## Chapter 8 – Advanced Theories of Covalent Bonding

The previous chapter dealt with the basics of chemical bonding and molecular geometry. Here we get into the details of what causes two atoms to bind to one another and why some covalent bonds are stronger than others.

11.1   Valence Bond (VB) Theory

There are two major theories that describe bonding. The one we cover first is more intuitive, but less accurate. Furthermore, it is usually used only for covalent bonds. You have already learned that a covalent bond was a shared pair of electrons. We now discuss what was meant by "shared" and why sharing occurs.

Consider a hydrogen atom. If an electron passes close by, the positive nucleus will capture it because the nucleus can't differentiate between its electron and the new one. In doing so, the system releases energy (electron affinity) and forms a hydride anion. Now consider two hydrogen nuclei that slowly approach one another. At large distances, each nucleus attracts only its own electron. However, as they get closer each nucleus begins to attract the electron on the other atom as well, resulting in the atoms pulling together. In an isolated atom, each electron moves freely around the nucleus creating a spherical shape. However, the electrons will now be drawn preferentially to the side of the atom facing the approaching hydrogen atom. At the distance of closest approach, both electrons will spend most of the time between the two nuclei because there is maximum attraction there (the electrons will be close to 2 nuclei in the middle, as opposed to one on the far side of either atom). The figure below shows the result of the interaction of two *s* orbitals starting at infinite distance and progressing to a bond. The final

two pictures show the overlap of atomic orbitals. The dashed lines show electrostatic attractions and the shaded portion is the region (volume) of overlap.
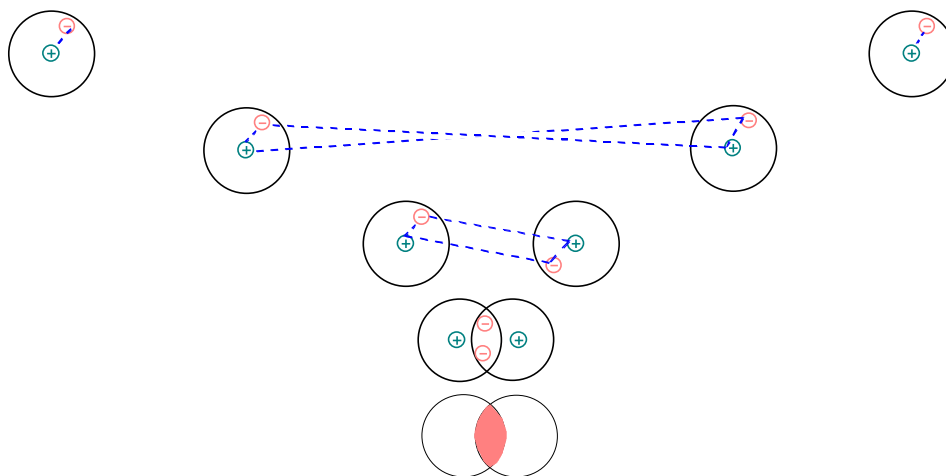
Why does the approach stop? The two nuclei repel each other and at some distance this repulsion offsets the added attraction of the two nuclei for its neighbor's electrons. The bond distance is the separation when these two forces are equal.

There are three ways orbitals can overlap. We will discuss two here. When two hydrogen atoms overlap, electron density concentrates along the line connecting the nuclei. Such "end-to-end" overlap is called a σ-bond (sigma bond). It occurs whenever an *s* orbital overlaps any other orbital or a *p* orbital overlaps through only one of its lobes.
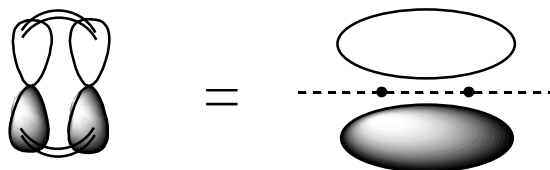
a *p-p* σ bond:

The second major bond type results from the side-to-side overlap of two orbitals either between two *p* orbitals or between *p* and *d* orbitals (shown below). This is called a π-bond (pi
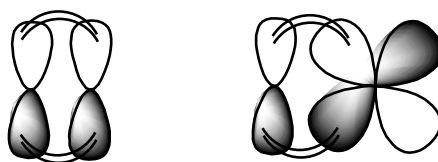
bond). In a π-bond, electron density concentrates above and below the internuclear axis with a

node in the plane separating the nuclei.

Single bonds are σ bonds, double bonds contain 1 σ bond and 1 π bond, and triple bonds contain a σ bond and 2 π bonds. There are a few exceptions to these rules, but you won't encounter any in this course.

8.2   Hybrid Orbitals

A problem that may have caught your eye with the previous description is that while it works for H_2, what about CH_4? There is no combination of orbitals that forms a tetrahedron. *S* orbitals are spherical, while *p* and *d* orbitals each form 90° angles. How are the shapes we actually see generated? Valence bond theory gives us an answer using "hybridized" orbitals.
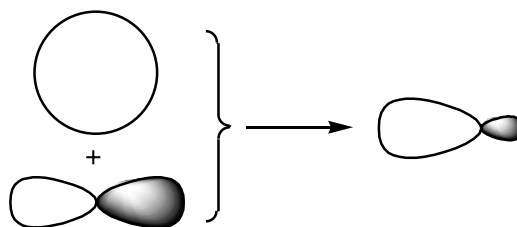
sp Hybrid Orbitals

Consider $BeCl_2$. VSEPR theory predicts a linear molecule with two identical bonds. The electron configuration of beryllium is [He] $2s^2$. If a covalent bond results from a shared pair of electrons and in a normal bond each atom contributes one electron to the bond, the initial electron configuration of beryllium does not allow a bond to form because all its atomic orbitals are either completely filled or empty. To obtain two orbitals containing one electron each, one of the electrons must be promoted from the 2*s* orbital to a 2*p* orbital.
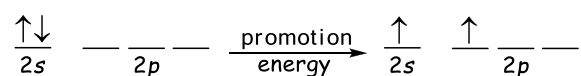
If the chlorine overlapped the 2*s* and 2*p* orbitals, the molecule would be linear, but with

bonds of different lengths, so something else must be happening.
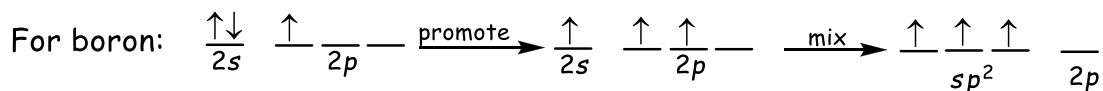
"Mixing" the orbitals solves the problem of different bond lengths. This process is a combining and averaging of the orbitals resulting in a <u>hybrid orbital</u>. In this example, one *s* and one *p* orbital mix, resulting in the generation of two *sp* hybrid orbitals. A useful rule to remember is that the number of atomic orbitals used will equal the number of product hybrid orbitals; in this case, two. Hybrid orbitals have the same basic shape regardless of whether they form from one *s* and one *p* orbital or one *s* and three *p* orbitals.

$$\underset{2s}{\uparrow\downarrow} \quad \underset{2p}{-\;-\;-} \quad \xrightarrow{\text{promote}} \quad \underset{2s}{\uparrow} \quad \underset{2p}{\uparrow\;\uparrow\;-} \quad \xrightarrow{\text{mix}} \quad \underset{sp}{\uparrow\;\uparrow} \quad \underset{2p}{-\;-}$$
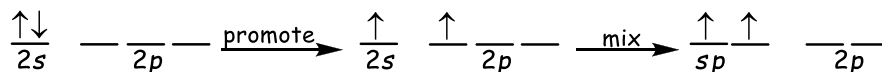
One lobe is very large because the amplitudes of the wave functions are both positive and reinforce one another (constructive interference). The other lobe is small because the amplitudes are opposed and partly cancel each other (destructive interference). There would also be the mirror image of this orbital as well. One reason why these orbitals form is that the shape leads to better overlap. The end of the large lobe is blunter (shorter and flatter tipped) than a *p* orbital. The better overlap provides the energy needed to promote the electron and mix the orbitals. A second reason is that second row atoms are too small to accommodate 90° angles between substituents. While most linear molecules possess sp hybridization, there are exceptions (e.g. XeF_2).

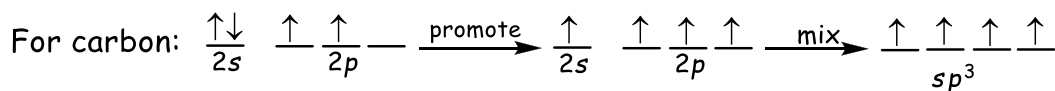## sp^2, sp^3, sp^3d, and sp^3d^2 Hybrid Orbitals

The same sort of thing is done to get the trigonal planar and tetrahedral geometries. If the atom has one p electron already, one of the s electrons is promoted into an empty p orbital.

For boron: $\underset{2s}{\uparrow\downarrow}\ \ \underset{2p}{\uparrow\ \ \rule{0.6em}{0.4pt}\ \ \rule{0.6em}{0.4pt}}\ \ \xrightarrow{\text{promote}}\ \ \underset{2s}{\uparrow}\ \ \underset{2p}{\uparrow\ \ \uparrow\ \ \rule{0.6em}{0.4pt}}\ \ \xrightarrow{\text{mix}}\ \ \underset{sp^2}{\uparrow\ \ \uparrow\ \ \uparrow}\ \ \underset{2p}{\rule{0.6em}{0.4pt}}$

The three sp^2 hybrid orbitals spread in a trigonal planar array, as in BF_3, with a vacant p orbital perpendicular to the molecular plane.
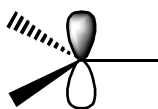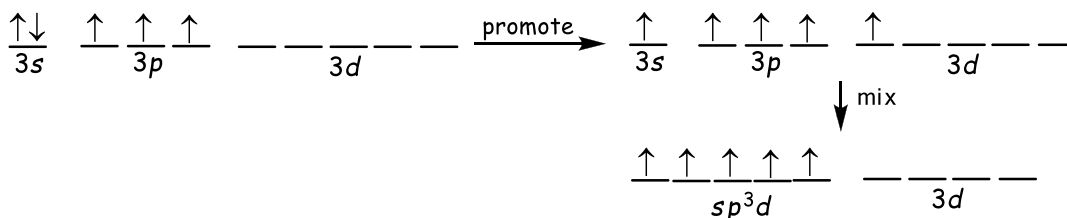

For a central atom with 2 p electrons, the s electron is promoted into the remaining vacant p orbital.

For carbon: $\underset{2s}{\uparrow\downarrow}\ \ \underset{2p}{\uparrow\ \ \uparrow\ \ \rule{0.6em}{0.4pt}}\ \ \xrightarrow{\text{promote}}\ \ \underset{2s}{\uparrow}\ \ \underset{2p}{\uparrow\ \ \uparrow\ \ \uparrow}\ \ \xrightarrow{\text{mix}}\ \ \underset{sp^3}{\uparrow\ \ \uparrow\ \ \uparrow\ \ \uparrow}$
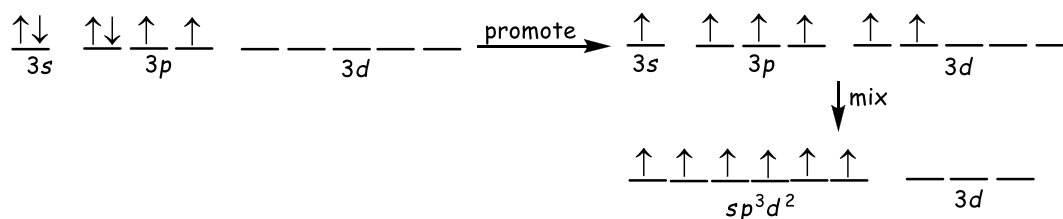
The four sp^3 hybrids spread in a tetrahedral array, as in CH_4.

As we have already discussed, expanded octets require the inclusion of d orbitals. Consider the phosphorus in PF_5:

$\underset{3s}{\uparrow\downarrow}\ \ \underset{3p}{\uparrow\ \ \uparrow\ \ \uparrow}\ \ \underset{3d}{\rule{0.6em}{0.4pt}\ \rule{0.6em}{0.4pt}\ \rule{0.6em}{0.4pt}\ \rule{0.6em}{0.4pt}\ \rule{0.6em}{0.4pt}}\ \ \xrightarrow{\text{promote}}\ \ \underset{3s}{\uparrow}\ \ \underset{3p}{\uparrow\ \ \uparrow\ \ \uparrow}\ \ \underset{3d}{\uparrow\ \ \rule{0.6em}{0.4pt}\ \rule{0.6em}{0.4pt}\ \rule{0.6em}{0.4pt}\ \rule{0.6em}{0.4pt}}$

$\downarrow \text{mix}$

$\underset{sp^3d}{\uparrow\ \uparrow\ \uparrow\ \uparrow\ \uparrow}\ \ \underset{3d}{\rule{0.6em}{0.4pt}\ \rule{0.6em}{0.4pt}\ \rule{0.6em}{0.4pt}\ \rule{0.6em}{0.4pt}}$

Finally, for the sulfur in SF_6, we obtain:

$\underset{3s}{\uparrow\downarrow}\ \ \underset{3p}{\uparrow\downarrow\ \ \uparrow\ \ \uparrow}\ \ \underset{3d}{\rule{0.6em}{0.4pt}\ \rule{0.6em}{0.4pt}\ \rule{0.6em}{0.4pt}\ \rule{0.6em}{0.4pt}\ \rule{0.6em}{0.4pt}}\ \ \xrightarrow{\text{promote}}\ \ \underset{3s}{\uparrow}\ \ \underset{3p}{\uparrow\ \ \uparrow\ \ \uparrow}\ \ \underset{3d}{\uparrow\ \ \uparrow\ \ \rule{0.6em}{0.4pt}\ \rule{0.6em}{0.4pt}\ \rule{0.6em}{0.4pt}}$

$\downarrow \text{mix}$

$\underset{sp^3d^2}{\uparrow\ \uparrow\ \uparrow\ \uparrow\ \uparrow\ \uparrow}\ \ \underset{3d}{\rule{0.6em}{0.4pt}\ \rule{0.6em}{0.4pt}\ \rule{0.6em}{0.4pt}}$

Finally, in geometries with lone pairs, those electrons go into a hybrid orbital.

8.3   Multiple Bonds

We now need to discuss the relationship of π bonds to hybridized orbitals.   Consider

ethylene $H_2C=CH_2$. The Lewis structure shows each carbon bound to three atoms and possessing

no lone pairs. Therefore, each exists in a trigonal planar arrangement. We've already learned

that molecules that have a trigonal planar base shape are sp^2 hybridized. Each of the hybrid

orbitals σ bonds, two to hydrogen atoms, one to the other carbon. But this leaves an extra p

orbital left over. The remaining p orbitals on the carbons overlap with each other to form the

π bond. The σ and π bonds between the carbons are the double bond represented by the double

line in the Lewis structure. The pictures on pp. 429 show this very nicely. A rougher sketch is

provided below.

sp^2 hybrids in a s bond
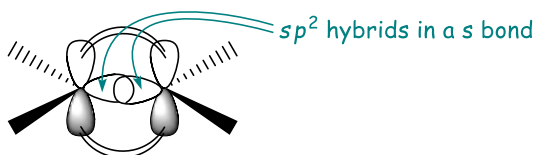
In molecules with triple bonds, the two π bonds lie at right angles to each other.

A consequence of π bonds is molecular rigidity. Consider the ethane molecule depicted in

Figure 8.17 (p. 423) of your book. The C-C bond is between two sp^3 hybrids and there is free

rotation about that bond. What that means is that if you were to grasp/immobilize one of the

CH_3 groups, you would see the other CH_3 spinning rapidly and, essentially, without restriction.

A major reason for this is that there no loss of bonding interaction as the CH_3 groups rotate.

Now contrast this with ethene, $CH_2=CH_2$, which possesses a π bond. In this situation, twisting

about the C-C axis would cause the p orbitals to unalign, which would lead to breaking the π bond. For this reason, there is a very high energy barrier to π bond rotation and that makes the molecule more rigid.

8.4   Molecular Orbital (MO) Theory

While valence bond theory is relatively simple to use (it is the simplest bonding theory), it sometimes makes major errors in predictions. For example, the Lewis structure of O_2 tells us a double bond exists between the oxygen atoms with two lone pairs of electrons on each oxygen atom. Experiment confirms the presence of two bonds, but the molecule is underlined paramagnetic (i.e. it has unpaired electrons). In the case of O_2, there are 2 unpaired electrons. A video shows the attraction of liquid oxygen to a strong magnet, something impossible if all electrons were paired. In VB theory, any molecule with an even number of electrons would be diamagnetic (all electrons paired). VB theory also poorly explains the transition between ionic and covalent bonding.

According to MO theory, when orbitals on two atoms interact, new molecular orbitals form. Just like in VB theory, for every atomic orbital put in, one product orbital forms. In this case, they are called molecular orbitals. In one case, the amplitudes on the waves reinforce one another and the atoms are attracted to one another. This is called a bonding molecular orbital. (See Section 6.3 for a similar discussion of the de Broglie atom.) In a bonding MO, the two electrons spend most of their time in the space between the nuclei.

The other MO results from the waves having amplitudes of different signs and destructively interfering with each other. This forces the electrons into the regions of space beyond the nuclei and creates a net **repulsive** force. This orbital is called an antibonding molecular orbital.

It is repulsive because without electrons between the nuclei the electrostatic repulsion between the nuclei becomes the predominant operating force.

bonding MO

antibonding MO

node
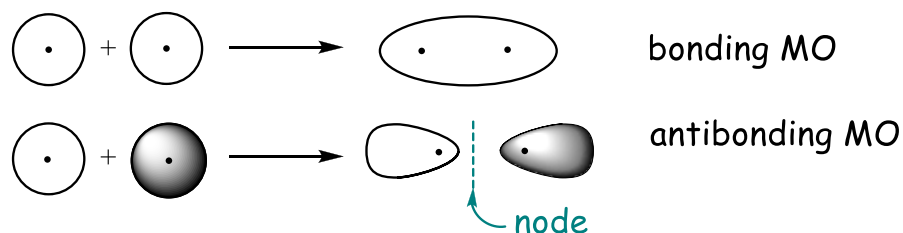
There is also a third type of molecular orbital that your book doesn't mention that you have already seen and are familiar with. These are nonbonding orbitals. Can you think of an example of these? Answer appears in the last line of the notes.

In MO theory, there are σ and π bonds, just as in VB theory, and they look pretty much the same too. To a first approximation, they arise from the same orbitals. They are represented very differently, however. We'll look at two examples: H_2 and He_2 which result from the interaction of two 1s orbitals.
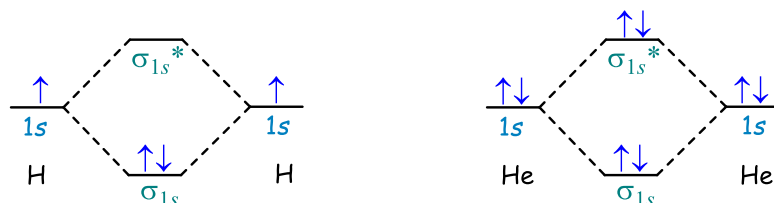

The σ_{1s} lies lower than the 1s in energy as much as the $\sigma_{1s}*$ orbitals rise above the 1s in energy. Thus, in H_2 a bond forms, while in He_2 the bonding and antibonding energies offset and no bond exists. Both yield the same predictions as VB theory.

Determining the number of bonds in VB theory can be straightforward: you simply count the lines. Resonance forms complicate counting because partial bonds don't exist in VB theory. MO theory uses a formula and <u>bond order</u> replaces the 'number of bonds,' although they are roughly synonymous.

B.O. = ½(no. bonding electrons - no. antibonding electrons)

Bond order eliminates the ambiguity of the number of bonds between two atoms. For H_2

and He_2 the bond orders are 1 and 0, respectively. In MO theory half-bonds can exist. An

example would be H_2^+ with a bond order of 0.5. Reassuringly, half bonds are roughly half the

strength of a full bond.

The MO diagrams for Li_2 and the hypothetical Be_2 molecule are shown below. The bond

order for Li_2 is one and for Be_2 is zero. In reality, Li_2 (dilithium, get it?) forms in the gas

phase, while Be_2 has never been detected.
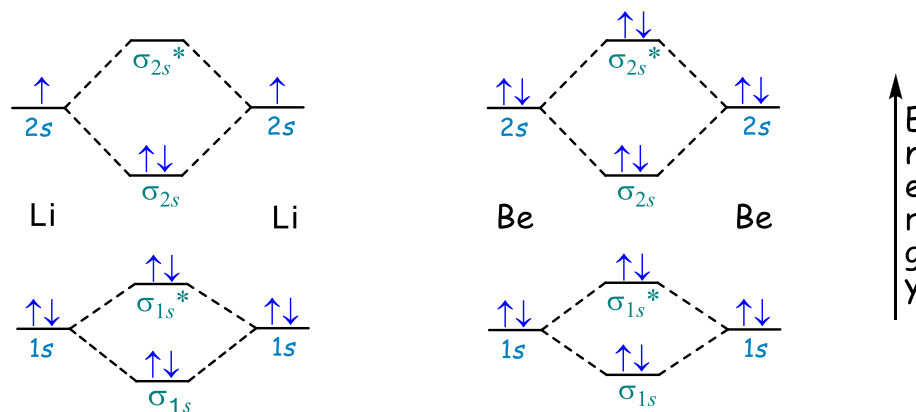
The interaction of the 2p orbitals is more complicated. Because the 2p orbitals are higher

in energy than the 2s orbitals, their resulting MOs lie higher in energy as well (just above the

previous figures).
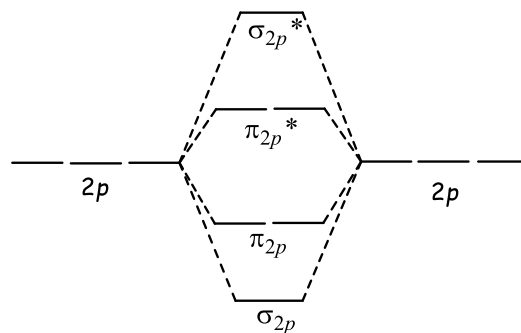
Electrons fill the well from the bottom up. Thus, B_2 has a bond order of one, C_2 is two, and

N_2 is three. This is the same as the triple bond predicted by VB theory with the same components a σ and 2 π bonds. At the beginning of Section 8.4, you were told O_2 has two unpaired electrons. This diagram predicts just such a scenario when the 8 p electrons on two oxygen atoms are filled in. Figure 8.38 (p. 443) presents a more technically correct MO diagram for second-row diatomic molecules. You may ignore this way of drawing the diagrams and use what are in these notes or use the book's method; your choice.

There is a notation for writing the location of electrons in an MO diagram that is very similar to that for an electron configuration. In it, the atomic orbital is replaced by an MO. For example, for Li_2 from the previous page, the electron configuration for the MO would be $(\sigma_{1s})^2(\sigma^*_{1s})^2(\sigma_{2s})^2$. The electron configuration for nitrogen gas would then be $(\sigma_{1s})^2(\sigma^*_{1s})^2(\sigma_{2s})^2(\sigma^*_{2s})^2(\sigma_{2p})^2(\pi_{2p})^4$. This method of providing the locations of the electrons has the obvious advantage of being very compact relative to the MO diagram.

The most common type of nonbonding orbital is the lone pair. We won't cover other types.

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