

Module 2 : Molecular Structure

Lecture 8 : Heteronuclear Diatomics

Objectives

In this lecture you will learn the following

- Construction of molecular orbitals of heteronuclear diatomics from the constituent atomic orbitals.
- Qualitative sketches of contours of MOs.
- The energy level diagrams.
- The electronic configurations.
- Quantitative picture of electronegativity.
- Construction of hybrid orbitals from atomic orbitals.

8.1 Introduction

The principles of chemical bonding in heteronuclear diatomics or any other class of molecules are the same as those of the homonuclear diatomics studied in the earlier Lecture (Lecture 7). Some differences naturally appear in heteronuclear diatomics (as compared to the homonuclear diatomics) such as the loss of symmetry, since the two participating nuclei are different. The plane perpendicular to, and bisecting the internuclear axis is not a plane of symmetry in heteronuclear diatomics.

As the nuclear charges and the atomic electron densities on the two participating atoms are different, the abilities of the two atoms to draw electron clouds towards themselves are different. The overall charge density in the molecule will be drawn towards the atom which has a greater value of electron negativity (the ability of an atom to draw electrons towards itself). The molecular orbitals will also lack the reflection symmetry (with respect to the perpendicular plane mentioned above) and the inversion symmetry (with respect to, or across the center of the molecule) present in the MOs of homonuclear diatomics will be absent in heteronuclear diatomics.

Furthermore, the energy levels of two orbitals trying to overlap and form a bond are different and the overlap is often not effective whenever the energy levels are very different. Atoms, therefore adopt new strategies so that the modified (or "new") energy levels of the two participating orbitals (of the two atoms) are much closer to one another. We will illustrate this principle, referred to as hybridization (which you would have already come across in molecules such as CH_4 , C_2H_4 and C_2H_2) in the molecule CO.

The nuclear charges now refer to the individual nuclear charges (generally distinct). The molecular orbitals are once again written as

$$\psi = \sum_i c_i \phi_i \quad (8.1)$$

The values of c_i are now not all the same/similar to the values they had in the homonuclear cases, but are determined by the nuclear charge, electron negativity and so on. Larger the value of c_i , greater the contribution of the corresponding AO, ϕ_i in the molecular orbital. Actually $|\psi|^2$ gives the probability density of the MO and if ψ is normalized c_i^2 gives a measure of the extent of the contribution of the AO in the MO. We shall now consider the sketches of the contours of the MOs of a heteronuclear diatomic.

8.2 Hybridization in LiF

In Fig 8.1, the energy levels of Li and F atoms are given at the left and right of the figure and the energy levels of the MOs are given in the middle.

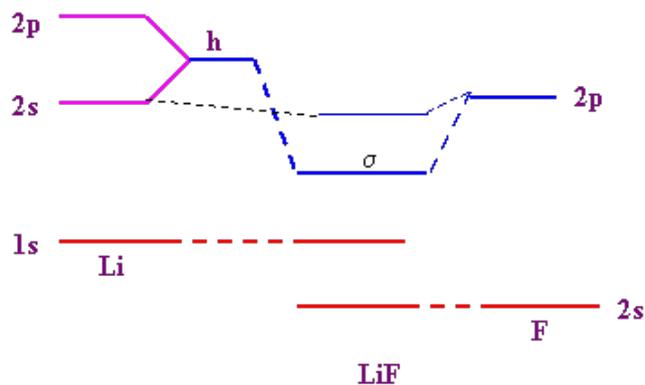


Fig 8.1 The energy levels of Li, LiF and F. One of the hybrid orbitals formed by the 2s and 2p orbitals of Li is denoted by h.

It is seen that the energy levels of F are lying much lower than those of Li. Such shifts are a common feature in atoms. As the atomic number (nuclear charge) is increased, the inner shells (1s, 2s, 2p .. and so on) are drawn closer to the nuclear charge. The values of energies of these orbitals (core electrons) are much lower than the energies of the "outer" or valence electrons.

The 1s and 2s electrons of F and the 1s electrons of Li hardly participate in bonding. The overlap between 2s orbital of Li and 2p orbital of F is not very strong. This is because the s orbital is spherically symmetrical and not directional and hence does not overlap strongly with the 2p orbital of F.

To "circumvent" this difficulty, the 2s and 2p orbitals of Li combine to give two hybrid orbitals h_1 and h_2 , of which h_1 is well directed towards the p-orbital of F to form a bonding orbital which has a lower energy than the unhybridized 2s (Li) + 2p (F) combination. The shapes of the hybrid orbitals h_1 and h_2 are shown in Fig 8.2

Fig (8.2) Hybrid orbitals in LiF, (a) s+p (h_1) and s-p (h_2) combinations in LiF (b) Bonding MO in LiF formed from the h_1 of Li and p of F.

8.3 Electronegativity

Electronegativity is defined as the tendency of atoms to draw electron clouds of other atoms towards them. Atoms such as fluorine, chlorine, oxygen, nitrogen and phosphorous have greater tendencies to draw electrons towards themselves. Compared to these, atoms such as Li, Na, Mg, K and so on have a tendency to release electrons away from them and are electropositive. Quantitative scales of electronegativity can be set up and in the Pauling's scale of electronegativity, F has an electronegativity of 4 and Li has an electronegativity of 1. Electronegativities of a few atoms are given in Table 8.1. It is not easy to quantify electronegativity. The differences in the ionization potentials, electron affinities, binding energies and electronic configurations of atoms and so on, all contribute to electronegativity.

Element	Value	Element	Value	Element	Value

H	2.2	Al	1.61	Cl	3.16
Li	0.98	C	2.55	Br	2.96
Na	0.93	Si	1.90	Cr	1.6
K	0.82	N	3.04	Fe	1.8
Be	1.57	P	2.19	Cu	1.9
Mg	1.31	O	3.44	Zn	1.6
Ca	1.10	S	2.58	Ag	1.9
B	2.04	F	3.98	Cd	1.7
Au	1.4	Hg	1.9		

When a highly electronegative atom binds to a strongly electropositive atom, the electron density in the molecules is significantly polarised towards the electronegative atom. This is illustrated by the contours of electron densities of Li, F, Li^+ , F^- and LiF which are shown in Fig 8.3.

(a)

(b)

Figure 8.3 Contours of charge densities in (a) Li, (b) F, (c) Li⁺, F⁻ and (d) molecule LiF.

Li atom is much larger than F (atom's sizes decreases along a period (row) in the periodic table due to increased nuclear charge). This is clearly reflected in the charge densities of separated Li and F in fig 8.3 (a) and (b). When Li and F approach up to a distance of $13.9 a_0$, Li⁺...F⁻ is more stable than Li...F at the same distance.

An electron from Li is captured by F, the electron density of F⁻ grows and that of Li⁺ shrinks drastically. When the molecule LiF is finally formed, the "small" electron cloud of Li⁺ is "captured" into the spherical cloud of F⁻. The molecular shape is closer to a spherical shape than to an elliptical shape (homonuclear cases). This discussion brings out an important feature. Molecules as well as their bonds need to be described in terms of their charge densities and writing the bonds as H - H or Li - F is a very crude representation. In the interaction between molecules, it is the charge densities that play a central role, and not the lines drawn between atoms!

Shapes of MOs of Heteronuclear Diatomics.

We have studied in detail the previous lecture the shapes, sizes and contours of MOs of homonuclear diatomics. The main difference in heteronuclear diatomics is the "distortion" or the "tilting" of electron clouds towards the electronegative atoms. The σ bond in LiF has been shown in fig 8.3(d) to be polarised towards the F atom. The π bonds formed by the sideways overlap of p- orbitals will also show the same distortion. The bonds in CO are sketched in fig 8.4.

Fig 8.4 π bond in CO

The other common heteronuclear diatomics are hydrogen halides and alkali halides, oxides and sulphides of elements of group II A, and other common gases such as NO, CO etc. There is hybridization in the valence orbitals of each of the participating atom. This not only yields stronger and more directed bonds, but helps in the bonding of these diatomics to other species such as metals or surfaces. We will illustrate this with the example of carbon monoxide (CO).

8.4 Hybridization in CO

In CO there are a total of 14 electrons, 6 from C and 8 from O. The oxygen orbitals are lower in energy due to its larger nuclear charge. We may construct the MOs in two ways, a) without taking into account the hybridization of the AOs of each atom and b) considering the hybridization of the AOs in each atom. The energy level diagram for both the cases are shown in fig 8.5

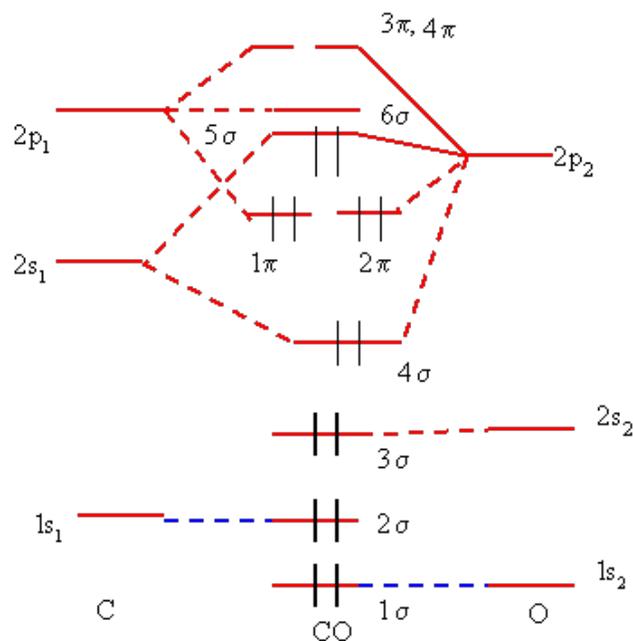


Fig 8.5 a) Orbital energy correlation diagram in CO without hybridization.

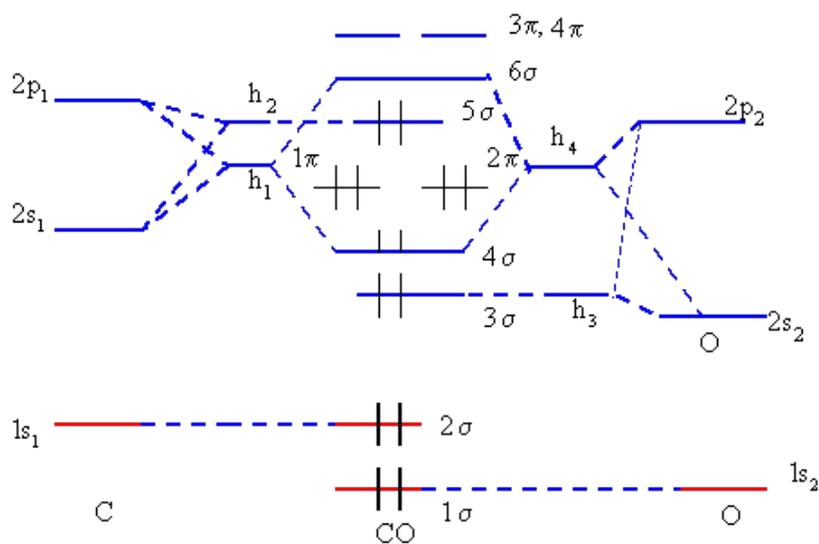


Fig 8.5 b) Orbital energy correlation diagram in CO with hybridization on C and O

The $1s$ orbital of O and the $1s$ orbital of C are very close to the nuclei and have very low values of energy and hence do not participate in bonding at all. The $2s$ orbital of O is also very low lying and does not take part in bonding. In a molecule, all atomic orbitals get converted to molecular orbitals. The inner orbitals may remain 99.999% "pure", but there will be a miniscule participation of other atoms converting them to MOs. This all orbitals in a molecule will be labeled as σ , π and so on. The first two orbitals 1σ (from $1s$ of O) and 2σ ($1s$ of C) hardly contribute to bonding and so their energy levels remain unchanged in the molecule.

The 3σ orbital, which is essentially the $2s$ of oxygen, (which is labeled as $2s_2$) is also "non bonding" and its energy is also "unaffected". The $2s_1$ (of C) and $2p_2$ (one of the three $2p$ orbitals of O, which is directed towards C) form bonding and antibonding orbitals 4σ and 5σ . The 4σ is a bonding orbital and 5σ is an antibonding orbital (it should have been written as $5\sigma^*$, * representing antibonding) because its energy is higher than the energy of both the participating atomic orbitals.

So far, we have taken care of $1s$ and $2s$ orbitals of C and $1s$, $2s$ and one $2p$, say $2p_z$ of O. The two other $2p$ orbitals of O, say $2p_x$ and $2p_y$ orbitals of C to give two bonding MOs (1π and 2π) and two antibonding MOs (3π and 4π) which are higher in energy. The $2p_z$ orbital of C has no counterpart in O to bond with and hence it remains a non bonding orbital (6σ). This diagram, which shows how the MO energy levels relate to the energy levels of the AOs of the atom is called a correlation diagram. The electronic configuration of CO will then be $1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 1\pi^2 2\pi^2 5\sigma^2$. This takes care of all the 14 electrons in CO.

There are no electrons in the 6σ , 3π and 4π levels. The highest occupied molecular orbital is 5σ , which has a dominant contribution from the $2p_z$ orbitals of oxygen. In an MO, the AO whose energy level is closer to the MO energy level, contributes to a greater extent ($> 50\%$) to the MO. In this model where hybridization is not invoked, the participating AO "pairs" such as $2s_1$ and $2p_2$

and $2p_1$ and $2p_2$ are not very close in their energy values) and hence the binding resulting from such overlaps is not very strong.

Now consider the MO correlation diagram in fig 8.5 (b). There is hybridization in both the atoms between their $2s$ and $2p_z$ AOs. The hybrid orbitals in C are h_1 and h_2 and h_3 and h_4 are the hybrid orbitals in O. Note that the energies of these hybrid orbitals lie between the energy levels of the corresponding AOs.

What has happened as a consequence of hybridization is that the energy level h_1 (of C) has come very close (in value, i.e. in height in fig 8.4 (b), where height represents the energy of the orbital) to the energy of h_4 which is the hybrid in the oxygen atom. The hybrid orbitals h_1 and h_4 together form a strongly bonding MO, 4σ and a highly antibonding MO, 6σ . The hybrid orbitals h_3 (of O) and h_2 (of C) remain non-bonding. The energies of the π orbitals take on the same values as in the unhybridized case. Although the electronic configuration in 8.5 (b) remains the same in case of CO as in the unhybridized case (8.5(a)), there are two crucial differences between these. One is that the bond order in the unhybridized CO is 2 while it is 3 in hybridized CO.

The binding energy in CO is -256 kcal/mol while the binding energy in N_2 is -240 Kcal/mol. CO is one of the strongest diatomics and the strength can be only explained using hybridization. The higher binding in CO (relative to N_2) is due to electronegativity differences between C and O and the consequent differences in the MO energy levels. The second difference is that the highest occupied MO (HOMO) in the unhybridized case is dominantly an oxygen orbital (mainly oxygen $2p$ with some contribution from carbon $2s$) whereas the HOMO in the hybridized CO is a nonbonding hybrid on C, which is mainly an atomic orbital. This lone pair of the outermost orbital of C is available for donating ("coordinate" bond) to electron deficient sites such as metal carbonyls. It is experimentally found that in metal carbonyls, CO binds to metals from the carbon end rather than the oxygen end (even though oxygen is more electronegative).

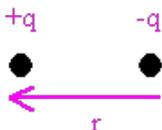
It should be apparent even from one example such as this as to how important and wide ranging the concept of hybridization is in chemistry. We will have more on this in the next chapter. While closing this lecture, you may be wondering how the energy levels such as the ones in fig 8.5 (a) and fig 8.5 (b) are obtained. These are all obtained as solutions of the Schrodinger equation for the molecule.

It is only from the coefficients of the AOs in the MO (Eq 8.1) that we can conclude that there is hybridization. The energy of hybrid $h_1 = 0.8(2s) + 0.6(2p)$ is $= (0.8)^2 E_{2s} + (0.6)^2 E_{2p} = 0.64E_{2s} + 0.36 E_{2p}$. The contribution of the AO in the hybrid is given by the square of the coefficient of AOs participating in the hybrid. The above hybrid may actually be represented as $2s^{0.64} 2p^{0.36}$. The other feature you may have noticed is that starting with two AOs, you can create two and only two hybrids.

Orbitals can neither be created nor destroyed! The other thing that you might be wondering is whether you can understand molecules using MOs alone. There is another approach called the valence bond approach (which uses electron pair [valency!] functions or non-linear combination of atomic orbitals to begin with) but that is perhaps more complicated to introduce than the MO approach. However, both approaches or theories give the same results which agree closely with experimental energy levels of most small molecules.

8.5 Problems

- 1) Calculate the bond order in hybridized CO and unhybridized CO. Extend the same analogy to hybridized and unhybridized NO, NO^+ and NO^- using the same energy level diagrams as those for CO.
- 2) What is the difference between a hybrid orbital and a molecular orbital? Let ϕ_s be an s orbital with energy E_s (ie $E_s = \int \phi_s^* H \phi_s d\lambda$ where H is the Hamiltonian operator for the atom) and E_p be the energy of ϕ_p , a p orbital. If the hybrid orbital is $C_s \phi_s + C_p \phi_p$, show that the energy of the hybrid orbital is $C_s^2 E_s + C_p^2 E_p$. Note that $\int \phi_s^* \phi_s d\tau = 1$, $\int \phi_p^* \phi_p d\tau = 1$ and $\int \phi_p^* \phi_s d\tau = \int \phi_s^* \phi_p d\tau = 0$
- 3) The dipole moment D is defined as the vector whose direction is from the -ve charge to the positive charge.



$D = qr$. q is the charge that is separated by distance r . For $+e$ and $-e$ separated by 1 \AA , $D = 4.8$ Debye $= 4.8 \times 10^{-18}$ esu.cm. The dipole moments of HF, HCl, HBr and CO are 1.9, 0.9, 0.7 and 1.05 Debye respectively and their bond lengths are 0.91, 1.27, 1.41 and 1.1 \AA . Assuming that the excess or separated charges are localised at the nuclei, what are the charges that are separated in these molecules?

- 4) Sketch the binding energy (vs internuclear distance r) for CO. What is the reference (or zero) value of energy that you have to subtract from the energy of CO to get the binding energy?

5) What are the electronic configuration of molecules HF, LiF and NO, CN and MgO?

6) KBr has a bond length of 2.94 \AA . If there is a separation of an unit of charge (i.e. electronic charge, e) in KBr with the molecule behaving as $K^+ Br^-$, what will be the dipole moment? Assuming that the repulsive forces between K^+ and Br^- are very small compared to attractive forces, how much energy is needed to separate K^+ from $K^+ Br^-$ at 2.94 \AA ?

Recap

In this lecture you have learnt the following.

Summary

In this lecture, we have studied the MO energy levels, contours and electronic configurations of heteronuclear diatomics. We also learnt the concept of electronegativity, which is the tendency of atoms to pull electrons towards themselves

Electronegativity is a very useful concept for the study of reaction mechanisms as well as chemical bonding. We also described the concept of hybridization in detail, with carbon monoxide as a special example. The concept of highest occupied molecular orbital (HOMO) is also a useful feature in chemical reactivity, and so are bond strengths and bond orders.