

Chapter 9 Covalent bonding: Orbitals

9.1 Hybridization and the Localized Electron Model

In Chapter 7 you were first introduced to the ideas of atomic orbitals. In Chapter 8 we focused on the molecule and what properties we could predict based on some simple models for covalent bonding. In this section of the chapter we will try to tie these together, that is show where molecular bonding comes from based on our knowledge of atomic orbitals. In section 9.2 then we will look at bonding from a different viewpoint, and develop molecular orbitals

Do in different order than book because easier to understand

In the last chapter we left off with the VSEPR. Saw that can have several different configurations of electrons around central atom. How did we get these different arrangements?

One explanation is that we can mix our old familiar atomic orbitals together in different ways to make new orbitals new and different geometries.

When we do this you will see two things.

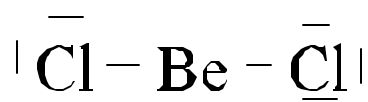
1. You can't gain or lose orbitals. If you mix two orbitals together, you will get two new orbitals out (3 give 3, 4 gives 4 etc.)

2. The mixing is done in 3 dimension, with wave functions that have + and - lobes. The book diagrams of orbitals does not show this +/- information, so sometimes things don't look obvious

Sp Hybridization

Let's look at BeCl_2 , concentrating on the Be

Be 2 electrons, Cl, 7 electrons apiece, total of 16 electrons or 8 pairs



Be is an exception to the general rule and can have < an filled octet; 2 electron regions, linear electronic and molecular structure, 180° Bond angle

What atomic orbital do you know that would give us two lobes of electron density 180 degrees apart? A p orbital. Thus one p orbital will give us the right geometry. However we need two orbitals, one to share a pair of electrons with each of two fluorines. How are we going to get this?

From the first principle above, if we want 2 orbitals we need to start with two orbitals. We want one to be a p. Let's make the other one an s and see what we get.

When we mix and one s and one p together the resulting 2 orbitals are called **sp hybridized** orbitals. [Figure 9.14 9.16 or models](#)

This hybridization makes sense graphically. $S + P$ gives us one lobe, $S - P$ gives

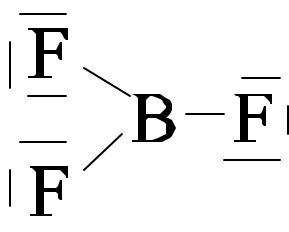
us a bond in the opposite direction.

The energy of these two bonds are intermediate between those of the s and p orbitals.

sp² Hybridization

Let's look at the Lewis structure of BF₃

3 electrons from boron, 21 electrons from fluorines a total of 24 electrons or 12 pairs

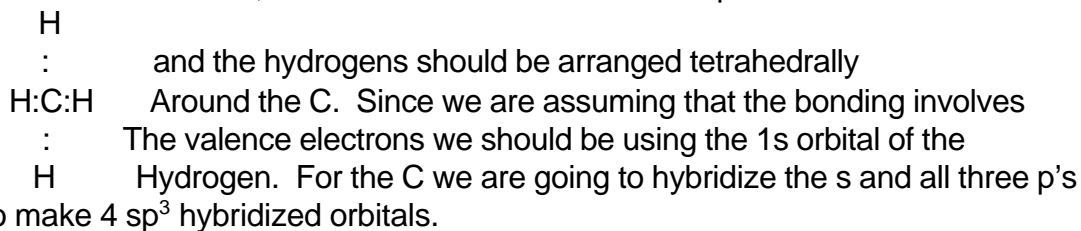


Again Boron is an exception and can have less than an octet, so we have trigonal planar electron and molecular geometry around the central atom and 120° bond angles. For hybridization let's try one s and two p orbitals into an **sp² hybridized orbital**. If we mix the s, a p_x and a p_y you can sort of see where the 120 degree comes from, but it's not quite as easy as it was for the sp case. [Figure 9.8 or models](#)

Note here we are using only 2 out of 3 of the p orbitals so we get a total of 3 sp² orbitals with equal energies (Figure 9.9) and we have 1 p orbital of higher energy left over.

sp³ hybridization

Let's move on to CH₄, methane. Based on our last chapter it has the Lewis structure



[Figure 9.3 or models like it](#)

Here are the 4 orbitals we get from various ways of mixing them together (like s+p_x+p_y+p_z, s+p_x+p_y-p_z). Now the pictured result, with a tetrahedral arrangement of lobes may not be obvious to you, but that is because these simple pictures are covering up a bit of complicated math. Just take my word for it that it is true.

Thus we get the result that if we want a tetrahedral set of orbitals we assume that the atom adopts the sp³ hybridized state. And we get the 109.5° bond angles we wanted. So that explains the geometry, what about the energy. If you remember the s atomic orbital has a lower E than the p atomic orbitals. When we hybridize these 4 orbitals together, we do it in such a way that the energy of our resulting

sp^3 orbitals are all the same and they are in-between the e of the s and p states (Fig 9.5 on board)

Thus the geometry and equal energy of the CH_4 molecule makes sense if we don't use the atomic orbitals per se, but instead blend them together into new hybrid orbitals

dsp^3 hybridization

How do we explain the trigonal bipyramid of something like PCl_5 . Here we hybridized s , $3p$'s and a d orbital together, and the result is just what we want, a trigonal bipyramid. Since we join 5 orbitals into this, we get places to put 5 electron pairs so a set of 5 effective pairs around an atom requires the use of dsp^3 hybridization around that atom.

The Cl's in this molecule have the configuration $-Cl:$

:

So what hybridization should they have? 4 effective pairs, 1 bonding, 3 nonbonding, sp^3

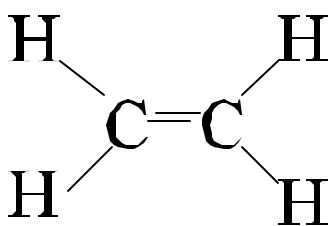
d^2sp^3 hybridization

I think you get the idea, to get the octahedral arrangement see with molecules like SF_6 we are going to hybridize $2d$, and s and $3p$'s together to get 6 hybrid orbitals of the right geometry. So octahedral geometry will require d^2sp^3 hybridization.

Now let's look at double and triple bonds

C_2H_4 , Ethene

$2(4) + 4 = 12$ electrons or 6 pairs



Around each C we have 3 electron regions, so trigonal planar and sp^2 hybridization for the first bond. But what about the second bond?

We are going to form the second bond with the leftover orbital. What are the leftover C orbitals? We have already used 1 s and 2 p 's on each C to make our three sp^2 orbitals, so the only one left is the remaining p

orbital. Thus our second part of the double bond is going to come from the unused p orbital. Where is this p located? Well, in making the sp^2 bonds we used the 2 p orbitals that were in one plane, the CH plane. Thus the remaining p , the one we are going to use for the second part of the double bond is not in the same plane, but must be sticking out above and below this plane.

Let's introduce a little terminology. When bond has its electrons located in the space between two atoms we will call it a **sigma (σ) bond**.

Now let's return to the P orbitals that we will use to make our second bond. Where are the electrons located when the two p orbitals? (Above and below) When we have a bond with the electrons above and below a line separating the atoms we will call this a **pi (π) bond**.

So our C=C double bond is consists of a σ made by sp^2 hybridized orbitals and a π bond formed from the remaining p orbitals merging together.

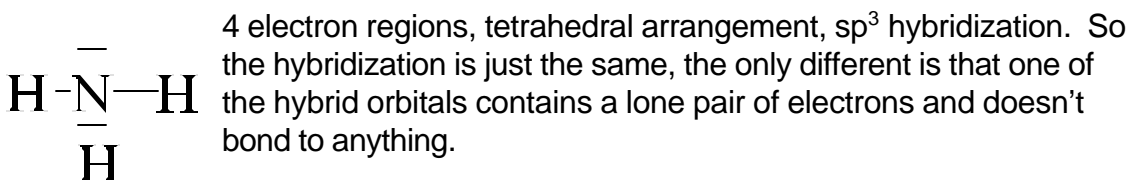
One other thing before we leave this molecule. This model has actually made a prediction that we haven't looked at. What is the relative orientation of the two sets of hydrogen? Since we need the second part of the double bond to be made of p orbital that are in the same plane so they overlap to form our bond, the bond to the hydrogens must be in a different plane. In that plane they cannot rotate otherwise will break the pi bond. This is, in fact the way the molecule actually behaves, thus our model predicted something we didn't know ahead of time!

What about H-C \equiv C-H, the triple bond in acetylene?

Around each C we have a linear arrangement, so that is sp hybridization and 2 p's are unused. Again we will use these p's in the multiple bond. We will merge 2 sets of p's one in the y plane and one in the Z plane to give us two additional π bonds, one in the Y and one in the Z plane. Thus our triple bond consists of 1 σ bond using the sp hybridization from each atom and 2 π bonds from the remaining p orbitals

What about lone pairs? Let's look at NH₃

5+5 = 8 electrons



Summary localized electron model

To describe molecule take following steps

1. Draw Lewis structure
2. Determine best arrangement of electron pairs with VSEPR
3. Select hybrid orbital needed to achieve given geometry

The idea here is that the molecule is trying to find its lowest energy, and it will rearrange thing like atomic orbitals to create hybridization to get to this lowest energy. Likewise don't get concerned about where any individual electron comes from in the molecule, the molecule will shuffle them around as it needs.

model did not give us. Both model work, both give information, we need both to get a fuller understanding of what is going on.

Let's start with the simplest molecule we can think of H_2 , 1 protons and 2 electrons. Basically what we are going to do is to use the same atomic theory we used in chapter 7 to explain the orbital of atom, say He with 2 protons and 2 electrons, only we are going to put some distance between the protons, rather than having them sit in the same nucleus.

To solve these problems we generate lots of complex math and this, in turn, generates **molecular orbitals (MO)** analogous to the atomic orbital we found for individual atoms

Since you already have a feel for atomic orbitals, we will describe what we find in terms of these atomic orbitals that you already understand. For instance let's the molecular orbital that binds H_2 together may be found by joining the individual s orbitals of the two atoms in different ways:

$$MO_1 = 1s_A + 1s_B$$

$$MO_2 = 1s_a - 1s_b$$

This is analogous to hybridizing s and p orbitals together to make sp orbitals, the only difference is that the orbitals are on different atoms!. Notice that just like before if we start with X orbitals we get out the same number of orbitals, thus MO_1 & MO_2

The shapes of these molecular orbitals are shown in figure 9.25, the shape of the a+b makes sense, while the a-b is again hard to understand without a little more math.

Notice that the MO_1 bond has the electron density between the atoms while the MO_2 bond has the highest electron density on either side of the nuclei. This localization of electrons along the nuclei centers means that both of these bonds are considered **sigma type bonds**

In this model the $1s_1$ and $1s_2$ atomic orbitals no longer exist, so our electrons can only fit into the molecular orbitals

The energies of these orbitals are shown in 9.26 (on board) whereas in our sp hybridization we could predict the bond energies because it had to be between the component energies, you can see here that our energies are going both higher and lower, and we have no idea how much higher or lower. However the fact that MO_1 orbital has a lower energy than the individual orbitals show that when the 2 electrons of the molecule occupy this orbital the energy of the molecule is lower than the energy of the individual atoms, hence we have a stable bond. This is called **probonding**. If we could force the electrons to sit in the MO_2 orbital the energy of the system would be higher than that of the individual atoms, and this would be **anti-bonding** because the molecule would want to fall apart to get to its lower energy state

If you look at the electron distributions this actually makes sense. In the bonding orbital the electrons are between the nuclei and help shield 1 + from the other. In the antibonding configuration they cannot keep the nuclei from being repelled from each other.

We have a bit of nomenclature for the orbitals

MO_1 will be referred to as σ_{1s} because it has the σ shape and is composed of 1s atomic

MO_2 will be called σ_{1s}^* because it has the σ shape and is composed of 1s atomic orbital and is antibonding.

Just like in the atomic orbital we will denote the number of electron in an orbital like: $(\sigma_{1s})^2$ as a filled orbital.

With these thoughts what would you predict for the stability of H_2^- ?

2 in bonding, 1 in antibonding, less stable? How much less stable? H_2 is 2 units stable, H_2^- is 1 unit stable, expect to be $\frac{1}{2}$ as stable and it is!

This leads us to how we can use the molecular orbital model to estimate the energy of a bond using a bond order calculation

Bond order

Let's expand the last observation further using the concept of **bond order**.

$$\text{Bond Order} = \frac{\# \text{ of electrons in bonding} - \# \text{ electrons in antibonding}}{2}$$

Why 2? Because we think in terms of electron pairs

What is bond order? It correlates with bond strength. The bigger the number the stronger the bond. Also correlates with single, double or triple bond. If B.O. is 3, have a triple. 2 a double, 1 a single. Note will also have fractional!

For H_2 we will have $(2-0)/2 = 1$

For H_2^- we will have $(2-1)/2 = \frac{1}{2}$

The larger the bond order, the greater the bond strength.

Let's try the on He_2

In He_2 we have each atom contributing a pair of 1s electrons, total of 4, and 1 σ_{1s} and 1 σ_{1s}^* orbital. Both bonding and antibonding are filled and our bond order is

$(2-2)/2 = 0$ this implies that H_2 is NOT stable.

9.3 Bonding in Homonuclear Diatomic Molecules

Homonuclear diatomic i.e. 2 of the same atoms. Will further restrict to 2ns period
Let's start with Li $1s^2 2s^1$

Remember that the radius of the 2s orbital is much larger than the 1s orbital. Thus when we form a diatomic molecule only the large 2s orbital overlap, and the smaller 1s orbital aren't close enough to overlap. *In order to participate in molecular orbitals, atomic orbital must overlap in space.* Thus our 1s orbital that do not overlap will not take part in the molecular bonding orbitals.

If we use 2s atomic orbital we can form σ_{2s} and σ_{2s}^* molecular orbitals. With 1 electron from each atom the bonding orbital is filled and the anti-bonding is unfilled, hence our Bonding order is $(2-0)/2 = 1$ so we predict that Li_2 is a stable compound (and it is. It is not, however, the most stable and Li can exist in many other bonded forms)

What about Be_2 . Same orbitals, but now have 2 electrons from each atom, so 2 in bonding and two in anti-bonding, Bond order $(2-2)/2 = 0$ so Be dimer is **less** stable than individual atoms, so predict will not be found. (Be metal however is technically many metals bonded together and it does exist, it will be discussed in chapter 10)

Moving on to Boron

$1s^2 2s^2 2p^1$ Now we have both S and P orbitals, what should we do? For now let's assume that the s and p do not mix together and can be treated separately. We will come back and reexamine this supposition in a minute.

Treating the 2s molecular orbital separate from the p orbital we can see that we have σ_{2s} and σ_{2s}^* orbitals and 4 electrons to put in them, so they give us a bonding order of $(2-2)/2 = 0$, so no net bonding on the s alone. Now let's look at the p.

Remember the shapes of the p's? We have 2 lobed dohickies, aligned along x, y, and z. 2 sets will be parallel with each other so overlap above and below or to the side of the line joining the atoms, the other set will overlap in the middle between the two. Also have antibonding of each set. **Pictures or models?**

Would you expect these molecular orbital to all have the same energy? (No the one with overlap between the atoms should be lower E). Because has the shape of electrons in the middle will call this molecular orbital a σ_{2p} . The other two orbitals have the same energy (called degenerate) will designate as π_{2p} Picture the energy diagram for this as: **Figure 9.36**

Filling this in with 2 electrons, we have the σ_{2p} bonding orbital filled

What is our **total or net** bonding order?

$(4-2)/2 = (\sigma_{2s})^2, (\sigma_{2s}^*)^2, (\sigma_{2p})^2$ so we predict a stable molecule. An this is Correct

However we are missing an important detail called **Paramagnetism**

Paramagnetism and Diamagnetism

One property we haven't talked about yet is magnetism. Most materials have no magnetism until they are placed in a magnetic field. If the material is attracted to the inducing field we call the material **paramagnetic**, if it is repelled from the inducing field we call it **diamagnetic**. It is really pretty simple to measure this. Put sample in magnetic field and weigh it, see if it has more or less weight.

If heavier, attracted to magnetic field, paramagnetic. If lighter, repelled by magnetic field, diamagnetic.

The reason we mention this now is that **paramagnetism is associated with unpaired electrons, diamagnetism is associated with paired electrons**

So we can use these magnetic properties to see if our molecules have unpaired electrons in them as a further check to see if our model is right!

Paramagnetic - unpaired electrons - attracted to magnetic field

Diamagnetic - paired electrons - slightly repelled by magnetic field

Let's look again at our B_2 compound. We just said that all orbitals had paired electrons, so we would predict B_2 to be diamagnetic.

We do the experiment, however, and we find out it is paramagnetic. So our model is wrong! We must either discard it or modify it.

We will modify it by changing one of our assumptions. When we started this we assumed that the s and p orbitals did not mix and treated them separately. If we allow them to mix we get different answers. Without proving it, I will simply say that when you allow the s and p orbitals to mix the bonding σ_{2p} and π_{2p} orbitals change places and the σ_{2p} bonding and anti-bonding levels change energy to get the diagram shown

Figure 9.38. The net result is that the 2 π_{2p} orbitals each get 1 electron, giving the molecule 2 unpaired electrons making it paramagnetic

Rather than doing all the other diatomics one by one, let's go to **figure 9.39** that summarizes out results past B_2

Summarizing table results

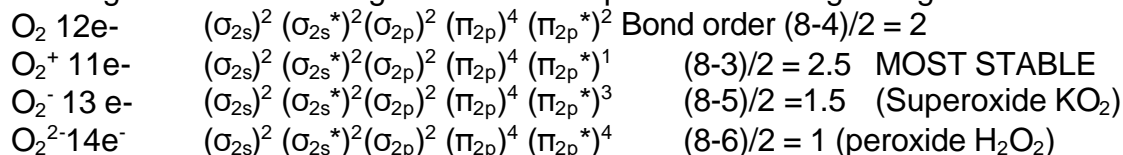
1. Bond order, bond strength and bond E all correlate
2. Bond order and bond strength correlation not perfect, can predict exact #
3. Note N_2 triple bond is very stable. That is why lots of explosives contain nitrogen.

As react to form N_2 give off lots of E

4. O_2 is paramagnetic, see demos

Let's work with O_2 a bit Predict the strength of O_2 , O_2^+ , O_2^- and O_2^{2-}
Elemental oxygen, ?, superoxide and peroxide

Looking at the orbital energies we would expect the following configurations



9.4 Bonding in Heteronuclear diatomic molecules

Now let's get even more complicated, let's let the atoms be different.

If we don't let them get too different, say must be adjacent in periodic table, we can do everything we have been. Thus let's try the CN^- anion

CN^- will have 4+5+1 or 10 valence electrons

You would guess that it would follow the same order as C and N so the configurations will be

$(\sigma_{2s})^2 (\sigma_{2s}^*)^2 (\pi_{2p})^4 (\sigma_{2p})^2$ so the bond order will be $(8-2)/2 = 3$ and will be quite a strong triple bond much like N_2 itself.

When the atoms are very different, then we need to generate entirely new bond energy diagrams as in [figure 9.43](#)

Note we are starting with the assumption that the 2p orbital of F is at a lower E than the 1s of H does this make sense? (Chapter 7 ionization of e for F is higher, electron more tightly bound to nucleus because not well shielded from +7 nucleus)

Assume other valence of F don't contribute

HF should be more stable than either H or F because E is lower

Because $2p^F$ orbital is lower E than $1s^H$ molecular orbital will have more 2p character, and will thus be more closely associated with F. This is consistent with earlier thought on electronegativity of F v H and net polarity of this bond

9.5 Combining both models

One of the problems with the Localized electron model was how to deal with molecules that had more than one equivalent Lewis structure. While the concept of resonance seems to be a reasonable fix, but it wasn't an intuitively great fix. For one thing it leaves us with the impression that there are a series of different structure, that 'flip' from one to another over time. In reality what we have is a molecular orbital in which the electrons are smoothly distributed over space rather than flipping between forms.

Let's use the molecule Benzene to help illustrate this:

Benzene has the formula C_6H_6 . All 6 C-C bonds are equivalent and all 6 CH bonds are equivalent. If we wrote Lewis structure for this molecule we would get X and Y any you tend to think of these two forms flipping from one to another.

To meld our atomic and molecular models together we will keep the thought that the sp^2 bonds are localized to individual atoms. This makes sense, since we have seen that the electrons are indeed localized between the nuclei of the atoms. Thus our σ bonds are localized in the plane of the atoms. The electrons in the π orbital are localized above and

below the plane of the molecule. These we will assume to be delocalized molecular orbitals, thus these electrons are more properly being smeared out over a large space rather than being tied down between a couple of atoms.

Same of NO_3 show picture on board.