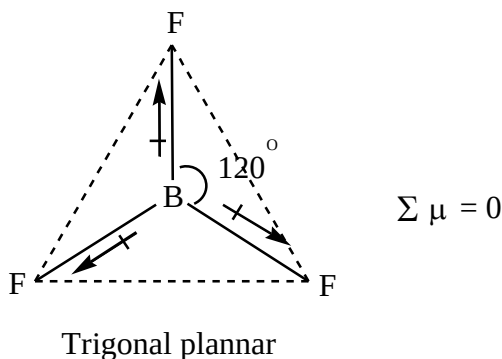
4.5.1. Boron trifluoride, BF_3

Boron forms many covalent compounds by bonding to three other atoms. Typical examples include BX_3 , where $\text{X} = \text{Cl}$, Br , or I .

VSEPR Theory

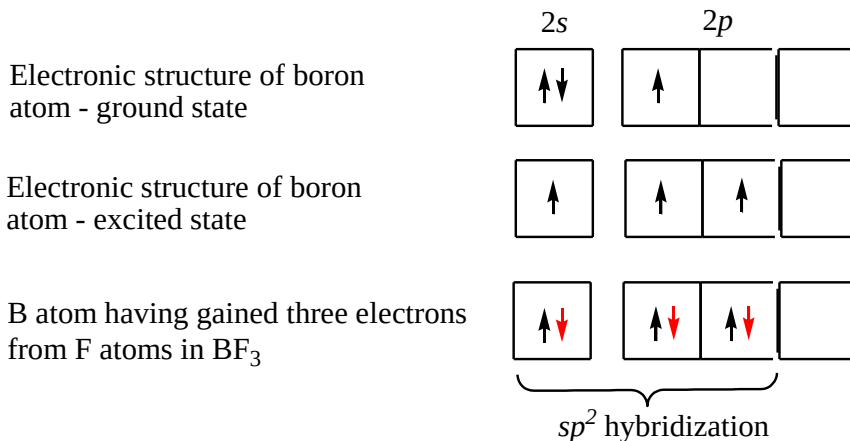
Lewis formula for BF_3 molecule (sec. 3.4) predicts three regions of high electron density (three bond pairs) around the boron atom. VSEPR theory predicts trigonal planar electronic geometry. there are no lone pairs of electrons associated with the boron atom, so fluorine atom is at each corner of the equilateral triangle, and the molecular geometry is also trigonal planar. All the four atoms are in the same plane with the boron atom in the center.

The electronegativity difference between boron and fluorine atoms is large, so the $\text{B} - \text{F}$ bonds are very polar. However, the three bond dipoles are symmetrical and cancel each other to give nonpolar molecule.



Valence bond theory

The boron atom in this molecule (the central atom) has the electronic structure $1s^2 2s^2 2p^1$ (we are concerned only with the valence shell). The atom in its ground state has only one unpaired electron, but in the excited state has three, so three bonds can be formed.



Now, the 2s orbital and two of the 2p orbitals of boron atom hybridize to form a set of three degenerate sp^2 hybrid orbitals. The three sp^2 hybrid orbitals point toward the corners of an

equilateral triangle and overlapped with the 2p orbitals of fluorine atoms, as shown in Figure (4.3).

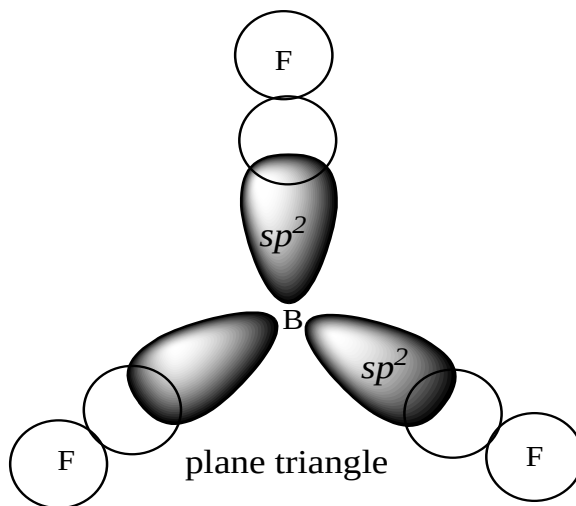


Figure (4.3): BF_3 molecule

4.6. Tetrahedral geometry

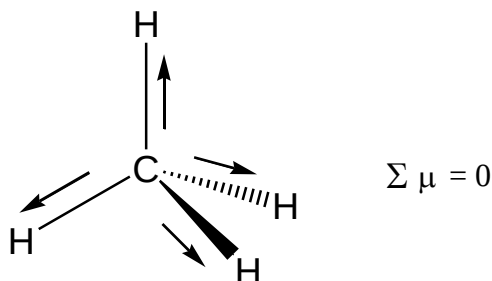
4.6.1. Methane, CH_4 molecule

According to Lewis dot formula the carbon atom (central atom) is surrounded with four regions of high electron density, all of them are bond pairs.

VSEPR Theory

The theory predicts a tetrahedral electronic geometry and also a tetrahedral molecular geometry (there are no lone pairs of electrons), and the HCH angle is $109^\circ 28'$. Although, the four C –

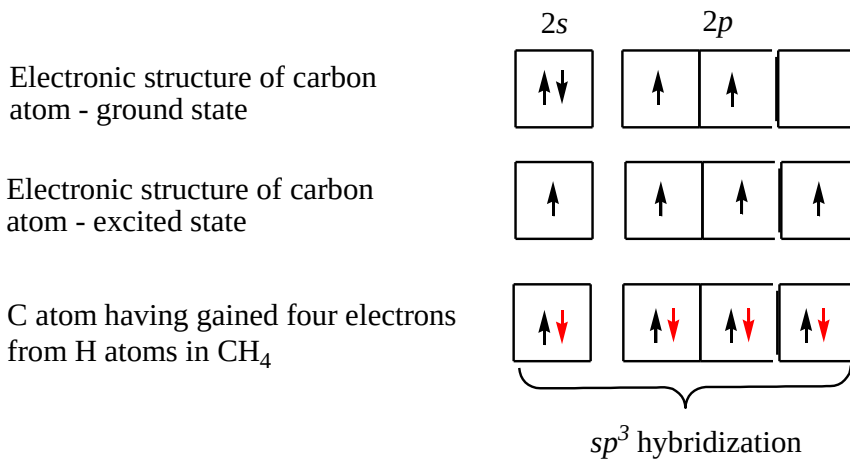
H bonds are polar, the net dipole moment of the molecule is zero,^ε
 $\mu = 0$.



Tetrahedral geometry

Valence bond theory

The carbon atom has four unpaired electrons in the excited state, so it can form four bonds with four hydrogen atoms. The $2s$ and the three $2p$ orbitals undergo hybridization of the type sp^3 which corresponds to tetrahedral geometry.



The obtained four sp^3 hybrid orbitals are now overlap with the $1s$ orbital of four hydrogen atoms, as shown in Figure (4.4).

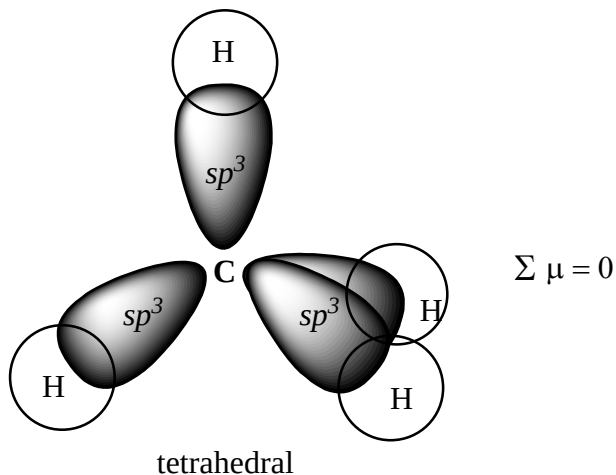


Figure (4.4); CH_4 molecule

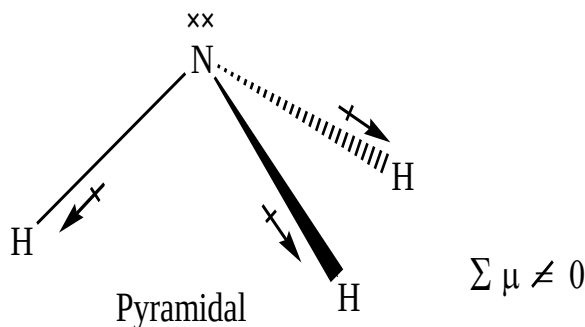
Typical examples showing the same geometry are CX_4 , (X = halogen), SiH_4 , SiF_4 are all tetrahedral, nonpolar molecules. Polyatomic ions such as ammonium, NH_4^+ , sulfate, SO_4^{2-} , fluoroborate, BF_4^- show tetrahedral geometry.

4.6.2. Ammonia, NH_3 , molecule

Lewis dot formula for NH_3 molecule shows four regions of high electron density around the nitrogen atom, three bond pairs and one lone pair.

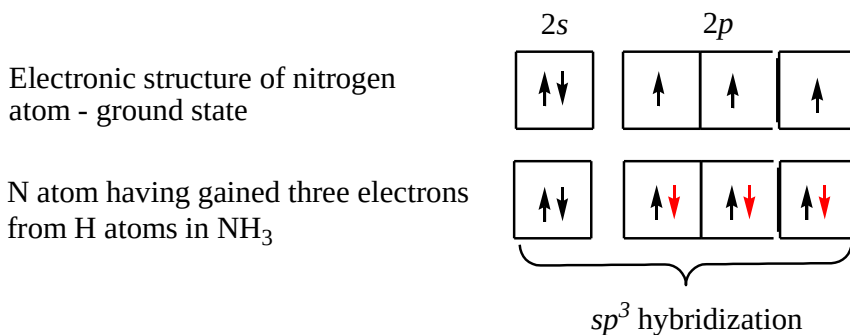
VSEPR Theory

The presence of four regions of high electron density around the central atom indicates that, the expected electronic geometry is tetrahedral. The presence of one lone pair among the regions of high electron density reveals that the molecular geometry is pyramidal, as shown below. On passing from methane to ammonia, a bond pair is replaced by a lone pair which repels the other bond pairs more strongly, thus reducing the bond angle, HNH from $109^{\circ}28'$ to $106^{\circ}45'$. The molecule is polar because the net dipole moment does not equal zero.



Valence bond theory

The nitrogen atom has three unpaired electrons, so it can form three bonds with three hydrogen atoms. The 2s and the three 3p orbitals undergo hybridization of the type sp^3 which corresponds to tetrahedral geometry.



Three of the four sp^3 hybrid orbitals can overlap with three $1s$ orbitals of hydrogen atoms and form three N – H bonds, while the fourth sp^3 is occupied by a lone pair. This gives a pyramidal molecular geometry, as shown in Figure (4.5).

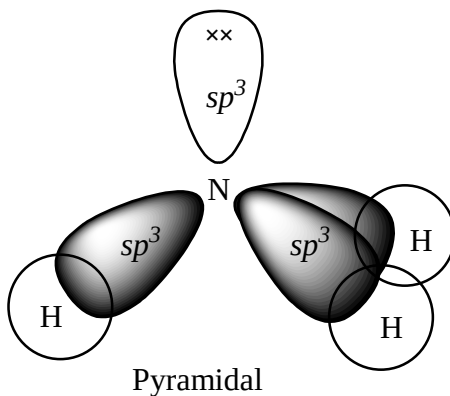


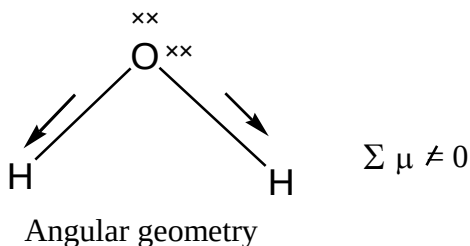
Figure (4.5): Ammonia molecule

4.6.3. Water H₂O molecule

Four regions of high electron density around oxygen (the central atom) in H₂O molecule (two lone pairs and two bond pairs).

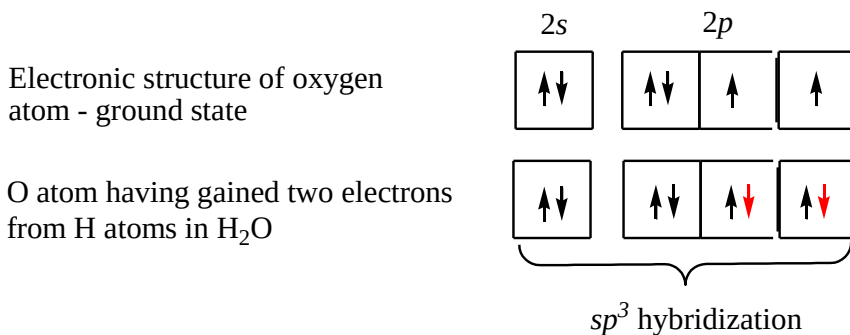
VSEPR theory

The theory predicts a tetrahedral electronic geometry. The presence of two bond pairs only renders the molecule is angular (bent) geometry. Here, the presence of two lone pairs distort the bond angle, H – O – H more than it was distorted by the one lone pair in NH₃, the bond angle in H₂O is 104°27'. Furthermore, the molecule is polar because the net dipole moment does not equal to zero, as shown;



Valence bond theory

The oxygen atom in water molecule has two unpaired electrons, which are sufficient to form the two bonds required.



The four outer orbitals hybridize, sp^3 and two of these hybrid orbitals overlap with two $1s$ orbitals of hydrogen atoms giving two hybrid orbitals are occupied by lone pairs, as shown in Figure (4.6).

Distortion of the ideal shape may be related also to the electronegativity. In a series of molecules such as NH_3 , PH_3 , AsH_3 , because of the electronegativity of the central atom decrease in the order $\text{N} \rightarrow \text{P} \rightarrow \text{As}$ the bonding electrons are drawn nearer to the hydrogen atoms, that is further away from the central atom, repulsion between bond pairs decreases and the bond angles decrease from $106^\circ 45'$ in NH_3 to $93^\circ 50'$ in PH_3 to $91^\circ 35'$ in AsH_3 .

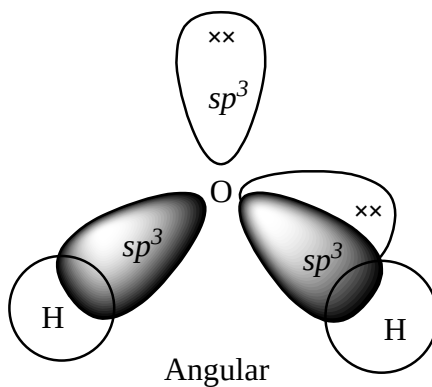


Figure (4.6): Water molecule

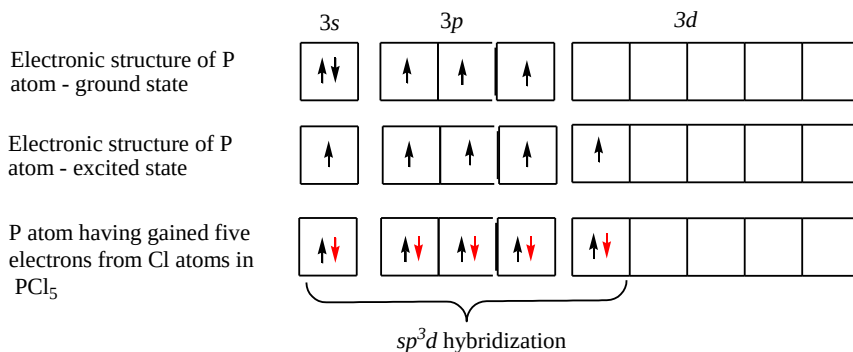
H₂S, H₂Se, H₂Te have the same molecular geometry as water molecule but the bond angles are 92°, 91°, and 89.5°, respectively. Account for this?

4.7. Trigonal bipyramidal geometry

4.7.1. Phosphorus pentachloride, PCl₅ (gaseous state)

VSEPR theory predicts trigonal bipyramidal electronic geometry because of five regions of high electron density are present around the central phosphorus atom. The five regions of high electron density are all bond pairs, so the theory predicts also a trigonal bipyramidal molecular geometry. The net dipole moment is zero, therefore the molecule is nonpolar.

Valence bond theory assumes sp^3d hybridization which corresponds to trigonal bipyramidal geometry. In this molecule, phosphorus atom contains only three unpaired electrons in its ground state. An electron must be unpaired to provide the correct number of unpaired electrons for bond formation, and the $3d$ orbital is involved in such hybridization.



Five orbitals (one $3s$ + three $3p$ + one $3d$) are being used and five sp^3d hybrid orbitals are produced which overlap with five $3p$ orbitals from chlorine atoms giving a trigonal bipyramidal structure, as shown below, Figure (4.7).

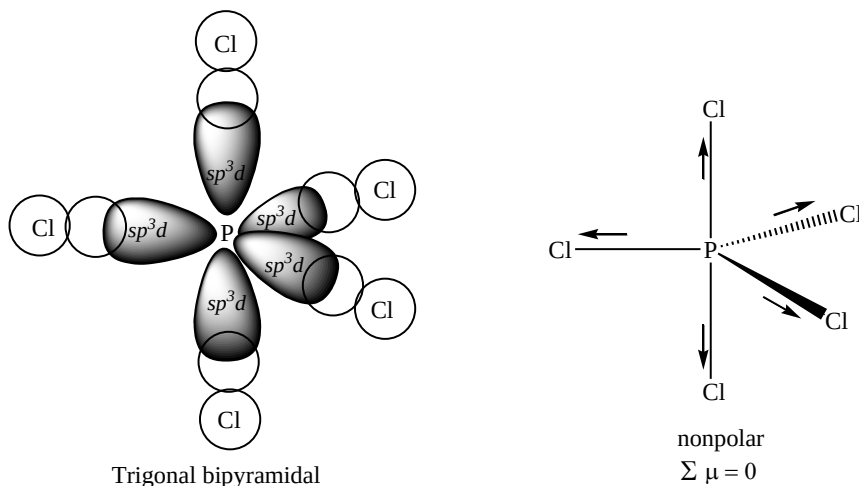


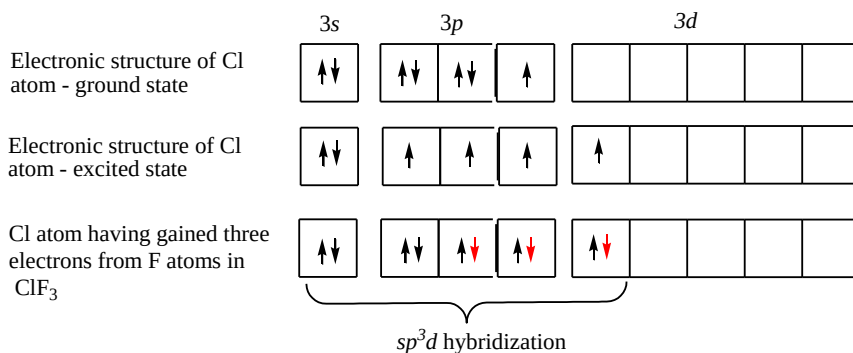
Figure (4.7): PCl_5 molecule

PCl_5 is highly reactive, and in the solid state splits into PCl_4^+ and PCl_6^- ions which have tetrahedral and octahedral structure, respectively. Symmetrical structures are usually more stable than unsymmetrical ones.

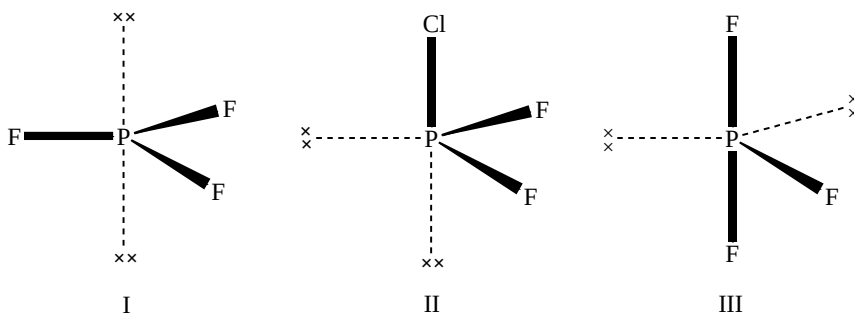
4.7.2. Chlorine trifluoride, ClF_3

The central atom, chlorine has five regions of high electron density (three bond pairs + two lone pairs) so; VSEPR theory predicts a trigonal bipyramidal electronic geometry. Valence bond

theory state that, chlorine atom must be excited to provide the right number of unpaired electrons.



Once again there are five orbitals in the outer shell which are hybridized to give five sp^3d orbitals and a trigonal bipyramidal arrangement. Three orbitals contain bond pairs and two contain lone pairs and several arrangements are theoretically possible, as shown in the following scheme;

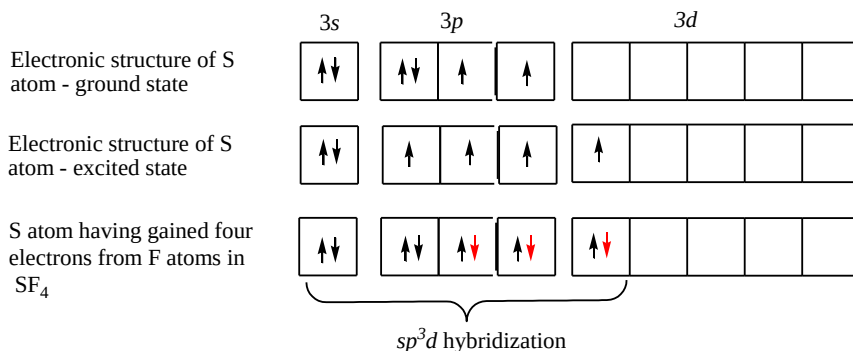


Structure (I) is the most symmetrical, but the most stable structure will be the one of lowest energy, that is the one with the least repulsion between the five orbitals. Normally lone pairs repel each

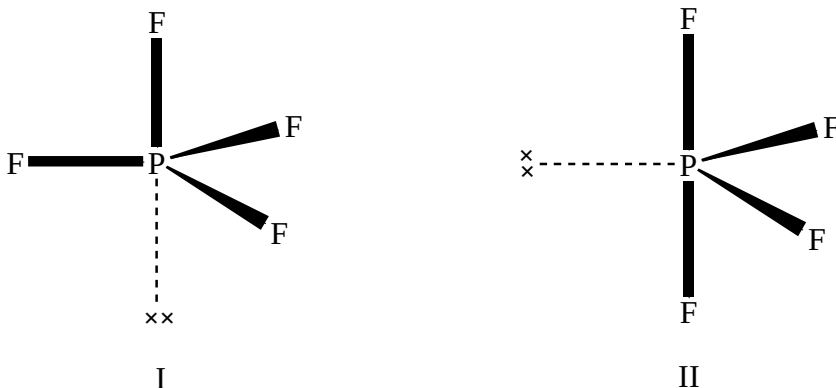
other the most strongly, lone pair – bond pair repulsions are next strongest, and bond pair – bond pair repulsions the weakest. However the trigonal bipyramidal structure is not regular and groups at 90° to each other repel each other very strongly, whilst repulsions between groups 120° apart are very much less. From consideration of these factors, structure (III) would seem the most probable. As a general rule, if lone pairs occur in a trigonal bipyramidal they will be located in the equatorial positions (round the middle) rather than the epical positions (top and bottom), since this arrangement minimizes repulsive forces. The bond angles have been found to be $\sim 87^\circ$, so the structure must be (III) and the slight distortion from a right-angle must be due to the repulsion of the two lone pairs.

4.7.3. Sulfur tetrafluoride, SF_4

Since there are five regions of high electron density around sulfur atom (four bond pairs + lone pair) the VSEPR theory predicts a trigonal bipyramidal structure, with four corners occupied by fluoride atoms and one by a lone pair. Valence bond theory assumes that sulfur atom must be excited to provide four unpaired electrons to form the required number of bonds.



sp^3d hybridization is then assumed giving the a trigonal bipyramidal shape. Two arrangements are theoretically possible as shown in structures I and II.



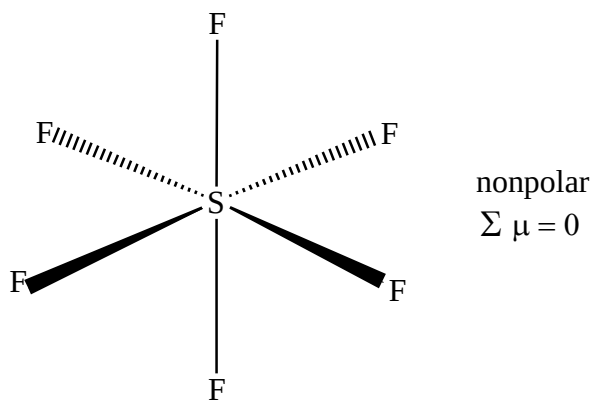
To minimize the repulsive forces the lone pair occupies an equatorial position, and the fluorine atoms are located at the other four corners. This means that structure II is more stable.

4.8. Octahedral geometry

4.8.1. Sulfur hexafluoride, SF_6

VSEPR theory

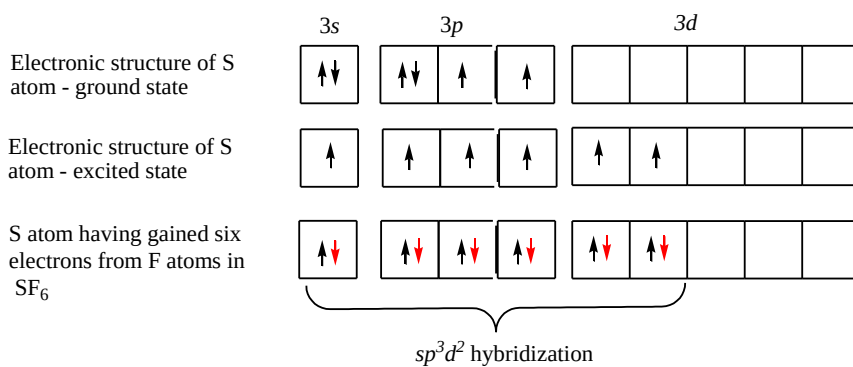
Sulfur atom in SF_6 is surrounded by six regions of high electron density; all of them are bond pairs. Hence, a regular octahedron for electronic as well as molecular geometry is assumed according to VSEPR theory, furthermore the molecule is nonpolar.



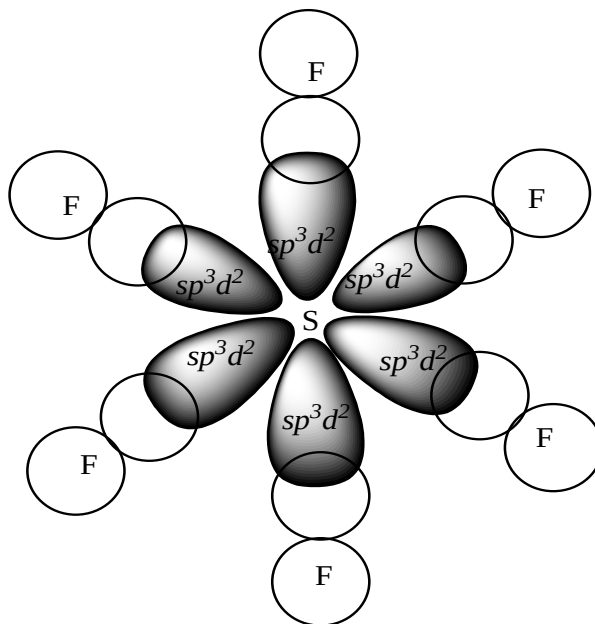
Octahedral shape

Valence bond theory

Valence bond theory proposes that, in SF_6 the sulfur atom is excited to provide six unpaired electrons sufficient to promote six bonds with six fluorine atoms, as follows;



sp^3d hybridization then occurs and the six hybrid orbitals are directed to the corner of a regular octahedron and overlapped with six p orbitals of six fluorine atoms, Figure (4.8).



Octahedral geometry

Figure (4.8): SF₆ molecule

4.9. Sigma and pi bonds

All the bonds formed in these examples results from end to end overlap of orbitals and are called sigma (σ) bonds. When double or triple bonds occur, some orbitals overlap laterally giving pi (π) bonds, Figure (4.9). π bonds are never included in hybridization

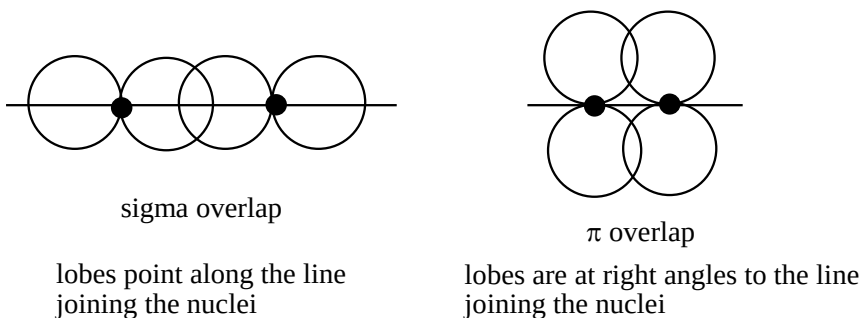
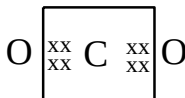
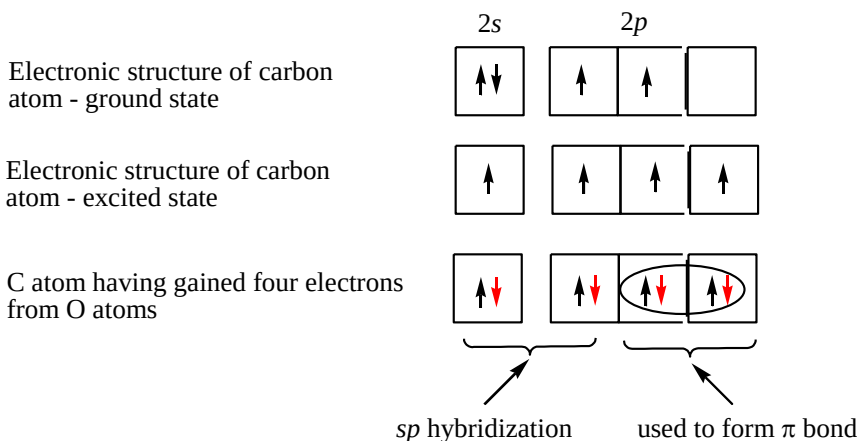


Figure (4.9): Sigma and pi overlap

Consider the structure of the carbon dioxide molecule, Lewis dot formula is; $\text{O} = \text{C} = \text{O}$ or



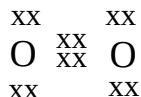
There are two regions of high electron density, so the VSEPR theory predicts a linear geometry with a bond angle of 180° . The same result can be obtained in terms of valence bond theory. In CO_2 , the carbon atom is excited to provide four unpaired electrons and sp hybridization is then obtained from $2s$ and one of the $2p$ orbitals.



In CO_2 molecule there are two pi bonds and two sigma bonds. Pi orbitals are not hybridized, and do not affect the shape of the molecule. Thus two electron pairs are reserved for pi bonding. The remaining s and p orbitals are used to form sigma bonds, and the two *sp* hybrid orbitals produced result in a linear molecule, with a bond angle of 180° . The two unhybridized *p* orbitals on the carbon atom are at right angles to the *sp* hybrid orbitals, and overlap sideways with *p* orbitals on the oxygen atoms at either side. This pi overlap shortens the carbon – oxygen distances, but does not affect the shape.

5. MOLECULAR ORBITALS (MO) THEORY

For oxygen molecule the valence bond theory predicts sp^2 hybridization at each oxygen atom, because there are three regions of high electron density and all the valence electrons are paired.



However, experiments show that the oxygen, O_2 , molecule is paramagnetic; therefore, it has unpaired electrons. Thus the valence bond structure is inconsistent with experiment and cannot be accepted as a suitable description of the bonding. Molecular orbitals theory predicts that O_2 has two unpaired electrons. This ability of MO theory to explain the Paramagnetism of O_2 brought it to the forefront as a major theory in bonding.

5.1. Molecular orbital method.

In hybridization of atomic orbitals so far discussed, atomic orbitals of the same atom have been combined to produce hybrid orbitals which can be overlap more effectively with orbitals from other atoms, thus producing stronger bonds. In molecular orbitals theory, the valence electrons are considered to be associated with all the nuclei concerned and to do this ***atomic orbitals from different atoms must be combined to produce molecular orbitals.***

Electrons may be considered either as particles or as waves. An electron in an atom may be therefore described as occupying an atomic orbital, or by a wave function ψ , which is a solution of to

the Schrodinger wave equation. Electrons in a molecule are said to occupy molecular orbitals. The wave function describing a molecular orbital may be obtained by one of two procedures:

- 1- Linear combination of atomic orbitals (LCOA).
- 2- United atom method.

5.2. Linear combination of atomic orbitals (LCOA)

Consider two similar atoms 1 and 2 which have atomic orbitals described by the wave functions ψ_1 and ψ_2 . When these atoms form a bond, the electrons originally in the atomic orbitals now occupy molecular orbitals, and the molecular orbital is formed by a linear combination of atomic orbitals ψ_1 and ψ_2 .

$$\Psi = N (C_1 \psi_1 + C_2 \psi_2)$$

Where N is a normalizing constant chosen to insure that the probability of finding the electron in the whole of the space is unity, and C_1 and C_2 are constant chosen to give a minimum energy for ψ .

5.2.1. s – s Combination of Atomic Orbitals

Suppose the atoms 1 and 2 are hydrogen atoms, then the wave functions ψ_1 and ψ_2 describe the 1s atomic orbitals on the two atoms. Two combinations of the wave functions ψ_1 and ψ_2 are possible;

- i. where the signs of the two wave functions are the same
- ii. where the signs of the two wave functions are the different.

If one of the wave function ψ_1 is arbitrarily assigned as a +ve sign, the other may be either +ve or -ve. Wave functions which have the same sign may be regarded as waves that are in phase, which when combined add up to give a larger resultant wave (**constructive interference**). Similarly wave functions of different signs correspond to waves that are completely out of phase and which cancel each other by **destructive interference**. The two combinations are

$$\Psi_g = N (\psi_1 + \psi_2)$$

and

$$\Psi_u = N (\psi_1 + -\psi_2) = N (\psi_1 - \psi_2)$$

This process can be represented schematically as shown in Figure (5.1).

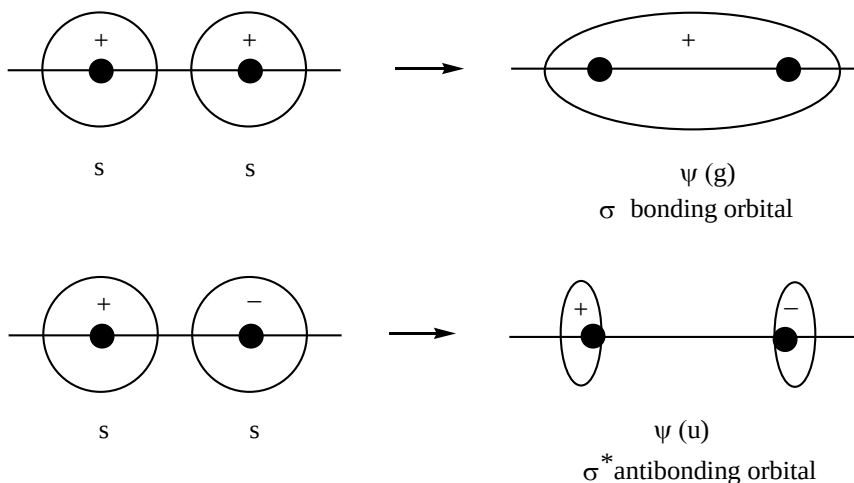


Figure (5.1): s – s Combination of atomic orbitals

When a pair of atomic orbitals ψ_1 and ψ_2 combines, they give rise to a pair of molecular orbitals Ψ_g and Ψ_u . The number of molecular orbitals produced must be equal to the number of atomic orbitals involved. The function Ψ_g leads to increased electron density in between the nuclei, and is therefore, a bonding molecular orbital. It is lower in energy than the original atomic orbitals. Conversely, Ψ_u results in two lobes of opposite sign cancelling Ψ and hence giving zero electron density in between the nuclei. This is antibonding molecular orbital which is higher in energy than the original atomic orbitals, Figure (5.2).

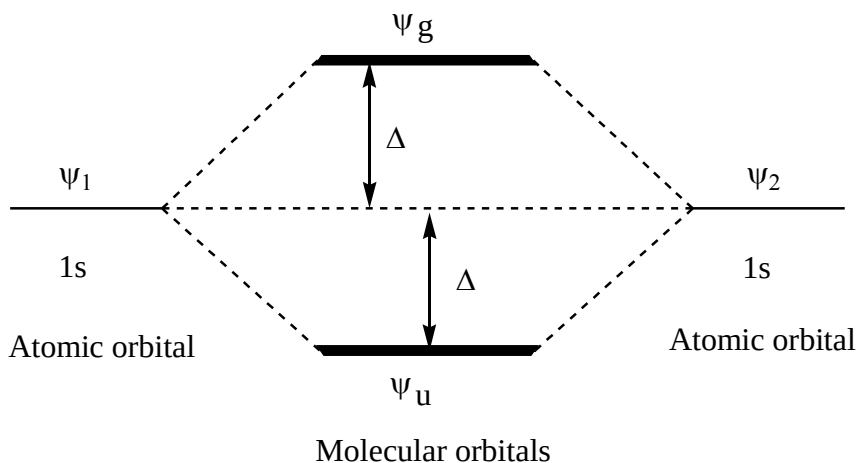


Figure (5.2): Energy levels of s – s atomic and molecular orbitals

In molecular orbitals wave functions are designated Ψ_g and Ψ_u ; g stands for gerade (even) and u for ungerade (odd). g and u refer to the symmetry of the orbital about its center of symmetry.

The energy of the bonding molecular orbital is lower than that of the atomic orbital by an amount Δ , known as stabilization energy. Similarly the energy of the antibonding molecular orbital is increased by Δ . Atomic orbitals may hold up to two electrons (opposite spins), and the same applies to molecular orbitals.

Overlap of atomic orbitals along the axis joining the nuclei produces σ molecular orbitals, whilst lateral overlap of atomic orbitals forms π molecular orbitals.

5.2.2. $s - p$ Combinations of Atomic Orbitals

An s orbital may combine with a p orbital provided that the lobes of the p orbital are pointing along the axis joining the nuclei. This results in a bonding molecular orbital (σ) with an increased electron density between the nuclei and an antibonding molecular orbital (σ^*) when the adjacent lobes are of opposite sign giving a reduced electron density in between the nuclei, as shown in Figure (5.3).

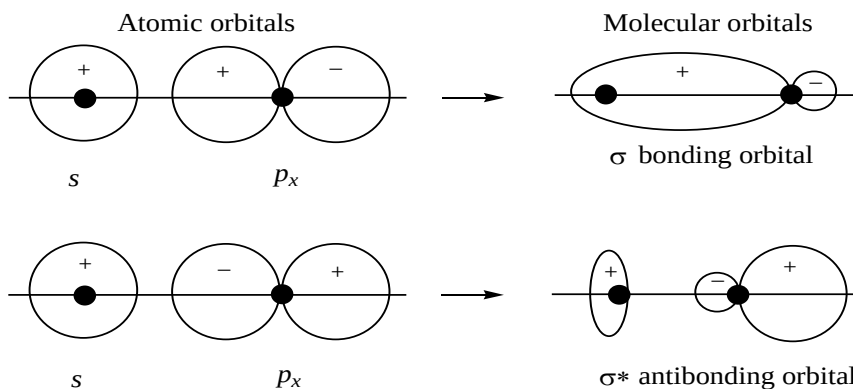


Figure (5.3): $s - p$ combination of atomic orbitals.

5.2.3. $p - p$ Combination of Orbitals

Consider first the combination of two p orbitals which have both lobes pointing along the axis joining the nuclei (face on overlap). Both a bonding MO and an antibonding MO are produced, Figure (5.4).

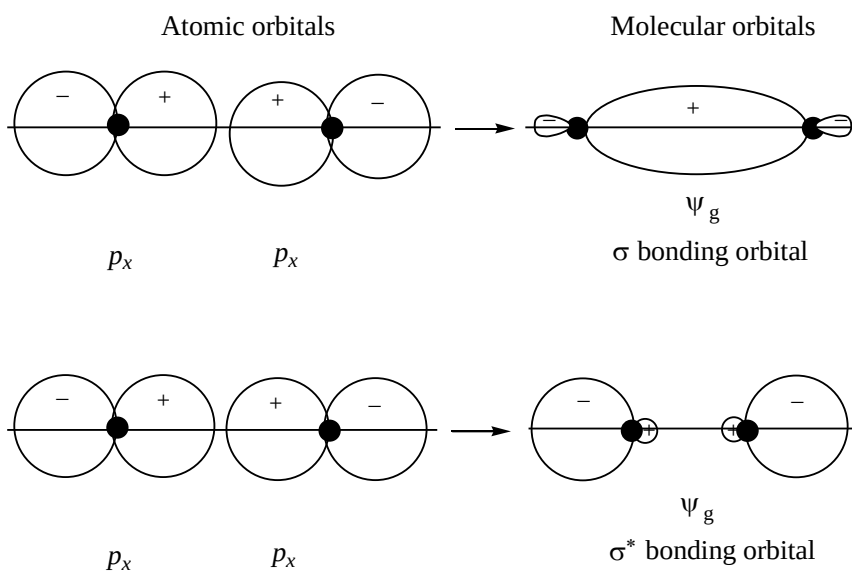


Figure (5.4): $p - p$ face on combination of atomic orbitals

Next consider the combination of two p orbitals which both have lobes perpendicular to the axis joining the nuclei. Lateral (side on) overlap of orbitals will occur resulting in π bonding and π^* antibonding molecular orbitals, Figure (5.5).

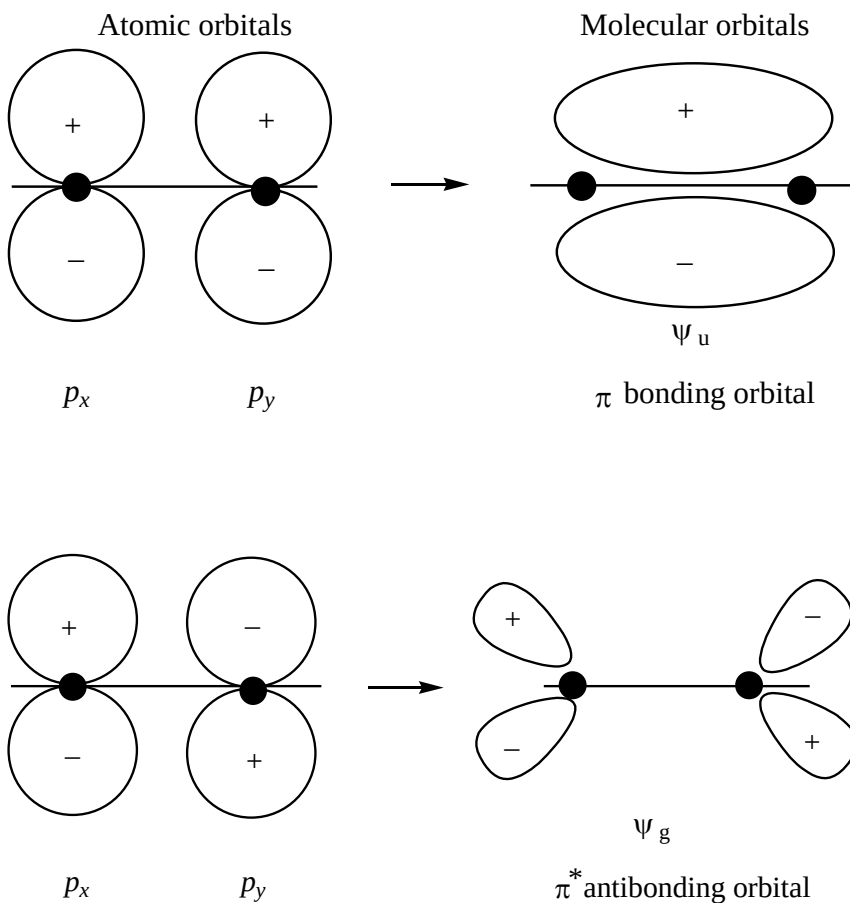


Figure (5.5): $p - p$ lateral combination of atomic orbitals

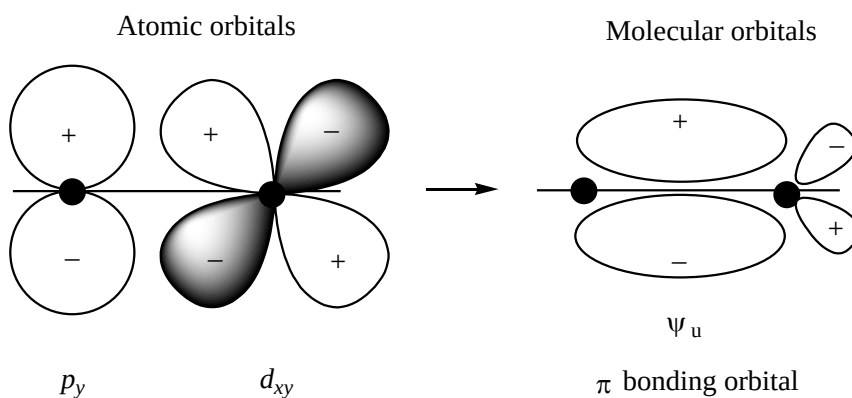
There are three points of difference between these σ and π molecular orbitals described previously:

- i. For π overlap the lobes of atomic orbitals are perpendicular to the line joining the nuclei. Whilst for σ overlap the lobes point along the internuclear axis.

- ii. For π molecular orbitals, Ψ is zero along the internuclear axis and consequently the electron Ψ^2 density is also zero. This is in contrast to σ orbitals.
- iii. The symmetry of π molecular orbitals is different from that shown by σ molecular orbitals. The π bonding orbital is ungerade (Ψ_u), whereas all σ bonding MOs are gerade (Ψ_g). Conversely the antibonding MO π^* is gerade (Ψ_g) whilst all σ^* molecular orbitals are ungerade (Ψ_u).

5.2.4. p – d Combination of Orbitals

A p orbital on one atom may overlap with a d orbital on another atom, as shown in Figure (5.6), giving bonding and antibonding molecular orbitals. Since the orbitals do not point along the internuclear axis, the obtained MOs must be of the π type.



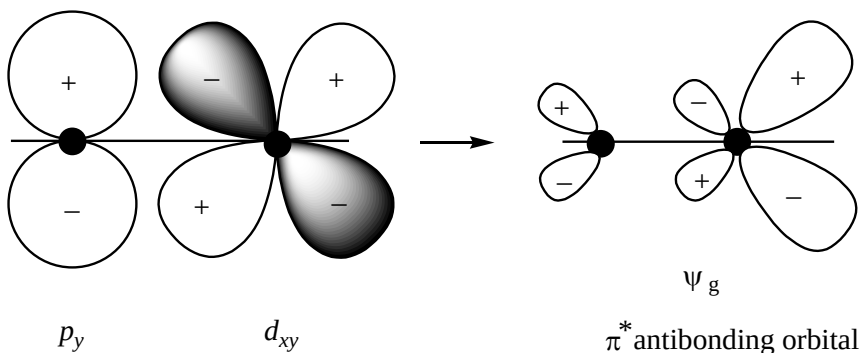


Figure (5.6): p – d combinations of atomic orbitals

5.2.5. d – d Combinations of Orbitals

It is possible to combine two d atomic orbitals producing bonding and antibonding molecular orbitals called δ and δ^* respectively.

5.2.6. Nonbonding Combinations of Orbitals

All the cases of overlap of atomic orbitals considered so far have resulted in a bonding MO of lower energy and an antibonding MO of higher energy. To obtain a bonding MO with a concentration of electron density in between the nuclei, the signs (symmetry) of the lobes which overlap must be the same. Similarly, for antibonding MO's the signs of the overlapping lobes must be different. In the combinations shown in Figure (5.7) any stabilization which occurs when overlapping + with + is destabilized by an equal amount of overlap + with -. There is no

overall change in energy, and this situation is termed nonbonding. It should be noted that in all of these nonbonding cases the symmetry of the two atomic orbitals is different.

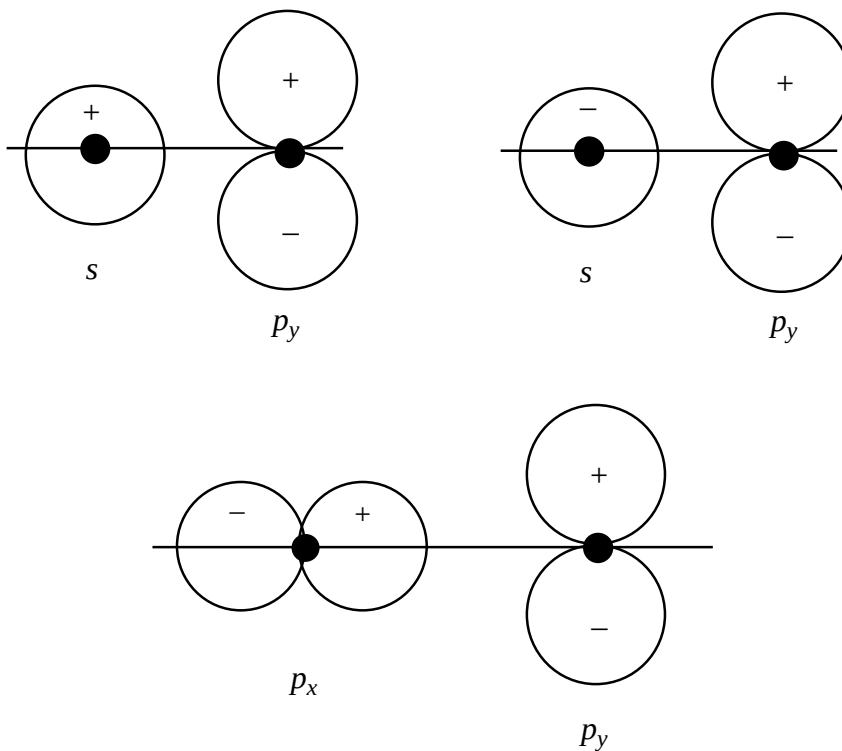


Figure (5.7): Some nonbonding combination of orbitals.

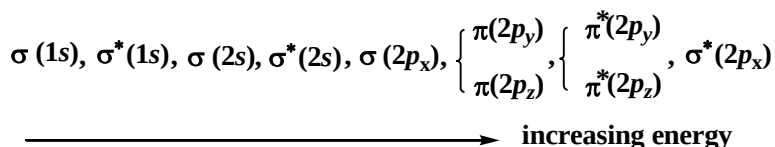
5.2.7. Rules for Linear Combination of Atomic Orbitals

In deciding which atomic orbitals may be combined to form molecular orbitals, three rules must be considered:

- i) The atomic orbitals must be roughly the same energy. This is important when considering overlap between two different types of atoms.
- ii) The orbitals must overlap one another as much as possible
- iii) In order to produce bonding and antibonding MOs, either the symmetry of the two atomic orbitals must remain unchanged when rotated about the internuclear axis, or both atomic orbitals must change symmetry in an identical manner.

5.3. Molecular Orbital Energy Level Diagrams

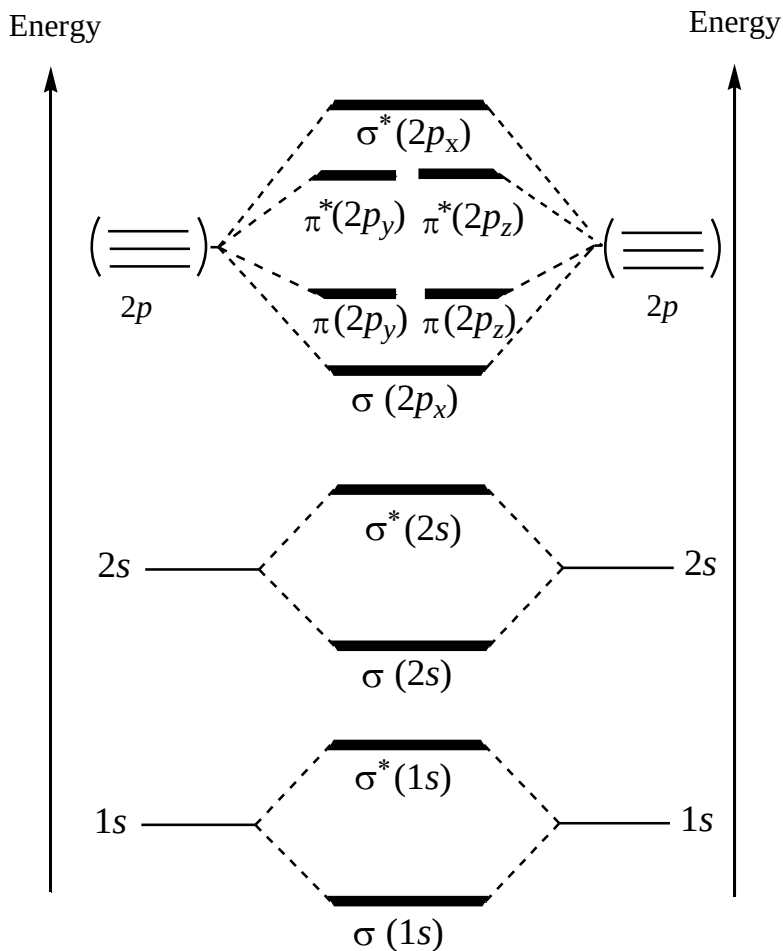
The order of energy of molecular orbitals has been determined mainly from spectroscopic data. For simple homonuclear diatomic molecules, the order is:



The $2p_y$ atomic orbital gives π bonding and π^* antibonding MOs of the same energy as those produced from the $2p_z$ orbitals. The

$\pi 2p_y$ and $\pi 2p_z$ orbitals are said to be doubly degenerate, and similarly $\pi^* 2p_y$ and $\pi^* 2p_z$ are doubly degenerate.

The same order of energy of molecular orbitals can be shown diagrammatically as in Figure (5.8).



Atomic orbitals Molecular orbitals Atomic orbitals

Figure (5.8)

The energies of the $\sigma 2p$ and $\pi 2p$ molecular orbitals are very close together, and the order shown is correct for nitrogen and heavier elements, but for boron and carbon the order is reversed and $\pi 2p_y$ and $\pi 2p_z$ are probably lower than $\sigma 2p_x$.

5.4. Bond Order and Bond Stability

All we need is a way to judge the stability of a molecule, once its level-energy diagram has been filled with the appropriate number of electrons. This criterion is the bond order (BO):

$$\text{BO} = \frac{\text{no. of bonding electrons} - \text{no. of antibonding electrons}}{2}$$

**Usually the bond order corresponds to the number of bonds described by the valence bond theory.*

**Fractional bond order exist in species that contain an odd number of electrons.*

**A bond order equal to zero means that the molecule has equal numbers of electrons in bonding and antibonding MOs, such a molecule would be unstable.*

**A bond order greater than zero means that there are more electrons in bonding than in antibonding MOs. Such a molecule would be more stable than the separate atoms. The greater the bond order, the shorter the bond length and the greater the bond strength.*

5.5. Examples of Molecular Orbital Treatment

5.5.1. Homonuclear Diatomic Molecules

The hydrogen molecule, H_2

The two electrons of the molecule occupy the lower energy σ_{1s} orbital (Figure 5.9). The molecule is represented as σ_{1s}^2 and the associated bond order equal to 1 $\{\text{BO} = (2 - 0) / 2 = 1\}$. Stabilization energy is 2Δ , so a σ bond is formed and the molecule exists and is well known.

H_2^+ molecule ion

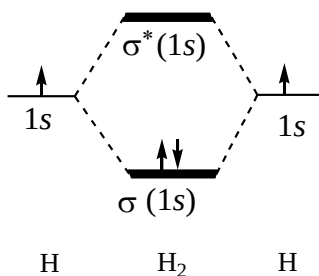
This may be considered as a combination of a H atom and a H^+ ion. The molecule is represented as σ_{1s}^1 with a bond order equal to $1/2 \{(1 - 0) / 2\}$ and associated with stabilization energy equal to Δ , as shown in Figure (5.9). This ion can be detected spectroscopically when hydrogen under reduced pressure is subjected to an electric discharge.

He_2 molecule

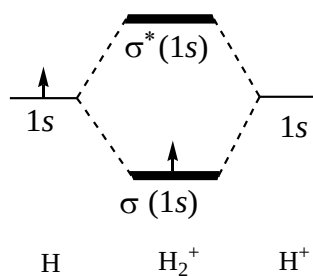
In the hypothetical helium molecule, there are four electrons arranged as; σ_{1s}^2 , σ_{1s}^{*2} , Figure (5.9). The stabilization and destabilization energies cancel each other, so there is no bond formation and the molecule does not exist ($\text{BO} = 0$).

He_2^+ molecule ion

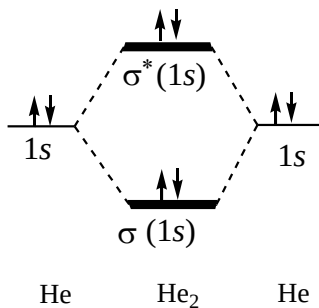
If this is considered as a He atom and a He⁺ ion there are three electrons, which are arranged as $\sigma 1s^2, \sigma^* 1s^1$. The filled $\sigma 1s$ bonding orbital gives 2Δ stabilization whilst the half-field $\sigma^* 1s$ gives one Δ of destabilization. Overall there is some stabilization, so the helium molecule ion should exist, and it has been observed spectroscopically.



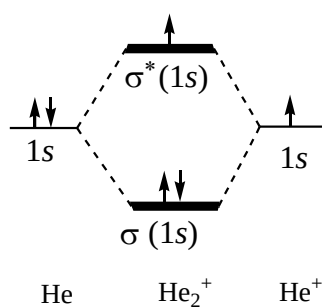
(a)



(b)



(c)



(d)

Figure (5.9): Molecular orbital diagrams for (a) H₂, (b) H₂⁺, (c) He₂ and (d) He₂⁺

Li₂ molecule

Each lithium has two electrons in the inner shell, and one electron in its outer shell, making a total of six electrons, arranged as; $\sigma 1s^2$, $\sigma^* 1s^2$, $\sigma 2s^2$. The inner shell of filled $\sigma 1s$ and $\sigma^* 1s$ do not contribute in the bonding, however, bonding occurs from the filling of the $\sigma 2s$ level, and though lithium is a metal, Li₂ molecules do exist in the vapour state, see Figure (5.10).

Be₂ molecule

A beryllium atom contains four electrons, so there are eight electrons to be considered in the molecule; $\sigma 1s^2$, $\sigma^* 1s^2$, $\sigma 2s^2$, $\sigma^* 2s^2$. Ignoring the inner shell as before, it is apparent that the effect of the bonding 2s and antibonding 2s levels cancel, so there is no stabilization and the molecule would not be expected to exist, see Figure (5.10).

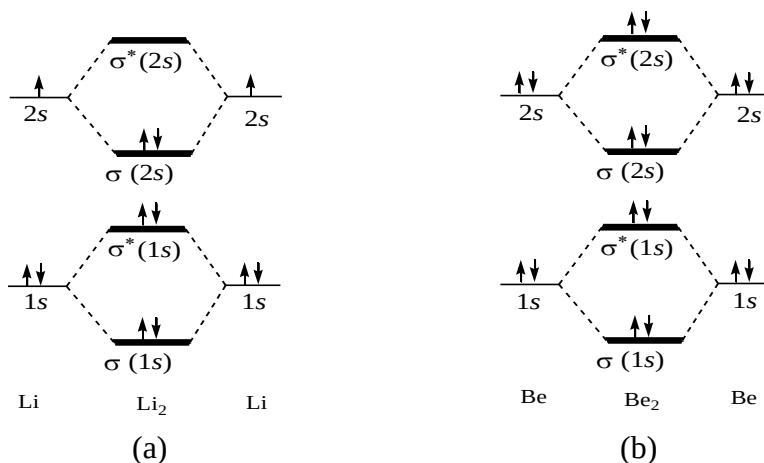


Figure (5.10): Molecular orbital diagrams for (a) Li₂, and (b) Be₂

B₂ molecule

Each B atom contains five electrons, making ten electrons in the molecule, distributed in the molecular orbitals as follows;

$$\sigma(1s)^2, \sigma^*(1s)^2, \sigma(2s)^2, \sigma^*(2s)^2, \begin{cases} \pi 2p_y^1 \\ \pi 2p_z^1 \end{cases}$$

Since the $\pi 2p_y$ and $\pi 2p_z$ orbitals are degenerate, Hund's rule applies, and each is singly occupied. The inner shell does not participate in bonding. The effect of bonding and antibonding $\sigma 2s$ orbitals cancel but stabilization occurs from the filling of the $\pi 2p$ orbitals, hence a bond is formed and B₂ exists, $BO = (4 - 2) / 2 = 1$. The molecule has two unpaired electrons, therefore a paramagnetic properties are expected, see Figure (5.11).

C₂ molecule

The carbon atom has six electrons, giving twelve electrons in the molecule.

$$\sigma(1s)^2, \sigma^*(1s)^2, \sigma(2s)^2, \sigma^*(2s)^2, \begin{cases} \pi 2p_y^2 \\ \pi 2p_z^2 \end{cases}$$

The molecule should be stable, since the $\pi 2p$ bonding orbitals provide 4Δ of stabilization energy and the bond order = $(6 - 2) / 2 = 2$, assuming that the inner shell does not participate in bonding.

The molecule with all electrons are paired should be diamagnetic, see Figure (5.11).

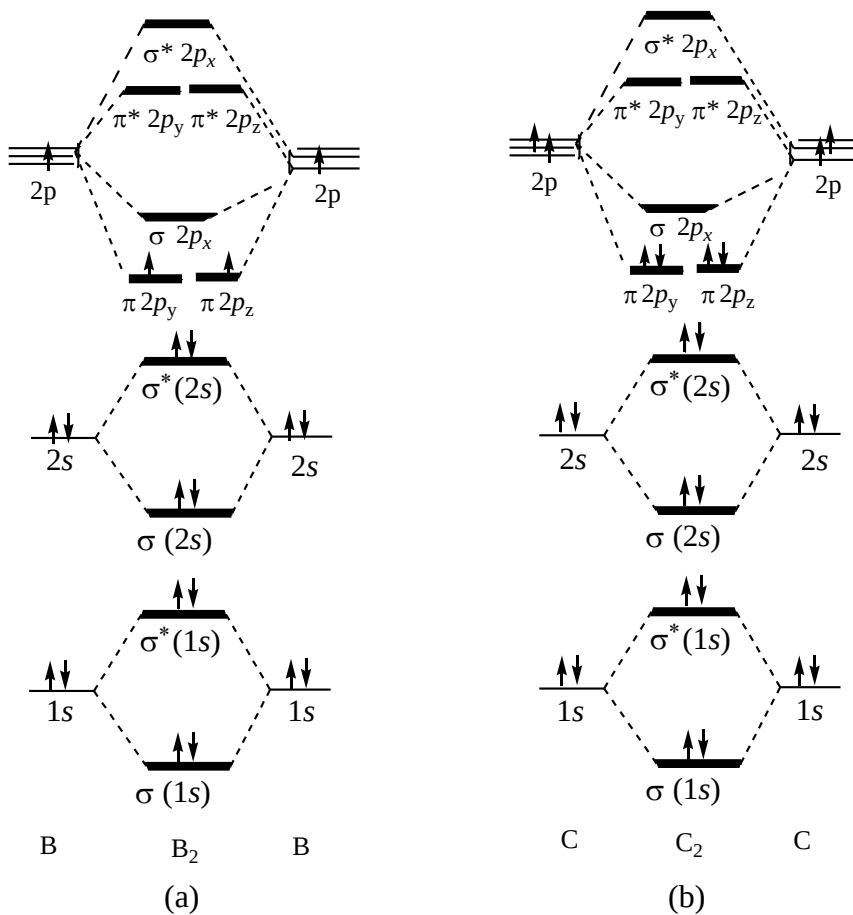


Figure (5.11): Molecular orbital diagrams for (a) B_2 , and (b) C_2

N₂ molecule

Each nitrogen atom has seven electrons, so the diamagnetic nitrogen molecule has 14 electrons, distributed as follows.

$$\sigma(1s)^2, \sigma^*(1s)^2, \sigma(2s)^2, \sigma^*(2s)^2, \sigma(2p_x)^2, \begin{cases} \pi 2p_y^2 \\ \pi 2p_z^2 \end{cases}$$

Remember that, for nitrogen and heavier elements $\sigma 2p_x$ is of lower energy than $\pi 2p_y$ and $\pi 2p_z$. The bond order is 3 $\{(8 - 2) / 2 = 3\}$, and all the electrons are paired, so the molecule should be diamagnetic, see Figure (5.12).

O₂ molecule

Recall that valence bond theory predicts that O₂ is diamagnetic. However, experiments show that it is paramagnetic, with two unpaired electrons. Molecular orbital theory predicts a structure consistent with this observation. Each oxygen atom has 8 electrons, so the oxygen molecule has 16, distributed as follows.

$$\sigma(1s)^2, \sigma^*(1s)^2, \sigma(2s)^2, \sigma^*(2s)^2, \sigma(2p_x)^2, \begin{cases} \pi 2p_y^2 \\ \pi 2p_z^2 \end{cases}, \begin{cases} \pi^* 2p_y^1 \\ \pi^* 2p_z^1 \end{cases}$$

BO = $(8 - 4) / 2 = 2$, and the molecule contains two unpaired electrons as shown in Figure (5.12).

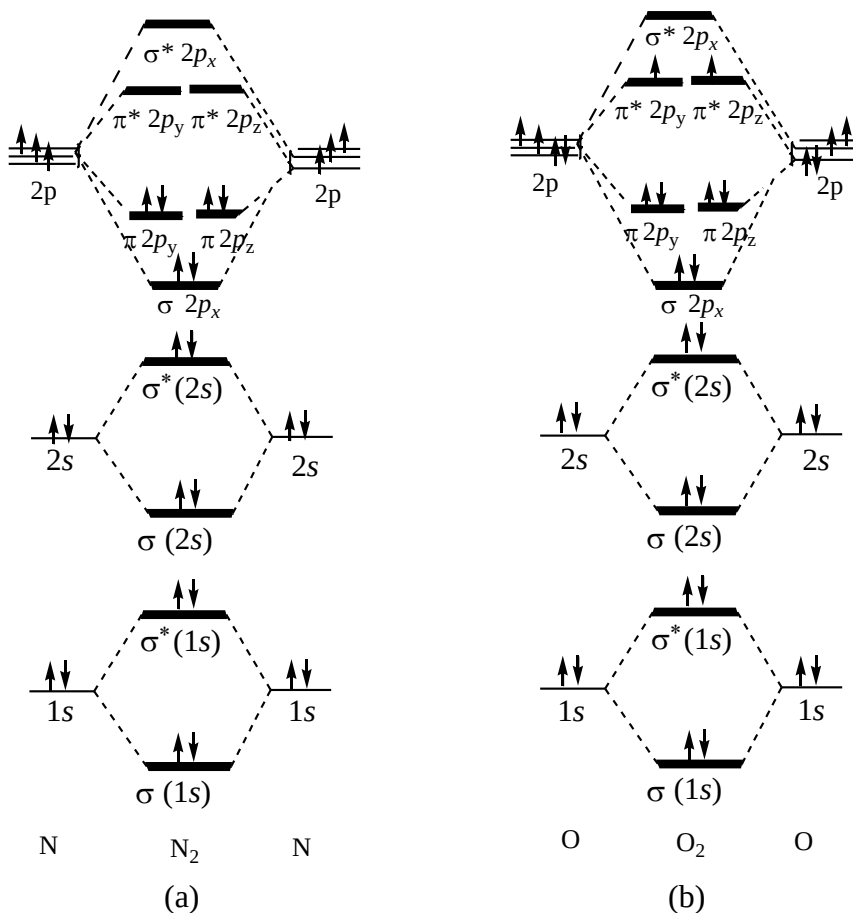


Figure (5.12): Molecular orbital diagrams for (a) N_2 , and (b) O_2

Predict the stabilities and bond orders of the ions O_2^+ and O_2^- ?

*For O_2^+ , we have to remove one electron from the highest energy orbital of O_2 molecule (π^*2p_y or π^*2p_z) and the configuration becomes,

$$\sigma(1s)^2, \sigma^*(1s)^2, \sigma(2s)^2, \sigma^*(2s)^2, \sigma(2p_x)^2, \left\{ \begin{matrix} \pi 2p_y^2 \\ \pi 2p_z^2 \end{matrix} \right\}, \left\{ \begin{matrix} \pi^* 2p_y^2 \\ \pi^* 2p_z^1 \end{matrix} \right\}$$

The bond order = $(8 - 3) / 2 = 2.5$.

*For O_2^- , we have to add an extra electron to the O_2 configuration as follows.

$$\sigma(1s)^2, \sigma^*(1s)^2, \sigma(2s)^2, \sigma^*(2s)^2, \sigma(2p_x)^2, \left\{ \begin{matrix} \pi 2p_y^2 \\ \pi 2p_z^2 \end{matrix} \right\}, \left\{ \begin{matrix} \pi^* 2p_y^2 \\ \pi^* 2p_z^1 \end{matrix} \right\}$$

The bond order = $(8 - 5) / 2 = 1.5$.

Build up molecular orbital diagram of O_2^+ and O_2^- molecule ions?

In a similar way you may conclude the bond order and stability of O_2^{2-} (peroxide ion)?

F₂ molecule

The eighteen electrons of F_2 molecule are arranged as;

$$\sigma(1s)^2, \sigma^*(1s)^2, \sigma(2s)^2, \sigma^*(2s)^2, \sigma(2p_x)^2, \left\{ \begin{matrix} \pi 2p_y^2 \\ \pi 2p_z^2 \end{matrix} \right\}, \left\{ \begin{matrix} \pi^* 2p_y^2 \\ \pi^* 2p_z^2 \end{matrix} \right\}$$

Build up molecular orbital diagram of F_2 molecule and predict the bond order?

5.5.2. Heteronuclear Diatomic Molecules

The corresponding atomic orbitals of two different elements, such as the 2s orbitals of carbon and oxygen atoms, have different energies because their differently charged nuclei have different attractions for the electrons. The atomic orbitals of the more electronegative element are lower in energy than the corresponding orbitals of the less electronegative element. As a result, a molecular orbital diagram such as shown in Figure (5.13) is appropriate for heteronuclear diatomic molecules such as CO, NO, and CN.

In general, the energy differences ΔE_1 , ΔE_2 , and ΔE_3 depend upon the difference in electronegativities between the two atoms. The greater these energy differences, the more polar is the bond joining the atoms i.e., the greater is its ionic character. On the other hand, the energy differences reflect the degree of overlap between atomic orbitals, the smaller these differences, the more the orbitals can overlap, and the greater is the covalence character of the bond.

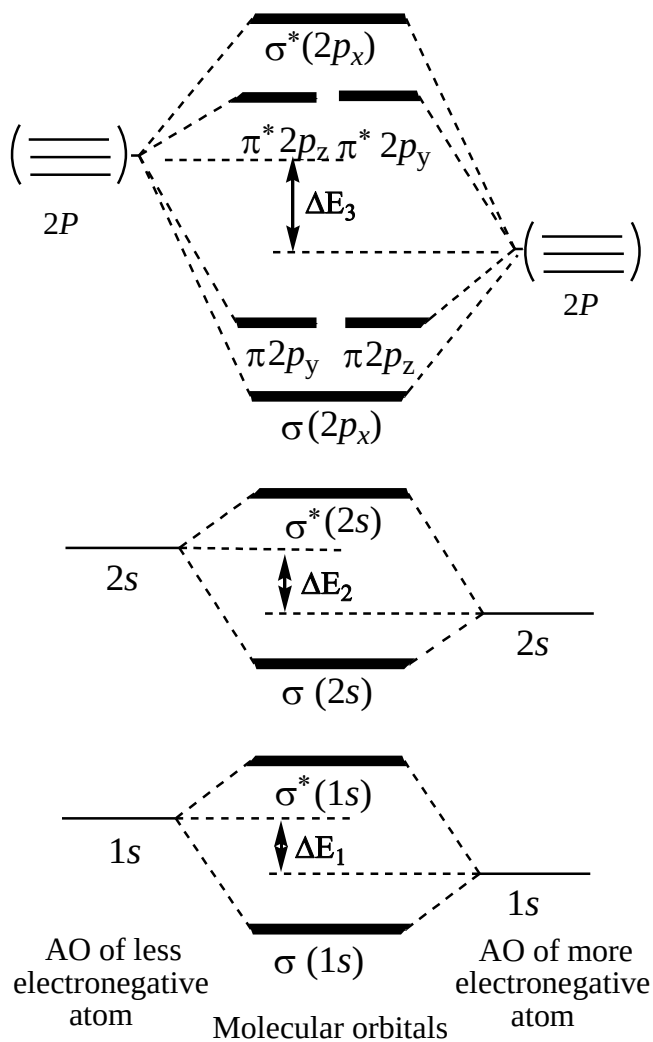


Figure (5.13): Molecular orbital diagrams for heteronuclear diatomic molecule, CO, NO or CN.

NO (nitric oxide) molecule

The nitrogen atom has 7 electrons and the oxygen atom has 8 electrons, making fifteen electrons in the molecule. So the electronic configuration of the molecule is,

$$\sigma(1s)^2, \sigma^*(1s)^2, \sigma(2s)^2, \sigma^*(2s)^2, \sigma(2p_x)^2, \begin{cases} \pi 2p_y^2 \\ \pi 2p_z^2 \end{cases}, \begin{cases} \pi^* 2p_y^1 \\ \pi^* 2p_z^0 \end{cases}$$

The inner shell is nonbonding as we have seen before, hence, the bond order is $(8 - 3) / 2 = 2.5$. The molecule is paramagnetic because it contains one unpaired electron.

Removal of one electron to make NO^+ results in a shorter and stronger bond because the electron is removed from an antibonding orbital, $\text{BO} = 3$. What about if an electron is added to make NO^- ?

Build up the molecular energy diagrams for NO , NO^+ , and NO^- ?

What is the bond order and magnetism expected for CN ?

CO molecule

The carbon has 6 electrons, and the oxygen has 8 electrons, making 14 electrons in the molecule, presumably arranged,

$$\sigma(1s)^2, \sigma^*(1s)^2, \sigma(2s)^2, \sigma^*(2s)^2, \sigma(2p_x)^2, \begin{cases} \pi 2p_y^2 \\ \pi 2p_z^2 \end{cases}$$

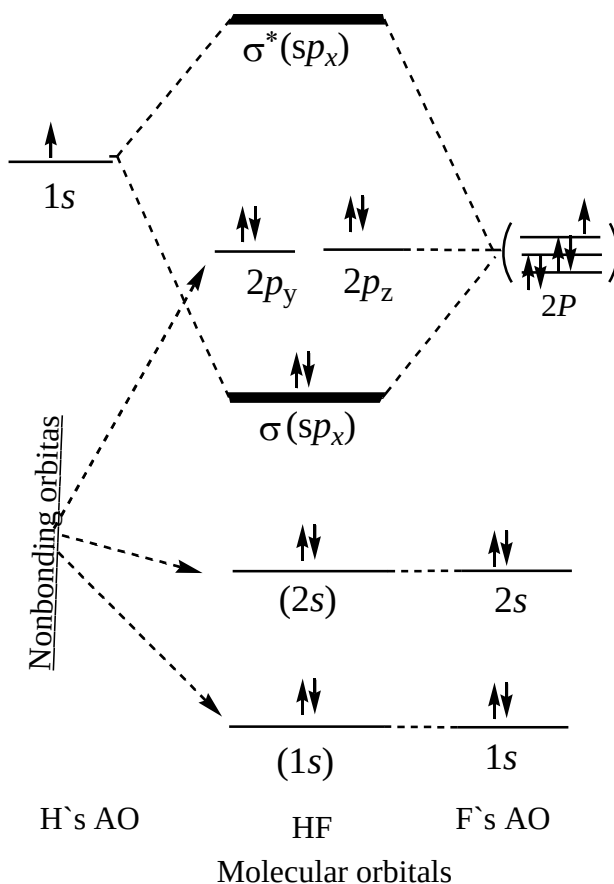
The expected bond order is $(8 - 2) / 2 = 3$, and the molecule is diamagnetic.

It should be mentioned that, this simple picture of bonding and sequence of energy levels in the molecule is not adequate, since if CO is ionized to give CO^+ by removal of one electron, it would be expected that the bond order would be reduced (and the bond length would be increased) since it apparently involves the removal of a bonding electron. In fact the bond length is decreased upon ionization indicating that the electron removed must come from an antibonding orbital. This indicates that in this molecule the order of molecular orbitals differs from that for simple heteronuclear diatomic molecules.

HF molecule

Combination between the hydrogen 1s atomic orbital and the fluorine 1s, 2s can be ruled out because their energy is too low. If overlap occurred between the hydrogen 1s and the fluorine $2p_y$ or $2p_z$ orbitals, it would be nonbonding (see Figure (5.7)) because the positive lobe of hydrogen will overlap equally with the positive and negative lobes of fluorine orbitals. Thus the only effective overlap is with the fluorine $2p_x$ orbital. The combination of $\text{H } 1s^1$ and $\text{F } 2p_x^1$ gives both bonding and antibonding orbitals, and the two electrons occupy the bonding molecular orbital.

Except $2p_x$ all the fluorine atomic orbitals have no net overlap with H orbital. They are called nonbonding molecular orbitals. These nonbonding orbitals retain the characteristic of the fluorine atomic orbitals from which they are formed, Figure (5.14).



The expected bond order = $(2 - 0) / 2 = 1$

6. United atom method

The LCAO method described above is equivalent to bring the atoms from infinity to their equilibrium positions in the molecule. The united atom method is an alternative approach. It starts with a hypothetical united atom, where the nuclei of two

atoms coalesce, so that we have a nucleus whose mass and charge are equal to the sum of the two nuclei, together with all the attendant electrons. The united atom has the same number of orbitals as a normal atom, but it contains the electrons from two atoms. Thus some electrons must be promoted to higher energy levels in the united atom. Furthermore, the energy of the united atom orbitals differs from that of the atomic orbitals because of the greater nuclear charge. Thus the molecular orbitals are in an intermediate position between the orbitals in the united atom and those in the separate atoms. If lines are drawn between the energies of the electrons in the separate atoms and in the united atom a correlation diagram is obtained, as shown in Figure (6.1).

The molecular orbitals associated with the formed molecule fall into two categories:

- i) Those levels or molecular orbitals corresponding to a decrease in energy as the atoms get closer together, i.e. related to lines sloping downwards from right to left are called bonding molecular orbitals.
- ii) Those corresponding to an increase in energy as the internuclear distance decreases, and so related to lines sloping upwards from right to left are called antibonding molecular orbitals.

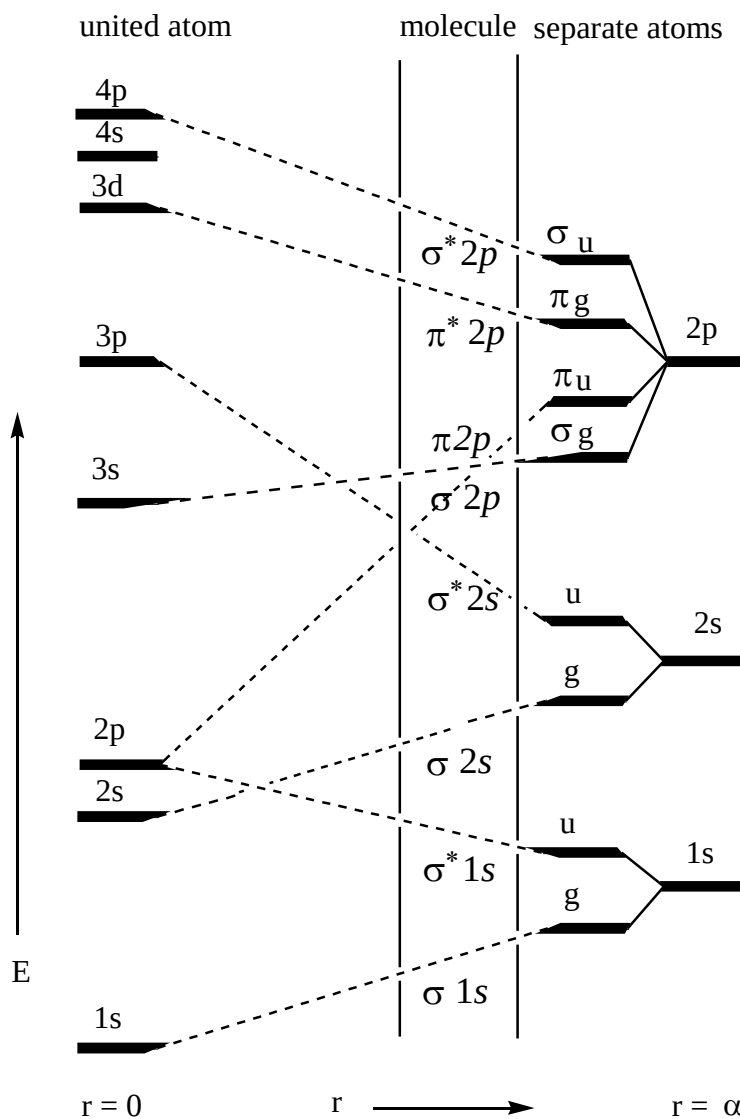


Figure (6.1): correlation diagram, energy levels in separated and united atoms

7. References

1. N. N. Greenwood, "Principles of atomic orbitals" Royal Institute of Chemistry Monographs for Teachers, No. 8 (1966).
2. H.G. Emeleus and A. G. Sharpe, "Modern aspects of inorganic chemistry" Routledge and Kegan Paul, 4th edition (1973), and references therein.
3. H. B. Gray, "Electrons and Chemical Bonding", Benjamin, (1964).
4. J. D. Lee, "A new concise inorganic chemistry" 3rd edition, Van Nostrand Reinhold(UK) Co. Ltd. (1982).
5. E. Cartmell and G.W.A. Fowles, "Valence and molecular structure" 4th edition, Butterworths (1983).
6. A. F. Wells, "Structural Inorganic Chemistry" 4th edition, Oxford University Press, (1975)
7. W. E. Addison, "Structural Principles in Inorganic Chemistry" Longmans, (1961).

8. D. S. Urch, " Orbitals and Symmetry" Penguin, (1970).
9. T. Moeller, "Inorganic chemistry", Wiley-Interscience, New York , (1952).
10. J. Kleinberg, W.J. Argersinger, and E. Griswold , " Inorganic chemistry", Heath, Boston, (1960).
11. F.A. Cotton and G. Wilkenson, "Advanced inorganic chemistry " Wiley-Interscience, New York , (1973).
12. W.L. Jolly, " Modern inorganic chemistry " Mc Graw Hill Book Co, (1984).
13. J.E. Huheey, " Inorganic chemistry " 2^{ed} edition Harper and Row Publishers, New York, (1978).
14. M.C. Day and J. Selbin, "Theoretical inorganic chemistry "Chapman and Hall., New York, (1962).
15. D.H. Andrews, and R.G. Kokes," Fundamental chemistry" 2^{ed} edition John Wiley & Sons, Inc., New York , (1965).
16. A. K. Barnard, " Theoretical Bases of Inorganic Chemistry" McGraw-Hill, (1965).

