Chapter 9 – More on Bonding

**VALANCE BOND HYBRIDIZATION THEORY**

The octet rule and the VSEPR model have told us about bonding (lone pairs, single bonds, double bonds, etc.) and about spatial geometry. The problem is they have done so a bit inconsistently in that if we accept that bonds are formed when orbital clouds on different atoms overlap and share electron cloud density, we would expect from the one ns and the three np type orbits that up to three other atoms could attach to the p orbital and from bonds that lay along the x, y, and z axis. This is not what VSEPR and experiment tell us. What’s wrong? The answer is that the atom’s valence picture is the lowest energy electron cloud arrangement for an isolated atom. But in a molecule the atom is not isolated and a lower energy cloud shape exists. This shape and sharing between newly shaped orbitals on different centers to form bonds lowers the energy by pointing the new bonds in directions where it can have maximum bond overlap and sharing while achieving the proper geometry according to the VSEPR. Actually the truth is that the geometry and bond shape both are the result of the fact that they maximally lower the energy. The new orbitals are called hybrid orbitals and the “reshaping” is called hybridization. The results of calculations that show the reshaping of the clouds tell us the following. Consider an atom in a molecule; if the atom has

1. 4 “sticks” (lone pairs or bonds) the new orbital are four sp^3 orbitals made by mixing the one s and three p orbitals of the same n (i.e. only orbitals near in energy are mixed.) Each of the 4 orbital looks as \[ \text{and the four points to the corners of a tetrahedron.} \]
   (we omit the little black lobes)

   ![Diagram](image)

   See Figure 1

2. If 3 sticks exist one s and two p orbits combine to give the sp^3 orbitals leaving one unaffected p orbital.

   ![Diagram](image)

   The sp^3 orbitals point to the edges of the triangle. See figure 11, 12, 13.
Figure 9.3
The formation of $sp^3$ hybrid orbitals

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Figure 9.8
The formation of $sp^2$ hybrid orbitals

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Figure 9.10
An $sp^2$ hybridized C atom

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(3) two sticks - the Pz and the Py orbitals are unaffected but the S and one P, called here Px, combine to two SP orbitals that look as \[ \text{SP}^2 \text{ and } \text{SP}^3 \] to give totally

\[ \text{SP}^2 \text{ and } \text{SP}^3 \text{, see Fig IV and Fig VI} \]

(4) 5 sticks as PCl₅ - now use one d and the S and the three 2P to form five dSP³ - as VSEPR says they must all point to the corners of a trigonal bipyramid see Fig VI #5

(5) 6 sticks as SF₆ - now use two d's and get six dSP³ orbitals each pointed to the corners of an octahedral see Fig VI #6
Figure 9.14
The formation of sp hybrid orbitals

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<table>
<thead>
<tr>
<th>Number of Effective Pairs</th>
<th>Arrangement of Pairs</th>
<th>Hybridization Required</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>Linear</td>
<td>$sp$</td>
</tr>
<tr>
<td>3</td>
<td>Trigonal planar</td>
<td>$sp^2$</td>
</tr>
<tr>
<td>4</td>
<td>Tetrahedral</td>
<td>$sp^3$</td>
</tr>
<tr>
<td>5</td>
<td>Trigonal bipyramidal</td>
<td>$dspd^2$</td>
</tr>
<tr>
<td>6</td>
<td>Octahedral</td>
<td>$d^2sp^3$</td>
</tr>
</tbody>
</table>

**Figure 9.24**  
The hybrid orbitals for various electron pair arrangements

Now let us make molecules. Step 1 is to get the Lewis bond picture. Step 2 is to look at each atom and from the "sticks" to pick the hybridization for the atom and Step 3 is to overlap to make bonds and to check the VSEPR geometry energies.

**Examples:**

\[ \text{H}_2 : \quad \text{H}+\text{H} = \bullet \quad \overset{\text{overlap}}{\text{H}} \rightarrow \cdot \cdot \rightarrow \quad \text{one } \sigma \text{ bond} \]

\[ \text{CH}_4 + \text{H} : \quad \overset{\text{sticks}}{\text{C}} + 4 \overset{\text{sp}^3}{\text{O}} \rightarrow \quad + 4 \overset{\text{sp}^3}{\text{H}} \rightarrow \text{CF}_4 \quad \overset{\text{sp}^3}{\text{C}} \quad \text{4 CH } \sigma \text{ bonds} \]

\[ \text{CF}_4 \text{ sp}^3 \text{4 sticks same as CH}_4 \text{ but H atom replaced by} \]

\[ \text{C} - \overset{\text{sp}^3}{\text{F}} : \quad \overset{\text{sp}^3}{\text{4 sticks sp}^3 \text{on F}} \]

\[ \text{so } 3 \quad \text{sp}^3 \text{ tetrahedrally pointed lone pairs on each F and} \]

\[ \text{four CF } \sigma \text{ bonds} \]

\[ \text{NH}_3 : \quad \overset{\text{sp}^3 \text{ lone space}}{\text{N}} \quad \overset{\text{sp}^3 \text{ hybrid on N}}{\text{N} + 4 \overset{\text{H}}{\text{H}} \text{ bond}} \]

**Ethylene:** \( \text{C}_2 \text{H}_4 \)

\[ \overset{\text{sp}^2}{\text{H}} \quad \overset{\text{3 sticks}}{\text{sp}^2} \quad \overset{\text{C}}{\text{C}} \quad \overset{\text{sp}^2}{\text{H}} \quad \overset{\text{sp}^2}{\text{H}} \]

See figures \( \text{Fig VI} \) and \( \text{Fig VII} \). A "C-C" sigma out of two carbon sp\(^2\). A "C-C" pi bond and 4 C-H each out of a carbon sp\(^3\). Note it's planar with \( \frac{1}{2} \) pi bond above and \( \frac{1}{2} \) pi bond below the plane with an an H 1s orbital.
Figure 9.6
The orbitals in CH$_4$

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Figure 9.7
The orbitals in NH$_3$
Figure 9.11
Sigma bonding in $\text{C}_2\text{H}_4$
Figure 9.12: Sigma and pi bonding

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Figure 9.13
The orbitals for C₂H₄
\[ \text{CO}_2 \]
\[ \overset{\text{O}}{\text{C}} = \overset{\text{O}}{\text{C}} \]
\[ \overset{\text{sp}^3}{\uparrow} \quad \overset{\text{sp}^2}{\uparrow} \quad \overset{\text{sp}^2}{\uparrow} \]

See Fig. XII

It is linear with two sigma CO bonds and out of a C sp and an O sp\(^2\) and two perpendicular CO, pi bonds.

\[ \text{N}_2 \]
\[ :\text{N} \equiv \text{N} : \uparrow \quad \overset{\text{sp}}{\text{sp}} \quad \overset{\text{2sticks}}{\text{2sticks}} \]

See figure XIII
One N-N sigma and two N-N pi bonds and one lone pair on each end.

\[ \text{PCl}_5 \]
\[ \overset{\text{Cl}}{\text{P}} \quad \overset{\text{Cl}}{\text{Cl}} \quad \overset{\text{Cl}}{\text{Cl}} \quad \overset{\text{sy}}{\text{Cl}} \quad \overset{\text{cl}}{\text{Cl}} \quad \overset{\text{ds}p^3}{\text{d}sp^3} \quad \overset{\text{Fig. VI}}{\text{Fig. VI}} \quad \overset{\text{R}}{\text{R}} \quad \overset{\text{R}}{\text{R}} \quad \overset{\text{R}}{\text{R}} \quad \overset{\text{Fig. XIV}}{\text{Fig. XIV}} \]

Five P-Cl sigma bonds made of a P d\(sp^3\) orbital and a Cl sp\(^3\) orbital. 3 sp\(^3\) lone pairs on each Cl.

\[ \text{SF}_6 \]
\[ \overset{\text{S}}{\text{F}} \quad \overset{\text{F}}{\text{F}} \quad \overset{\text{F}}{\text{F}} \quad \overset{\text{F}}{\text{F}} \quad \overset{\text{F}}{\text{F}} \quad \overset{\text{6sticks} \quad \text{sp}^3}{\text{6sticks} \quad \text{sp}^3} \]

So six S-F sigma bonds and out of one \(2sp^3\) orbital and an F sp\(^3\) orbital. Also 3 sp\(^3\) lone pairs on each F.

\[ \text{XeF}_4 \]

See Fig. XV

Square plane (See exercise 9.4). So Xe has two d\(sp^3\) lone pairs and four Xe-F d\(sp^3\) and one F sp\(^3\) orbital. Each F has three sp\(^3\) lone pairs.
Figure 9.19
The orbitals for CO$_2$

(a) Sigma bond (1 pair of electrons)
(b) Pi bond (1 pair of electrons)
Figure 9.20
The orbitals for $N_2$
Each chlorine atom has a lone pair. The other sp^3 orbitals on the five chlorine atoms share electron pairs with sp^3 orbitals on the five phosphorus atoms. The phosphorus bonds in the PCl_5 molecule are formed using the sp^3 orbitals shown above.

Figure 9.22
Xenon uses six $ds^2p$ hybrid orbitals to bond to the four fluorine atoms and require an octahedral arrangement.

Six electron pairs are required to hold these electrons, and the xenon atom is $ds^2p$ hybridized. In an octahedral set of six atomic orbitals, the xenon atom minimizes repulsions. An octahedral arrangement requires an octahedral arrangement of six electron pairs. Exercise 8.13, $\text{XeF}_4$ has six pairs of electrons around xenon that are lone pairs.
Linear molecule and Xe has 3 trigonal planar lone pairs.

SEE FIG XVII - BENZENE BONDING

An Alternate Theory of Bonding needed because our previous theory couldn’t explain odd electron molecules and couldn’t explain why say O₂. Also theory was not really predictive. Hence a new model (model—not the truth— the truth involves big calculations using quantum theory and yields good number by a very complicated way of picturing things) is needed. The new model, called the Molecular Orbital Theory, designs orbitals that are “natural” for molecules as atomic theory did for atoms. These new orbitals will not be 1s, 2s, 2p etc which were solution of one electron atomic problem. They will be solutions of a one electron molecular problem. For example as H₂⁺ for a homonuclear diatomic molecule and as LiH⁺ for a heteronuclear case. The new orbitals can then be lined up in energy and electrons can be dropped in one at a time, using a Pauli and Hunds rule build by “aufbau” a bonding orbital configuration.

To generate the orbitals takes large quantum calculations but we can get a qualitative idea about them if we consider them to be sums and differences of atomic orbitals centered on the “to be” bond atoms. Now the mathematical theory tells us that orbitals on different centers that have greatly different energy, average radii (See fig XVIII), or orientations (See fig XIX) can’t overlap to form the new orbitals. As such in a homonuclear species AB (here A and B are the same nucleus but A is on the left of B) 1sₓ can combine with 1sₓ, 2sₓ with 2sₓ, 2pₓ with 2pₓ (here); ditto 2pᵧ, 2pᵧ etc. Now each pair forms two molecular orbitals; one the plus combination and the minus combination. For 1sₓ, 2sₓ and 2pₓ, the plus combination puts electron density between A and B thereby causing stability and lowering the energy. The minus combination puts its electron density outside (B) the bonding area (Fig. XX) and its’ energy is raised relative to the atomic orbital energies by amount equal to the lowering of the plus combination. All these bonding orbitals are called sigma bonds (e.g., 1sₓ₁, 1sₓ₂, 2sₓ₁, 2sₓ₂, 2pₓ₁, 2pₓ₂ etc).
c. The XeF₂ molecule has 22 valence electrons. The Lewis structure shows 5 electron pairs on the xenon atom, which requires a trigonal bipyramidal arrangement:

Note that the lone pairs are placed in the plane where they are 120 degrees apart. To accommodate five pairs at the vertices of a trigonal bipyramid requires the xenon atom adopt a set of five $dsp^3$ orbitals. Each fluorine atom has two electron pairs and can be assumed to be $sp^3$ hybridized. The XeF₂ molecule has a linear arrangement of atoms.

Figure 9.48
The π system for benzene

(a)
Figure 9.31
Overlap of the 1s and 2s orbitals in Li₂
Figure 9.33
The atomic orbitals in B2
The molecular orbitals for $H_2$

(a) Electron probability distribution

(b) Energy diagram

$E$

$1s^2$

$1s^1$

$H_1$

$H_2$

$H_3$

$H_4$

$MO_1$

$MO_2$
The * denotes an "anti-bonding" or "raised energy (i.e. anti-stability) orbital. The subscript indicates which the atomic orbitals combined to give the new orbital. Fig XX shows the orbitals coming out of the 5 (15 with 15, 25 with 25) combinations. The 5 being larger in radius than the 15 (by radius I mean the view from the end of the molecule down the molecular axis). The 2p\textsubscript{z} mergers are shown in Fig XXIa. The orbitals for the 2p\textsubscript{y} merger is in Fig XXIb and are called \( \Pi_2 + \Pi_2^* \) and they have the same energy as the perpendicular set \( \Pi_2 + \Pi_2^* \) (i.e. \( \Pi_2 + \Pi_2^* \) are degenerate as are \( \Pi_2^* + \Pi_2^* \) and \( \Pi_2^* + \Pi_2^* \)). The energy level diagram is now given in the l.h.s. of Fig XXII. Note the definition of "bond order". This definition recognizes that equally
Figure 9.34
The molecular orbitals from $p$ atomic orbitals

For $O_2$ and $Be$:

- Atom $O_2$: $2p$ orbitals.
- Molecule $O_2$: $\sigma_2^*$, $\pi_2^*$ orbitals.

For $Be_2$, $C_2$, $N_2$:

- Atom $Be_2$: $2p$ orbitals.
- Molecule $Be_2$: $\sigma_2^*$, $\pi_2^*$ orbitals.

Bond order = $\frac{\text{# of electrons in bonding orbitals}}{\text{# of electrons in anti-bonding orbitals}}$.
occupied or \( \sigma \) orbitals cancel each other leaving a bonding atomic orbitals.

The bond order is roughly the number of bonds. The figure also recognizes that for Be, C, and N, that because of the \( \sigma \rightarrow \pi \) interaction which we ignored and which dies out by \( \text{O}_2 \) and \( \text{F}_2 \) that the \( \pi \) energy order and that the \( \sigma^* - \pi \pi^* \) and \( \sigma^* \pi \pi^* \) spacing is affected. Relative to \( 2s \), energy is lowered more than the \( \pi^* \) is raised.

Many things to note from Figure 6. We will do it molecule by molecule. Adding usually 2 electrons as we go to bigger atoms, \( \pi^* 2p \) is the configuration. It is a very strong short bond. It is diamagnetic (not attracted into but repelled out of a magnetic field because it has no unpaired electrons). Bond order is 1 and measures the number of bonds.

\( \text{He}_2 \): M.O. theory fails here. We expect \( \sigma(1s)^2 \pi(1s)^2 (\sigma^* 2s)^2 \). Note if \( \text{BO} = 0 \) and atoms far apart the molecular orbital product of molecular orbitals becomes the product of atomic orbitals. This molecule has never been observed.

\( \text{Be}_2 \): \( \text{BO} = 0 \) but \( \sigma_{2s} \) lower down than \( \pi \), so we expect a very weak bond. This is correct. It is "Dia".

\( \text{B}_2 \): \( \text{BO} = 1 \); but only two perpendicular 1 electron \( \Pi \) orbitals outside atom and Be-like cores \( \downarrow \downarrow \Pi \) so it is also a weak 1 bond. Uses new diagram which interchange of \( \Pi_{2p} \) and \( \sigma_{2p} \).

But it is found it is paramagnetic and weak bond; so a victory for M.O. theory.

\( \text{C}_2 \): Held together by two doubly occupied \( \Pi \) bonds and a weak \( \sigma_{2s} \). \( \text{BO} = 2 \) or a bit more and it is stronger and shorter. It is predicted to have no unpaired electrons and is "dia". It has a Be-like core i.e. weak \( 2s \). Old diagram gave \( \sigma(\Pi_{2p})^2 (\sigma^* 2s)^2 \) and "para" but its "dia". From experiment:

\( \text{N}_2 \): A \( \sigma(2p)^2 \) is added to \( \text{C}_2 \). Therefore a BO of 3 and a triple bond; it is very strong, has no unpaired electrons and it "dia".

\( \text{O}_2 \): Bonding \( \sigma(2p)^2 (\Pi_{2p})^4 (\sigma^* 2p)^4 \). Note the order change. \( \text{BO} = 2 \); one \( \sigma_{2p} \) bond and two \( \Pi \) bonds that are perpendicular to each other. It is "para" and it is true. See Fig. 9.40 of the book; it shows \( \text{O}_2 \) being "held" by the magnet.

\( \text{F}_2 \): \( \sigma(2p)^2 (\Pi_{2p})^4 (\sigma^* 2p)^4 \). \( \Pi_{2p} \) and \( \sigma^* 2p \) cancel and a single \( \sigma(2p)^2 \) bond exists with \( \text{BO} = 1 \) and it is "dia". It is found to be very weak. It has big electron repulsion – a big surprise. A half victory.

\( \text{Ne}_2 \): \( \sigma(2p)^2 \) now cancels \( \sigma(2p)^2 \) and no bond exists. \( \text{BO} = 0 \) and it is not observed.

\( \text{P}_2 = \) Phosphorus; like \( \text{N}_2 \) but 2 \( \rightarrow \) 3.

Heteronuclear:

Simple case – adjacent atoms use homonuclear model as the atoms are "similar" in their orbitals. - atoms in same 0.

Ex: CO use \( \text{N}_2 \) as model
\( \text{CN}^- \) use \( \text{N}_2 \) as model.
\( \text{NO}^+ \) use \( \text{N}_2 \) as model.

All triple bonds \( \sigma(2p)^2 (\Pi_{2p})^4 \).
Now NO$^+$ use N$_2$ diagram and add one electron i.e. ($\text{N}^{2+}$)$^2$ (2p$^2$) (1s$^2$ 2p$^4$) $\text{NO}^+$ So bond order = 2.5 and we expect a triple bond but with the system "weakened". Also "para", an unpaired electron exists. NO is "para": a victory.

Heteronuclear- greatly different atoms as H and F to form HF. Note that the LP. of the unpaired 2p$_z$ in F is much larger than for the 1s in H. Since being free is zero energy, the separated atoms are as.

Now when they interact we again get two states as in fig.XXI. Bonding is achieved by putting the two electrons in the lowest molecular orbital $\sigma^-$ whose energy is below that of the free atoms. Since $\sigma^-$ is closer to 2p than 1s$^2$. Hence $\sigma^+$ has a larger fraction of 1s than 2p$_z$. Since $\sigma^-$ is occupied, the electrons are closer, since they are more in the 2p part than the 1s, to F$_2$. We expect a big dipole with F being the negative end (See Fig.XXV) A victory- we can explain "electronegativity" and dipoles from first principles.

An explanation of "Resonance" and the reason for the delocalized bonds.

Recall NO$_3^-$ 1e $\xrightarrow{\text{N}}$ $\xrightarrow{\text{O}}$ $\xrightarrow{\text{O}}$ $\xrightarrow{\text{O}}$ $\xrightarrow{\text{O}}$

The N is sp$^2$ (i.e. localized electron theory).

Now bring up 3 oxygens hybridized as sp$^2$.

We must assume 3 sticks.
The overlapping of O sp$^2$ and N sp$^2$ form 3 $\sigma^-$ bonds as expected and now the p$_z$ as in fig.XIX forms a cloud above and below by forming out of the 4 p$_z$ orbits, 4 delocalized molecular orbitals, the lowest energy of which are bonding and are as shown in the figure.

Figures XX and XIX show a similar idea for the resonance of benzene.

HwK 23, 35, 37, 41, 43, 45
Figure 9.43
The molecular orbital diagram for HF

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Figure 9.44
The electron density map for HF

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Figure 9.49
(a) The p orbitals used to form the π bonding system in the NO$_3^-$ ion. (b) A representation of the delocalization of the electrons in the π molecular orbital system of the NO$_3^-$ ion.
Figure 9.47
The sigma system for benzene

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Figure 9.46

The π system for benzene

(q)

(a)