

## Module 2 : Molecular Structure

### Lecture 9 : Polyatomics

#### Objectives

In this lecture you will learn the following

- Construction of energy level diagrams of triatomics.
- Qualitative sketches of hybrid orbitals.
- Overlap diagrams in the case of multiple bonding.
- Molecular geometries of a few molecules.
- $\pi$  molecular orbitals of butadiene and benzene.

#### 9.1 Introduction

The next stage in the study of chemical bonding is the study of polyatomics. The solutions of the Schrödinger equation for polyatomics will involve the molecular orbitals that are functions of the coordinates of the electrons. With the possible exception of core orbitals (such as 1s orbital of Cl in NaCl or 2s orbital of I in KI ) all the molecular orbitals (especially those involving valence shell orbitals) are spread throughout the molecule.

A natural way to depict these MOs is to show the contour diagrams of various MOs. Since these involve detailed calculations, we shall study the simpler examples of binding in triatomics, shapes of hybrid orbitals and overlap diagrams in multiple bonding and towards the end of the lecture, consider some quantitative aspects of bonding in ethylene, butadiene and benzene.

The "simplest" polyatomic is  $H_3$ . Let us consider how the 1s orbitals of the three hydrogen atoms in a linear  $H_3$  contribute to the formation of the MOs in  $H_3$ . The binding energy in  $H_3$  is relatively small and the purpose here is simply to show the nature of the MOs. We will not do a quantitative calculation, but an intuitive approach will bring out many interesting aspects of bonding. In the lowest energy MO, all the three s orbitals overlap positively giving the shape shown in Fig 9.1 (a). There is an envelope of electron cloud throughout the molecule. Only two electrons (one with spin "up" and another with spin "down" can be placed in this orbital. The third electron ( $H_3$  has 3 electrons) has to go a higher level .

**Fig 9.1 The three orbitals of linear H<sub>3</sub> (a) bonding (b) nonbonding (c) antibonding.**

For the second MO, we chose  $1s_A - 1s_C$ . Had we chosen (i)  $1s_A - 1s_B$ , an equally acceptable candidate would have been (ii)  $1s_C - 1s_B$  or any combination of these two. We have actually chosen the difference of these two (i) - (ii) which has a greater degree of symmetry / asymmetry. For the third MO we take the sum of these two. The three MOs for linear H<sub>3</sub> are

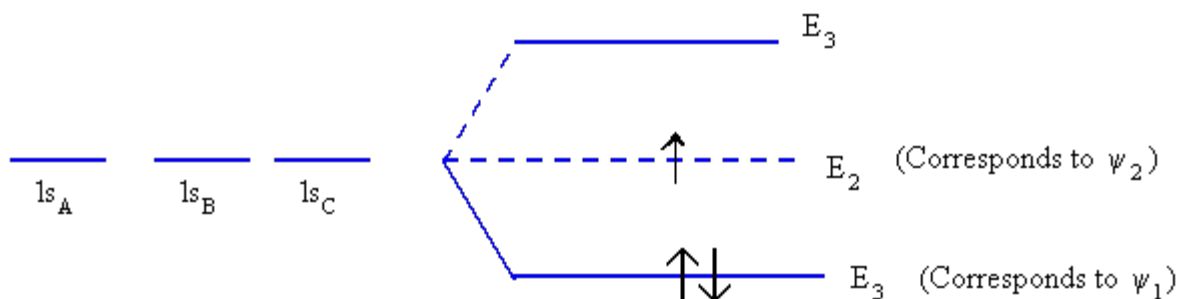
$$\psi_1(r_1) = 1s_A(r_1) + 1s_B(r_1) + 1s_C(r_1) \quad (9.1)$$

$$\psi_2(r_3) = 1s_A(r_3) - 1s_C(r_3) \quad (9.2)$$

$$\psi_3(r) = 1s_A(r) - 2s_B(r) + 1s_C(r) \quad (9.3)$$

When the second electron is placed in  $\psi_1$ , we assign the coordinate  $r_2$  to it giving  $\psi_1(r_2)$ . This will have a spin opposite to the spin of the electron described by  $\psi_1(r_1)$  so that the wave function does not disobey the Pauli exclusion principle. The third electron goes to  $\psi_2$ . There is no electron in  $\psi_3$ . The energy of H<sub>3</sub> depends on how much lower is  $\psi_1$  compared to the 1s level of an isolated H atom and also the relative placement of  $\psi_2$ .

Here  $1s_A(r_1)$  is the 1s orbital of a hydrogen atom labeled A and  $r_1$  is the electron coordinate. Note that  $\psi_2$  has one node and  $\psi_3$  has two nodes. This is a routine feature now. As the energies keep increasing, so do the number of nodes. An energy level diagram for H<sub>3</sub> is shown in fig 9.2.



**Figure 9.2 Energy level diagram for H<sub>3</sub>**

## 9.2 Bonding in triatomics CH<sub>2</sub>, XeF<sub>2</sub> and H<sub>2</sub>O

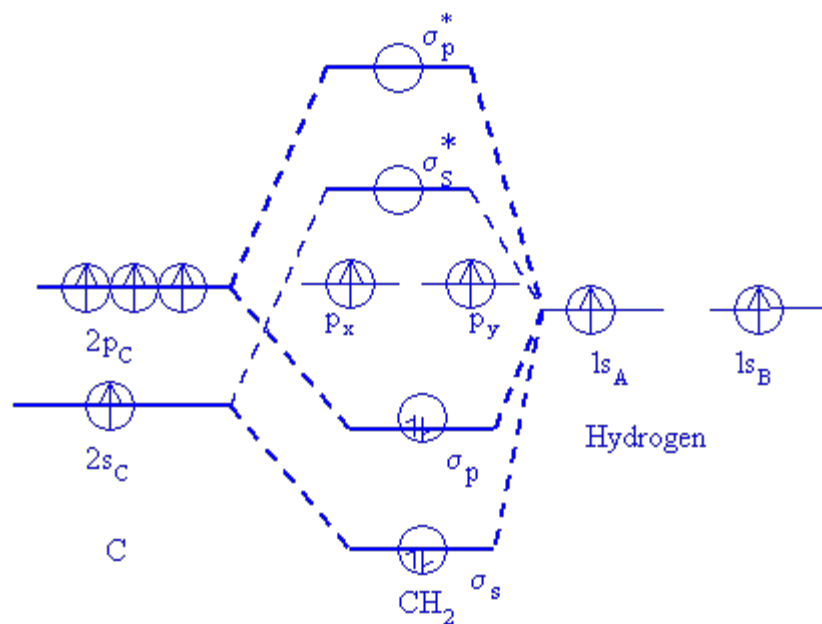


Figure 9.3 (a) Energy level diagram for CH<sub>2</sub>

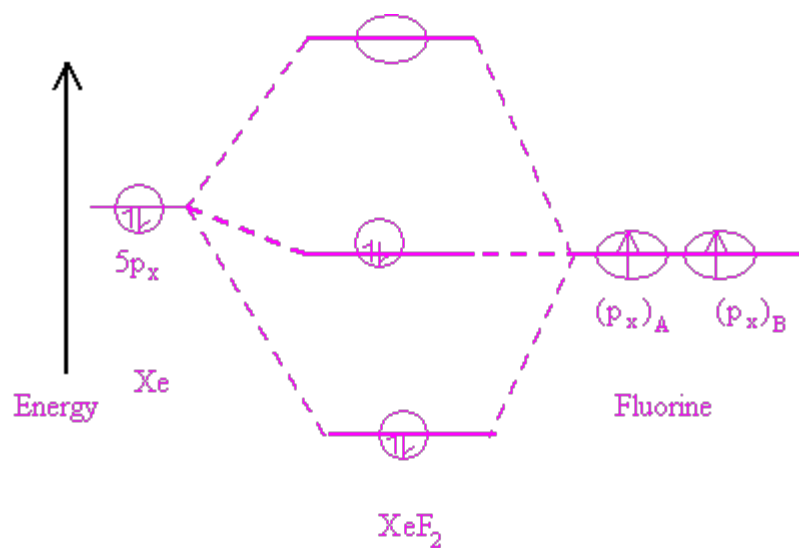


Figure 9.3 (b) Energy level diagram for XeF<sub>2</sub>.

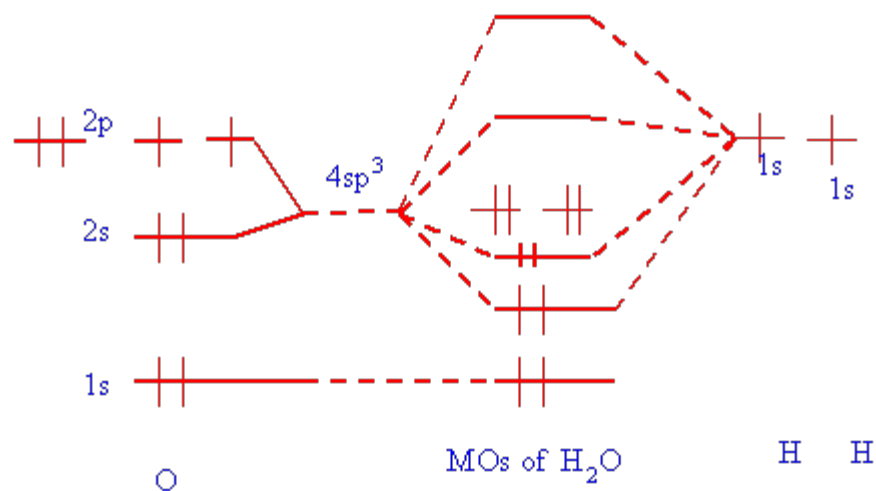


Figure 9.3 (c) Energy level diagram for H<sub>2</sub>O

We shall consider three more triatomics, namely  $\text{CH}_2$ ,  $\text{XeF}_2$  and  $\text{H}_2\text{O}$ . Water is a stable molecule.  $\text{XeF}_2$  is not as strongly bonded as water and  $\text{CH}_2$  is a radical. Their MO diagrams are shown in Fig 9.3 (a), (b) and (c). In  $\text{CH}_2$ , the four orbitals of carbon ( $2s$ ,  $2p_x$ ,  $2p_y$  and  $2p_z$ ) and the two  $1s$  orbitals of the two hydrogen together form the six MOs as shown in fig 9.3 (a). The  $1s$  orbital of C is not shown as it is much lower in energy. One of the two electrons of the  $2s$  orbital is shown "promoted" to  $2p$ . In  $\text{CH}_2$ , there are two bonding pairs ( $\sigma_s$  and  $\sigma_p$ ) of electrons and two unpaired electrons (in  $p_x$  and  $p_y$ ; which are non bonding) to give  $\text{CH}_2$  the free radical character. In  $\text{XeF}_2$  (fig 9.3 (b)), the paired electrons in a  $2p$  orbital of Xe interact with two electrons (one each in a  $p_x$  orbital of each F) of F to give two pairs of bonding electrons.

The "old" concept that rare gases do not form molecule due to their "closed" shell is gone! All (and the only thing!) that is needed to form a stable species is that in the MOs formed, there should be more number of electrons in bonding orbitals. Even if the numbers are equal, some stability can arise if the lowering in energy due to bonding MOs is more than the rise in energy due to the occupied antibonding MOs. Fig 9.3(c) shows the bonding in  $\text{H}_2\text{O}$ . Formation of four hybrid orbitals in O (from the  $2s$  and the three  $2p$  orbitals) is shown in the figure. There are two pairs of bonding electrons and two pairs of "non bonding" electrons on the oxygen. These are the lone pairs. These principles illustrated in simple triatomics work in other larger molecules. We shall next turn to the details of hybridization.

### 9.3 Hybridization.

Hybridization is a ubiquitous concept in molecular chemistry. A pictorial description runs like this. As four hydrogen approach a carbon atom, one of the  $2s$  electrons of C gets "promoted" to a vacant  $2p$  giving four unpaired electrons. These four orbitals rearrange into a regular tetrahedral arrangement and combine with the four  $1s$  orbitals of the four hydrogens to give a tetrahedral  $\text{CH}_4$ . Remember orbitals are mathematical functions. In quantum chemistry (the subarea of chemistry which studies the bonding in molecules using quantum mechanical principles), the bonding MOs are calculated for the most stable configuration of a molecule and from these levels (when the results agree with spectroscopic and other thermal data), inferences regarding hybridization are conclusively drawn. In  $\text{LiF}$  we have already seen  $sp$  hybrids.

In  $\text{H}_2\text{O}$  we mentioned hybrids formed by combining one  $s$  and three  $p$  orbitals on O. These are referred to as  $sp^3$  hybrids. These occur in all saturated carbon compounds. The tetrahedral bonding in a saturated carbon atom is a result of this hybridization. The four combinations for the four  $sp^3$  hybrids are given below.

$$h_1 = 2s + 2p_x + 2p_y + 2p_z \quad (9.4a)$$

$$h_2 = 2s + 2p_x - 2p_y - 2p_z \quad (9.4b)$$

$$h_3 = 2s - 2p_x - 2p_y - 2p_z \quad (9.4c)$$

$$h_4 = 2s - 2p_x + 2p_y - 2p_z \quad (9.4d)$$

The angle between any two  $sp^3$  hybrids can be found by the same argument. Take two  $sp^3$  hybrids (Eq 9.4). Two unit vectors along the hybrids  $h_1$  and  $h_2$  are  $1/\sqrt{3}(\hat{i} + \hat{j} + \hat{k})$  and  $1/\sqrt{3}(\hat{i} - \hat{j} - \hat{k})$ . The dot product is  $-1/3$  and  $\cos^{-1}(-1/3) = 109^\circ 28'$  which is the tetrahedral angle.

It should be noted that all hybrid combinations are not completely regular. E.g. in  $\text{CH}_3\text{Br}$ , the hybrid in the direction of Br is likely to be more directed (due to the electronegativity of Br) towards Br than the others towards hydrogens. The actual coefficients of e.q. 9.3 and 9.4 in these molecules are obtained from detailed calculations.

In this lecture, we have considered hybridization among  $s$  and  $p$  orbitals. In molecules wherein there is participation of  $d$  orbitals, other combination such as  $pd$ ,  $sp^3d^2$  and so on naturally emerge.

The next case of hybridization is  $sp^2$ , which predominantly occurs in carbon compounds containing double bonds. The best example is ethene  $\text{CH}_2 = \text{CH}_2$ . Each carbon atom is "connected" to three "centers", one adjacent carbon and two hydrogens.

To get 3 equivalent orbitals in 3 directions in a plane, one s (2s) and two 2p (2p<sub>x</sub> and 2p<sub>z</sub>) orbitals in the xz plane are used. The three sp<sup>2</sup> orbitals on the first carbon are:

$$\begin{aligned} h_1 &= (1/\sqrt{3}) [s + \sqrt{2} p_z] \\ h_2 &= (1/\sqrt{3}) [s - (1/\sqrt{2})(p_z) + \sqrt{3/2}(p_x)] \\ h_3 &= (1/\sqrt{3}) [s - (1/\sqrt{2})(p_z) - \sqrt{3/2}(p_x)] \end{aligned} \quad (9.5)$$

#### Figure 9.4 Hybrid Orbitals.

Orbital  $h_1$  is directed towards the second carbon to its right. Orbitals  $h_2$  and  $h_3$  are directed towards negative z. To get the angle between the orbitals, treat the p orbitals as vectors. The s orbitals are spherically symmetrical and independent of direction. They are like scalars and do not contribute to directionality. If z axis is  $\hat{k}$  and x axis is  $\hat{i}$ , then the unit vectors corresponding to  $h_2$  and  $h_3$  are  $-1/2 \hat{k} + \sqrt{3/2} \hat{i}$  and  $-1/2 \hat{k} - (\sqrt{3/2}) \hat{i}$ . The dot product or  $\cos \theta$  ( $\theta$ , the angle between the two vectors) is  $(+1/4 - 3/4)$ .

Since  $\cos \theta = -1/2$ ,  $\theta = 120^\circ$ , which is the angle between the two sp<sup>2</sup> hybrids. The same angle is found between any pair among the three hybrids. Among the four electrons in C, three can be placed, with one electron in each orbital to bind with an adjacent C or two hydrogens. All these three hybrid orbitals are in the molecular plane of C<sub>2</sub>H<sub>4</sub>. The fourth electron is in the p<sub>y</sub> orbital which is in a plane perpendicular to the molecular plane. This electron binds with its counterpart on the other carbon atom to give a  $\pi$  bond, which is the double bond in C<sub>2</sub>H<sub>4</sub>.

#### 9.4 Overlap diagrams of d-orbitals.

We have already studied the overlap diagrams of s and p orbitals in lectures 7 and 8. We shall consider the

overlap diagrams of d orbitals here. Just as s and p orbitals combine to form  $\sigma$ ,  $\sigma^*$ ,  $\pi$  and  $\pi^*$  orbitals, d orbitals can also overlap to give bonding and antibonding combinations. We will consider combinations between two d orbitals of two atoms. Combinations between d and s and d and p can be constructed by analogy.

The "head on" overlap of d orbitals gives a sigma bond (comparison to p is confusing) and is shown in fig 9.5 (a). The "sideways" overlap of two d orbitals gives a  $\pi$  orbitals which is shown in fig 9.5 (b). This MO has a plane of symmetry which contains the molecular axis and is perpendicular to the plane of paper. The third kind of overlap is also sideways but with each lobe of the d orbitals facing a corresponding lobe of the other. This third type of overlap is called a  $\delta$  bond. In  $\sigma$  and  $\pi$  bonds [ fig. 9.5(a) and (b) ] only one or two lobes overlap.  $\delta$  bond occurs in quadruple bonding which is found among bimetallic compounds of transition elements.

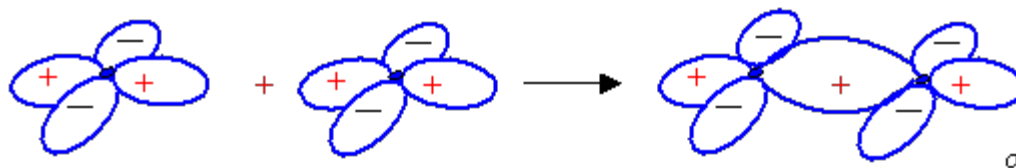


Fig 9.5 (a)  $\sigma$  bond from two d orbitals.

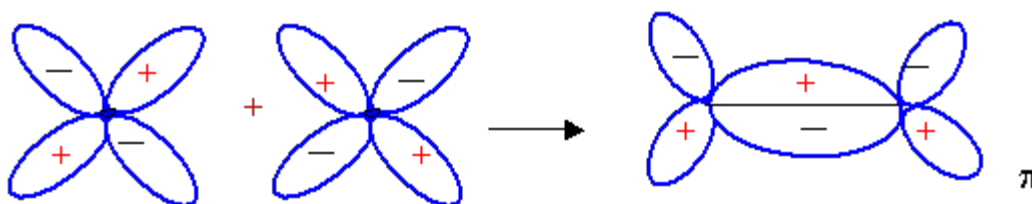


Figure 9.5 (b)  $\pi$  bond from two d orbitals.

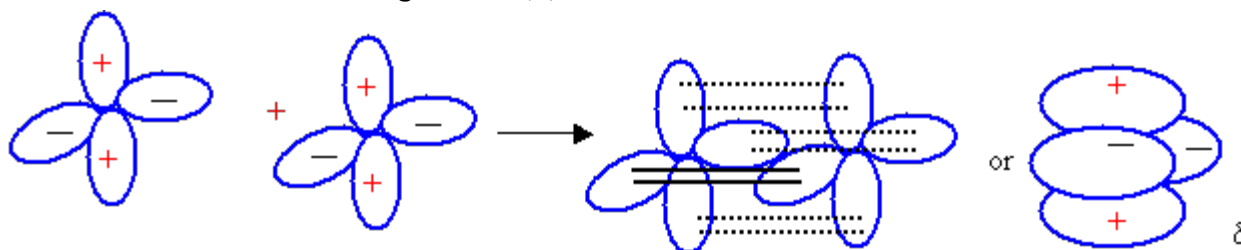


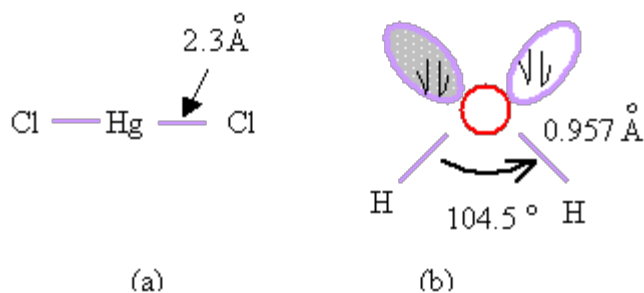
Figure 9.5 (c)  $\delta$  bond from two d orbitals.

Figure 9.5 Orbital overlap diagrams for different types of bonds using d orbitals.

By comparing Fig 9.5 with the corresponding figures of lectures 7 and 8, construct the antibonding combinations

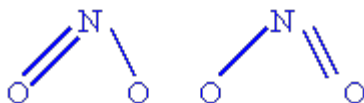
## 9.5 Molecular Geometry

This is a topic which has always remained at the center of attention of chemists. Chemistry has progressed with increasing knowledge of molecular geometry. The tetrahedral geometry of  $\text{CH}_4$ , the planar nature of benzene, the tunnel structure of pyramidal shape of ammonia, helical structure of proteins and the double helical structure of DNA and the emerging structures of nanomaterials are all problems in extended molecular and material structures. We will consider a few representative examples. Once a minimum energy configuration of a collection of atoms is arrived at, the molecular geometry gets defined. In water, the HOH bond angle is  $104.5^\circ$  and the bond length is  $0.957 \text{ \AA}$ .

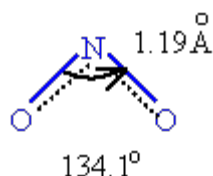


**Figure (9.6) The structure of (a)  $\text{HgCl}_2$  and (b)  $\text{H}_2\text{O}$**

$\text{CO}_2$  is a linear structure while  $\text{NO}_2$  is bent. The bent structure of  $\text{NO}_2$  and the equivalence of the two NO bonds can be explained by the two resonance structures of  $\text{NO}_2$  (Fig 9.7).



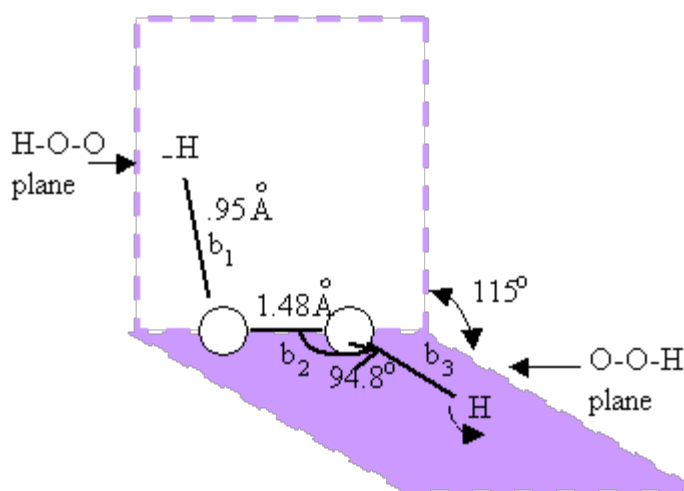
**Figure 9.7 (a) The two resonance structures of  $\text{NO}_2$**



**Figure 9.7 (b) Structure showing the equivalence of the two NO bonds**

In water, the hybridization in O is  $\text{sp}^3$ . The HOH bond angle is less than the tetrahedral ( $109^\circ 48'$ ) angle because of the strong lone pair - lone pair repulsion between the two lone pairs in water. In  $\text{NO}_2$ , although the hybridization on N is  $\text{sp}^2$ , the ONO bond angle is  $134.1^\circ$  because of the repulsion between the two NO bonds. Qualitative concepts such as lone pair - lone pair repulsion being greater than bond - pair - lone pair repulsion are very useful in rationalizing the deviations of chemical structures from the expected structures based on hybridization, differences in electronegativity, size differences and so on.

$\text{H}_2\text{O}_2$  is a nonplanar molecule with the bond lengths and bond angles as shown in fig 9.8.

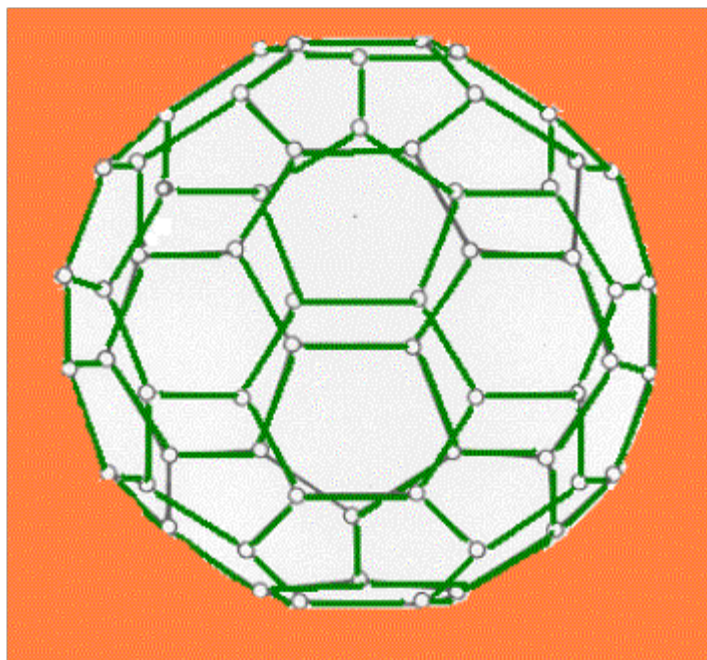


**Figure 9.8 The structure of  $\text{H}_2\text{O}_2$ .**

The angle between the first HOO plane and the next connecting OOH plane is  $115^\circ$  and this is called the dihedral angle. The different bond lengths in  $\text{H}_2\text{O}_2$  are shown in fig 9.8. Methane is tetrahedral,  $\text{XeF}_4$  is planar (with the two lone pairs on either side of the  $\text{XeF}_4$  molecular plane),  $\text{PCl}_5$ , trigonal bipyramidal,  $\text{SF}_4$ , a distorted tetrahedron and  $\text{ClF}$ , T shaped. In the latter two cases, the lone pair - bond pair repulsions cause

the distortion from regular shapes. The hybridization in both  $\text{PCl}_5$  and  $\text{ClF}_3$  may be thought of as  $\text{sp}^3\text{d}$  or  $\text{sp}^2\text{pd}$  with the three electron pairs of the  $\text{sp}^2$  group lying in a plane and the two electron pairs of the  $\text{pd}$  group lying perpendicular to this plane. One should remember not to get carried away by electron pairing or close shell concepts.

During bonding, the shells of atoms can easily expand to include higher available orbitals. For example, in  $\text{IF}_7$  the structure is pentagonal bipyramidal with five atoms lying in a plane and the other two at the apices of the bipyramid.  $\text{C}_{60}$ , buckminsterfullerene has the shape of a truncated icosahedron (appears like a football, of course, it is a molecular football ! ) with 20 hexagonal faces and 12 pentagonal faces. For a molecule with 60 atoms, it is one of the most symmetrical.



**Fig 9.9 (a)** The structure of  $\text{C}_{60}$



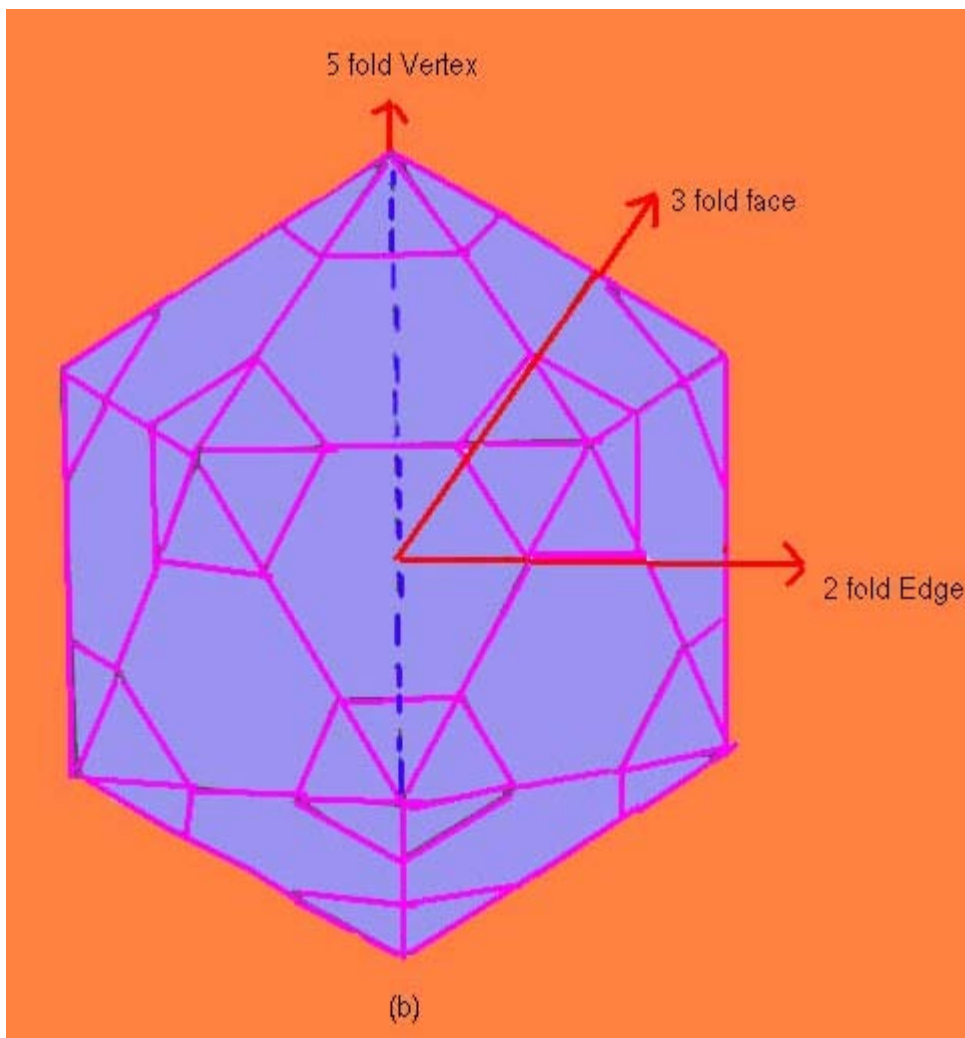


Figure 9.9 (b) Symmetry elements of  $C_{60}$

## 9.6 Bonding in butadiene and benzene

It is instructive to study the bonding in unsaturated compounds as it gives good insights into the nature of MOs. It is convenient to study the  $\pi$  bonding independent of the sigma bonds which can be treated as constituting the "rigid" framework of the molecule. In ethene, for example, the  $\pi$  bond is in the plane perpendicular to the molecular plane. In butadiene, all the carbons and hydrogens lie in a plane and all the bonds in the plane are  $\sigma$  bonds. The  $\pi$  bonds are in a plane perpendicular to this plane and are formed from the four p orbitals (one on each of the four carbon atoms) perpendicular to the plane. The four  $\pi$  bonds that can be constructed from the four p orbitals (represented as  $\varphi_1$ ,  $\varphi_2$ ,  $\varphi_3$  and  $\varphi_4$  in the following equation) are shown in the following figure (fig 9.10).

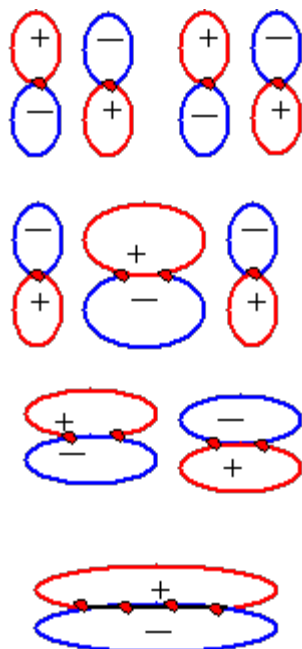


Figure 9.10 (a) The molecular orbitals of butadiene

Figure 9.10 (b) Top view of the MOs and (c) The energy level diagram.

The equations for the 4  $\pi$  orbitals are as follows.

$$\pi_1 = 0.37 \varphi_1 + 0.60 \varphi_2 + 0.60 \varphi_3 + 0.37 \varphi_4 \quad (9.6 \text{ a})$$

$$\pi_2 = 0.60 \varphi_1 + 0.37 \varphi_2 - 0.37 \varphi_3 - 0.60 \varphi_4 \quad (9.6 \text{ b})$$

$$\pi_3 = 0.60 \varphi_1 - 0.37 \varphi_2 - 0.37 \varphi_3 + 0.60 \varphi_4 \quad (9.6 \text{ c})$$

$$\pi_4 = 0.37 \varphi_1 - 0.60 \varphi_2 + 0.60 \varphi_3 - 0.37 \varphi_4 \quad (9.6 \text{ d})$$

Observe that  $\pi_1$  has no node perpendicular to the molecular plane.  $\pi_2$ ,  $\pi_3$  and  $\pi_4$  have one, two and three nodes respectively. The energies of  $\pi_3$  and  $\pi_4$  are above the energies of the p orbitals and hence they are antibonding. Although butadiene is often represented as  $\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$ , wherein the two  $\pi$  bonds are shown as equivalent and distinct, the correct bonding picture is that there are two electrons in  $\pi_1$  and two in  $\pi_2$  which are not degenerate (not having the same value of energy).

The case of benzene, which is a cyclic or ring compound, can be studied in a similar fashion. There are six p electrons (one on each carbon atom) in p orbitals perpendicular to the molecular plane. Starting with 6 p orbitals, we get six  $\pi$  orbitals,  $\pi_1$  to  $\pi_6$  as shown below in Fig 9.11 and the coefficients are given in Eq 9.11. The energy levels are shown in fig 9.11 (b).

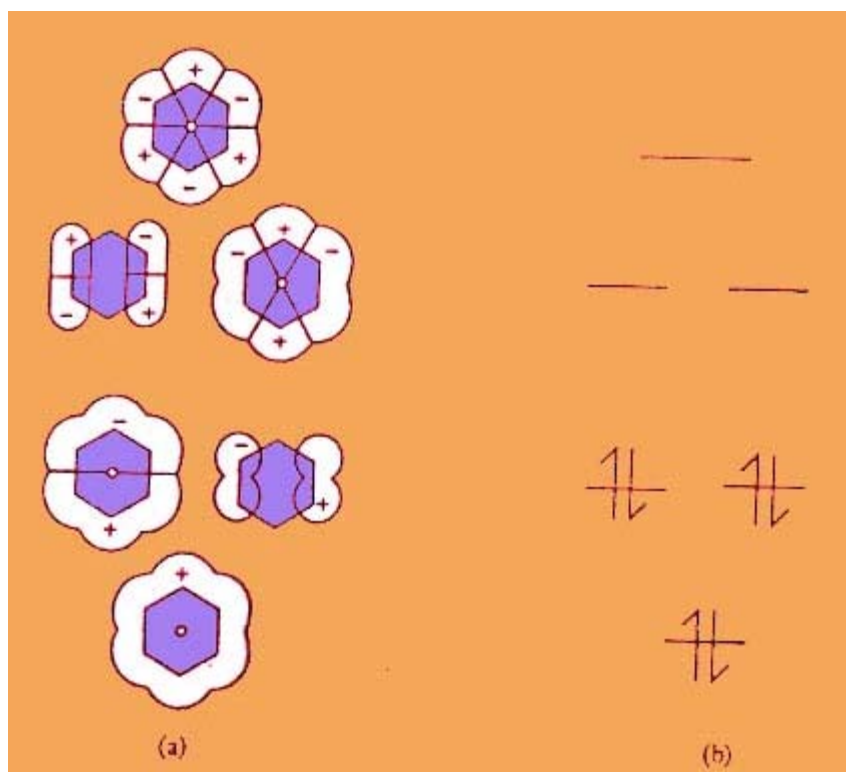


Figure 9.11 (a) The  $\pi$  molecular orbitals of benzene (b) The energy level diagram.

$$\pi_1 = \varphi_1 + \varphi_2 + \varphi_3 + \varphi_4 + \varphi_5 + \varphi_6 \quad (9.7a)$$

$$\pi_2 = \varphi_1 - \varphi_2 - \varphi_3 - \varphi_4 + \varphi_5 + \varphi_6 \quad (9.7b)$$

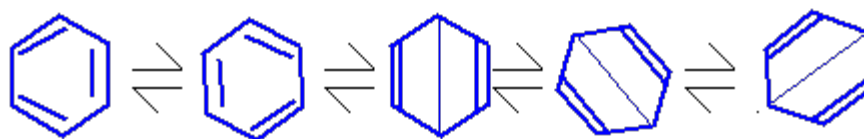
$$\pi_3 = \varphi_1 + \varphi_2 - \varphi_4 - \varphi_5 \quad (9.7c)$$

$$\pi_4 = \varphi_1 + \varphi_2 - \varphi_3 + \varphi_4 + \varphi_5 - \varphi_6 \quad (9.7d)$$

$$\pi_5 = \varphi_1 - \varphi_2 + \varphi_4 - \varphi_5 \quad (9.7e)$$

$$\pi_6 = \varphi_1 - \varphi_2 + \varphi_3 - \varphi_4 + \varphi_5 - \varphi_6 \quad (9.7f)$$

MOs  $\pi_2$  and  $\pi_3$  are degenerate. The six bonding electrons are placed in  $\pi_1$ ,  $\pi_2$  and  $\pi_3$ . The antibonding orbitals are  $\pi_4$ ,  $\pi_5$  (degenerate) and  $\pi_6$ . Benzene is "aromatic". The word aromatic does not simply refer to the odour of the molecule but it also refers to the additional stability in the molecule resulting from the spread of  $\pi$  orbitals throughout the six carbon atoms of the ring. If the three  $\pi$  bonds in benzene were separate, the stabilization due to the three double bonds would be approximately three times the stability due to an isolated double bond as in ethylene. But the stabilization in benzene is 36 kcal/mol more than the stabilization due to three separate double bonds. This is called as stabilization due to "resonance" and the following pictures reflect this feature.



**Figure 9.12 Resonance structures for benzene.**

The resonance structures do not imply that the molecule is present as one of these at various times. The actual structure is a combination of all these structures (with the first two contributing predominantly). In benzene, all the adjacent C-C bond lengths are identical and none of the structures in fig. 9.12 satisfy this criterion individually.

## 9.7 How are the coefficient of MOs and their energy levels obtained?

You must have been wondering how the coefficients like 0.37 and 0.60 in butadiene or the energy levels in benzene can be determined. Each one of the MOs can be represented as

$$\psi_1 = \sum_i C_i^{(1)} \varphi_i$$

$$\psi_2 = \sum_i C_i^{(2)} \varphi_i,$$

where the subscript in  $\psi_k$  refers to the  $k^{\text{th}}$  MO and the superscript  $i$  in the  $C_i^{(k)}$  again refers to the  $k^{\text{th}}$  MO, i.e., it is the coefficient of the  $i^{\text{th}}$  atomic orbital in the  $k^{\text{th}}$  MO. Each one of the MOs satisfies the Schrödinger equation.

$$H \psi_1 = E_1 \psi_1$$

$$H \psi_2 = E_2 \psi_2$$

These can be combined into the following determinantal equation.

$\det | H_{ij} - E S_{ij} | = 0$ , where  $H_{ij} = \int \psi_i H \psi_j d\tau$  and  $S_{ij} = \int \psi_i \psi_j d\tau$  are elements of the matrices for  $H$  and  $S$ . The symbol  $\det | M |$  refers to the determinant of the matrix  $M$ .

For butadiene, the above equation is a 4 x 4 equation which can be solved for the four energies  $E_1$ ,  $E_2$ ,  $E_3$  and  $E_4$ . By substituting each energy in the above two equations, the values of the coefficients are obtained. The central theme in MO theory is to get good coefficients for the MOs, using improved forms of the above equations.

## 9.8 Problems

(9.1) What is the angle between the two  $sp$  hybrid orbitals on a carbon atom of acetylene? What are the energy levels of these two hybrids?

(9.2) Construct the antibonding combinations corresponding to figs 9.5 (a) , (b) and (c).

(9.3) Draw the overlap diagrams for bonding and antibonding combinations between (a) a p and an s orbital (b) between a d and an s orbital and (c) between a p and a d orbital. Indicate whether the MOs are  $\sigma$  ,  $\pi$  , etc.

(9.4) We discussed the resonance stabilization in benzene. Will there be a resonance stabilization in butadiene? Draw the resonance structures in butadiene.

(9.5) Draw the resonance structures in  $\text{SO}_3$  .

(9.6)  $\text{NO}_3^-$  and  $\text{CO}_3^{2-}$  are electronic with (i.e., having the same number of electrons as in )  $\text{SO}_3$  . What are the bond angles and bond orders in these molecules?

(9.7) Calculate the value of the  $\pi_1$  MO in benzene at the center of the molecule and at  $\pm 1 a_0$  on the molecular axis above and below the molecular plane. Assume each C-C bond length to be  $1.35 \text{ \AA}$  .

(9.8) We have considered the bonding in linear  $\text{H}_3$  in an earlier lecture. Draw the MO overlap diagram for the lowest MO in triangular  $\text{H}_3$

(9.9) What is the expected hybridization on the phosphorous atom in  $\text{PCl}_5$  and  $\text{PCl}_3$ ?

(9.10) What are the values of energies of a) sp, b)  $\text{sp}^2$  and c)  $\text{sp}^3$  hybrid orbitals in terms of the energies of s and p orbitals? Always remember that each hybrid orbital has to be normalised. E.g.,  $\psi_1 = (1/\sqrt{2}) (s + p_x)$  for a sp hybrid, because  $\int \psi_1^* \psi_1 d\tau = 1$

(9.11) Is an electron the same as its orbital? What is the difference between an orbital of a molecule and its wavefunction?

(9.12) What is the electronic configuration of Mg? What is the hybridization in Mg in  $\text{MgCl}_2$ ?

(9.13) Does water use  $\text{sp}^2$  hybrid orbitals or  $\text{sp}^3$  hybrids? justify your answer.

(9.14) What is the FBF bond angle in  $\text{BF}_3$  and the HNH bond angle in  $\text{NH}_3$ ? What are the hybridizations in B and N in these two molecules?

(9.15) If the three double bonds in benzene did not interact at all and contributed separately to the binding energy of benzene, then the contribution to the binding energy of benzene would be thrice the value of the energy of the C = C double bond in ethylene. From the MO energy level diagram of benzene we see that the energies of the three electron pairs are not same and the lowest MO gives a lot more stabilization than the double bond in ethylene. This additional stabilization in molecules is called the resonance energy. In which of the following molecules do you expect to have resonance energy (or resonance stabilization) ? Justify your answer

a) butadiene, b) hexatriene, c) 1,5 hexadiene, d)  $\text{NO}_2$ , e)  $\text{CO}_2$  f) buckminsterfullerene ( $\text{C}_{60}$  ) and g) cyclopropene

## Recap

In this lecture you have learnt the following

## Summary

In this lecture, we have studied the energy level diagrams of triatomics and polyatomics and drawn the MO overlap diagrams for the simpler cases. The sketches of hybrid orbitals which participate and contribute to the distinct directionalities in chemical bonding have been given.

The unique geometries of a number of common molecules were considered in detail. The role of the coefficients of AOs in hybrids as well as the MOs was elucidated.  $\pi$  molecular orbitals in butadiene and benzene were investigated in some detail and a method to determine the MO energy levels and the MO coefficients was outlined.