The previous chapter dealt with chemical bonding. Now we discuss molecular geometry; i.e. the shapes of molecules. Most enzymes will react with molecules possessing only a certain, specific shape. Small, sometimes seemingly trivial, changes in a molecule may prevent it from interacting with the enzyme. While usually less dramatic with small molecules, the shapes of substances can have a significant impact on their reactions and on their physical properties. For example, two isomers of pentane, C₅H₁₂, are normal pentane (CH₃CH₂CH₂CH₂CH₃) which melts at -130 ºC and neopentane (C(CH₃)₄) which melts at -16 ºC. This 114 ºC melting point difference arises almost solely from the differences in the shapes of the molecules.

11.1 Valence Bond (VB) Theory and Orbital Hybridization

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). 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.

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. $s$ is spherical, while $p$ and $d$ orbitals each form $90^\circ$ angles. How are the shapes we actually see generated? Valence bond theory gives us an answer using "hybridized" orbitals.
**sp Hybrid Orbitals**

Consider BeCl₂. VSEPR theory predicts a linear molecule with two identical bonds. The electron configuration of beryllium is [He] 2s². 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 2s orbital to a 2p orbital.

\[
\begin{array}{c}
\uparrow \downarrow \\
2s & 2p
\end{array}
\xrightarrow{\text{promotion energy}}
\begin{array}{c}
\uparrow \\
2s
\end{array}
\xrightarrow{\uparrow}
\begin{array}{c}
\uparrow \\
2p
\end{array}
\]

If the chlorine overlapped the 2s and 2p 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 hybrid orbital. 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.

\[
\begin{array}{c}
\uparrow \downarrow \\
2s & 2p
\end{array}
\xrightarrow{\text{promote}}
\begin{array}{c}
\uparrow \\
2s
\end{array}
\xrightarrow{\uparrow}
\begin{array}{c}
\uparrow \\
2p
\end{array}
\xrightarrow{\text{mix}}
\begin{array}{c}
\uparrow \uparrow \\
sp & 2p
\end{array}
\]

\[
\begin{array}{c}
\text{promotion energy}
\end{array}
\]

\[
\begin{array}{c}
\text{sp hybrid orbital}
\end{array}
\]

\[
\begin{array}{c}
\text{sp orbital}
\end{array}
\]

\[
\begin{array}{c}
\text{bond formation}
\end{array}
\]

\[
\begin{array}{c}
\text{sp hybrid orbital}
\end{array}
\]
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:  
\[
\begin{array}{c}
\uparrow \downarrow \\
2s \\
\uparrow \\
2p \\
\end{array} \quad \text{promote} \quad \begin{array}{c}
\uparrow \\
2s \\
\uparrow \\
2p \\
\end{array} \quad \text{mix} \quad \begin{array}{c}
\uparrow \uparrow \uparrow \\
\text{sp}^2 \\
\uparrow \\
2p \\
\end{array}
\]

The three \( \text{sp}^2 \) hybrid orbitals spread in a trigonal planar array, as in BF\(_3\), with a vacant \( p \) orbital perpendicular to the molecular plane.

For carbon:  
\[
\begin{array}{c}
\uparrow \downarrow \\
2s \\
\uparrow \uparrow \uparrow \\
2p \\
\end{array} \quad \text{promote} \quad \begin{array}{c}
\uparrow \uparrow \uparrow \\
2s \\
\uparrow \uparrow \uparrow \\
2p \\
\end{array} \quad \text{mix} \quad \begin{array}{c}
\uparrow \uparrow \uparrow \uparrow \\
\text{sp}^3 \\
\end{array}
\]

The four \( \text{sp}^3 \) 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\(_5\):

\[
\begin{array}{cccc}
\uparrow & \uparrow & \uparrow & \uparrow \\
3s & 3p & \text{promote} & 3d \\
\uparrow & \uparrow & \uparrow & \uparrow \\
\text{mix} & \text{sp}^3d & 3d \\
\end{array}
\]

Finally, for the sulfur in SF\(_6\), we obtain:

\[
\begin{array}{cccc}
\uparrow & \uparrow & \uparrow & \uparrow \\
3s & 3p & \text{promote} & 3d \\
\uparrow & \uparrow & \uparrow & \uparrow \\
\text{mix} & sp^3d^2 & 3d \\
\end{array}
\]

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

11.2 Modes of Orbital Overlap and the Types of Covalent Bonds

There are three ways orbitals can overlap. We will discuss two here. When two hydrogen atoms overlap (picture on p. 2 of notes), electron density concentrates along the line connecting the nuclei. Such “end-to-end” overlap is called a \( \sigma \) bond. It occurs whenever an \( s \) orbital overlaps any other orbital or a \( p \) orbital overlaps through only one of its lobes. Hybrid orbitals always \( \sigma \) bond.

A \( p-p \) \( \sigma \) 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 \( \pi \) bond. In
the $\pi$ bond, electron density concentrates above and below the internuclear axis with a node in the plane separating the nuclei.

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

We now need to discuss the relationship of $\pi$ bonds to hybridized orbitals. Consider ethylene $\text{H}_2\text{C}=$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 $\sigma$ 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 $\pi$ bond. The $\sigma$ and $\pi$ bonds between the carbons are the double bond represented by the double line in the Lewis structure. The pictures on p. 336 show this very nicely. A rougher sketch is provided below.

In molecules with triple bonds, the two $\pi$ bonds lie at right angles to each other.
A consequence of \( \pi \) bonds is molecular rigidity. Consider the ethane molecule depicted in Figure 11.9 (p. 336) 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 \( \pi \) bond. In this situation, twisting about the C-C axis would cause the p orbitals to unalign, which would lead to breaking the \( \pi \) bond. For this reason, there is a very high energy barrier to \( \pi \) bond rotation and that makes the molecule more rigid.

Ignore the discussion on Bond Order (p. 337).

10.3 Molecular Orbital (MO) Theory and Electron Delocalization

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 paramagnetic (i.e. it has unpaired electrons). In the case of O\(_2\), there are 2 unpaired electrons. This is not possible using VB theory. 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. 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.

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 $\sigma$ and $\pi$ 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 $\sigma_{1s}$ 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 bond order replaces the 'number of bonds,' although they are roughly synonymous. (Earlier, your book incorrectly discusses bond order with respect to VB theory. B.O. is exclusive an MO concept.)

$$B.O. = \frac{1}{2}(\text{no. bonding electrons} - \text{no. antibonding electrons})$$

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.

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 2$p$ orbitals is more complicated. Because the 2$p$ orbitals are higher in energy than the 2$s$ orbitals, their resulting MOs lie higher in energy as well (just above the
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 $\sigma$ and 2 $\pi$ bonds. At the beginning of Section 10.3, 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 11.20 (p. 343) presents a more technically correct MO diagram for second-row diatomic molecules. You should ignore this way of drawing the diagrams and use what are in these notes.

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

August 24, 2015