

Thoughts for the Day  
CH301 Fall 2010  
10/26/10

Heteronuclear Molecular Orbitals.

What if the two atoms in the diatomic molecule are not the same?

If they are similar, then the situation is very much like homonuclear. What is very similar? The AO should have similar energies which means they need to have a similar  $Z_{\text{eff}}$ .

So HeH or  $\text{CN}^-$ . What is not similar? HF

What can we do now.

For similar situations we can predict the energy level diagram. It is just like the homonuclear but the AO orbitals have slightly different energies. Now the MO will be closer in energy to one of the AO than the other. Thus if the molecule dissociates the electrons may have a preference for one element or the other.

Where are the electrons when HeH dissociates? Well this is a three electron species. The 1s orbital in He is lower in energy than H so we expect that of the three electrons two will go to He and one will go to the higher energy 1s in H. This is not a surprise. HeH dissociates into He and H. What about the two electron species  $\text{HeH}^+$ ? Now we can ask will this dissociate into  $\text{He}^+ + \text{H}$  or into  $\text{H}^+ + \text{He}$ ?

Finally what happens when the AO have very different energies. Only orbitals with similar energies will combine to make MO. There may be some AO that don't combine with any orbital from the other atom and are essentially the same energy in the molecule. These are non-bonding electrons. They don't count in figuring out the bond order as they have the identical energy in the molecule as in the atom. Thus they have no effect on bonding.

How to predict the MO diagrams in this case. This is difficult and we won't do it. However, given a diagram you should be able to interpret it. That is, you need to be able to fill in the electrons. Figure out how many bonding, anti-bonding, and non-bonding electrons there are. You should also be able to comment on bond order, bond strength, bond length (these are essentially all the same question) and on whether a molecule is paramagnetic or diamagnetic.

Finally, there is polyatomic molecules. Now the MO come from AO on more than two atoms. And the MO are for the whole molecule (not just a bond between two atoms). These again are not

something you can predict. However they are something you can interpret. [How many bonding, anti-bonding, and non-bonding electrons there are. You should also be able to comment on bond order, bond strength, bond length (these are essentially all the same question) and on whether a molecule is paramagnetic or diamagnetic.]

A local bond picture. Valence bond theory.

It is difficult to interpret MO's as they involve the entire molecule. We'd rather talk about particular bonds. This distinction is not clear when we are looking at diatomics. But for larger molecules it is more obvious.

Valence bond theory states that bonds result from overlap of atomic orbitals. However, we have a problem since we know that molecules take on geometries that we cannot achieve with our set of AO (everything would have bond angles of  $90^\circ$  or  $180^\circ$ ).

Therefore, we conceive a new set of hybrid orbitals that are linear combinations of AO which we will use to look at the bonding. The new AO are still atomic orbitals. They are just hybrids of what we had before that have the "correct" geometry.

For example, we want to have a tetrahedral geometry. We can combine the 2s and three 2p's into a new set of 4  $sp^3$ . (4 AO's make 4 hybrid AO's). The  $sp^3$  orbitals all have the same energy and are arranged in space in a tetrahedral geometry.

Thus if we look at the bonding in  $CH_4$ . The C-H bond results from the overlap of a  $sp^3$  on C and a 1s on H. Note: Carbon has 4 valence electrons. Before we had 2 x 2s and 2x 2p. Now we have one electron in each  $sp^3$ .

If we want to make a trigonal planar shape we take the 2s and combine it with two of the 2p's to make three  $sp^2$  hybrid AO. This leaves one 2p "left over" that is perpendicular to the plane with the three  $sp^2$ . Now look at ethane.  $C_2H_6$ . Check it out in chapter 7 of the book. It has a sigma bonding backbone. One C-C bond is from the overlap of a  $sp^2$  on one carbon and a  $sp^2$  on the other carbon. The C-H bonds are from the  $sp^2$  on the carbon with the 1s on the hydrogen. The "left-over" p orbitals on the carbons overlap to make a pi bond. This overlap only occurs if the whole molecule is in the same plane. If it rotates this will break the pi bond. Thus there is a large energy barrier to rotation for this molecule.

Linear molecules form from hybrids made to be at  $180^\circ$ . They are formed from one 2s and one 2p. This makes two sp hybrids and leaves 2 p orbitals left-over. These molecules can then form 2 pi bonds with the overlap of both the 2p's. For example  $C_2H_2$ .