3. Orbitals and hybridization.

3.1 Atomic and Molecular Orbitals.

We can use molecular orbital (MO) theory to describe the structure of molecules in more detail. MO theory also provides a means of predicting the shapes of molecules. In MO theory, our first hypothesis is that bonding occurs by the overlap of singly occupied atomic orbitals. So if we look at $\text{H}_2$, we see that two singly occupied $s$ orbitals, each with a spherical shape, come together in space to form a new MO with an oblong shape. Electrons in this new MO have less energy than electrons in either of the two atomic orbitals with which we started. As a result, energy is released, and the molecule that is formed is more stable than the individual atoms from which it was formed. You might think that the atoms could keep coming together until they were merged, but at a certain distance the repulsion between the positively charged nuclei becomes important. The balance point is called the bond distance. At this point the energy of the system is at a minimum. We can draw diagrams like the ones below.

The diagram on the right shows how two atomic orbitals come together to form a bonding orbital of lower energy than either constituent orbital. It also shows that an anti-bonding orbital of correspondingly higher energy is formed. If two He atoms come together, we can draw exactly the same picture, except that we would have to put the two extra electrons in the anti-bonding orbital. Then we would have equal amounts of loss and gain in energy. The net result would be no gain in energy for the system, and the two He atoms would be happier to fly apart than they would be to stick together.
3.2 \( sp^3 \) Hybridization.

Remember that C has four valence electrons in the configuration \( 2s^22p_x^12p_y^1 \), where \( p_x \) and \( p_y \) are two of the three \( p \) atomic orbitals (AOs) in shell 2. Since C has two singly occupied AOs, we might expect that it would form two bonds. In fact, C almost always likes to form four bonds, as in methane, \( CH_4 \). What can we do? The first thing we can do is promote one electron from \( 2s \) to \( 2p_z \). Then we have the configuration \( 2s^12p_x^12p_y^12p_z^1 \), with four singly occupied AOs. This helps a lot. Now we can say that each AO is used to form one bond to H in \( CH_4 \).

![Diagram of sp3 hybridization]

There is still a problem, though. The angle between each of the \( p \) orbitals is 90°, so we might guess that three of the four C–H bonds in methane are 90° apart. In fact every bit of evidence shows that all four C–H bonds are equivalent. Something must be done. What we do is to

![Diagram of sp3 hybridization with d orbitals]

excited atomic C; can make 4 bonds, one different from others
average the four s and p AOs mathematically. This gives us four equivalent AOs. We call them sp\(^3\) orbitals, because they consists of 1 part s orbital and 3 parts p orbital. Their energy is 3/4 of the distance between s and p. They point at 109.5° angles from each other, that is, to the four corners of a tetrahedron. C can use each hybrid AO to overlap with a H(s) orbital to make two new MOs.

[How do we derive 109.5°? Look at the depiction of the CH\(_4\) tetrahedron within the octahedron. Consider the midpoint, M, of the line connecting any two H atoms. If the length of a side of the octahedron is 1, the distance from M to either H must be \((\sqrt{2})/2\), and the distance from M to C must be \(1/2\). The H-M-C angle is 90°, so we can use trigonometry (remember SOHCAHTOA?) to conclude that the H–C–M angle is \(\tan^{-1}(\sqrt{2})\), or 54.74°. The H–C–H angle is twice this number, or close to 109.5°.]

The concept of hybridization is very different from that of bond-making, even though both involve mixing orbitals to make new orbitals. In hybridization, a single atom takes its AOs and uses mathematics to convert them into the same number of new AOs. No physical change has taken place; the total energy of the AOs is the same, and the amount of space covered by those AOs is the same. In bonding, two different atoms come together, and one AO from each overlap to form new MOs. When two AOs come together in this way, one new MO is lower in energy, and one is higher in energy. If each constituent AO contained one electron, then two electrons go into the bonding MO, and a bond is formed because the two electrons have lower energy than they would if the two atoms were far apart. That is, the new hybrid AOs are used to make bonds just as the individual “pure” AOs might have done.
3.3 Hybridization in Alkenes.

We can hybridize orbitals in other ways, too. If we combine the s orbital with two p orbitals and leave the third one unaltered, we have \( sp^2 \) hybridization. An \( sp^2 \)-hybridized atom has three equivalent \( sp^2 \) orbitals, each with 1/3 s and 2/3 p character, and one unadulterated p orbital. The \( sp^2 \) orbitals are 120° apart. If we combine the s orbital with one p orbital and leave the other two unaltered, we have \( sp \) hybridization. An \( sp \)-hybridized atom has two equivalent \( sp \) orbitals, each with 1/2 s and 1/2 p character, and two unadulterated p orbitals. The \( sp \) orbitals are 180° apart. The two p orbitals are perpendicular to each other and to the line containing the \( sp \) orbitals. Cartoons of \( sp^3 \), \( sp^2 \), and \( sp \) orbitals all look like a fishy, although in fact they have slightly different shapes.

Under what circumstances do we find \( C(sp^3) \), \( C(sp^2) \), and \( C(sp) \) hybridization, and how does C "choose" a particular hybridization? Suppose \( CH_4 \) were \( sp^2 \)-hybridized. Three H atoms would be coplanar, and the fourth, whose s orbital overlapped with the p orbital, would have a 90° angle with respect to the other three. Moreover, half the p orbital's bonding density would be wasted on the side of the C atom opposite the unique H atom. So we can see that \( sp^3 \) hybridization is best for a C atom that is bound to four different atoms.

\[
\text{CH}_4 \text{ with } C(sp^2)
\]

However, when a C atom is bound to three different atoms, the situation changes. Consider ethene (ethylene, \( H_2C=CH_2 \)). If the C atoms were \( sp^3 \)-hybridized, we would need to use two hybrid orbitals to construct the double bond. They would need to be canted with respect to the C–C axis, thus putting only a small amount of electron density between the two C nuclei. Not a good situation!

\[
H_2C=CH_2 \text{ with } C(sp^3)
\]
To put maximum density between the two C nuclei, the C atom must place an orbital in the same plane as the C–H bonds. This arrangement is achieved by sp² hybridization. The three C(sp²) orbitals on one C atom are used to form two σ bonds to H atoms and one σ bond to the other C. The p orbital is used to form the second bond to the other C atom. The C(p) orbitals overlap with each other lengthwise, giving a bond that does not look like the σ bonds we have seen already. This bond is a π bond. It has a node, i.e., a plane in which no electron density resides. The C(p) orbital has a higher energy than the C(sp²) orbital used to make the σ bond, and the C(p)–C(p) overlap is poorer than the C(sp²)–C(sp²) overlap, so the energy of the C–C π bond is higher than the energy of the C–C σ bond. Whenever you have a double bond between two atoms, there is one σ MO and one π MO. The energy of the C(sp²)–C(sp²) σ bond is lower than the energy of the C(sp³)–C(sp³) bond of ethane, because the C(sp²) orbitals are lower in energy than a C(sp³) orbital.

Just like there is a σ* orbital associated with a σ orbital in the H–H bond, so there are antibonding orbitals associated with the C(sp²)–C(sp²) σ bond and the C(p)–C(p) π bond. A C atom that makes one double bond and two single bonds is sp²-hybridized.
3.4 Hybridization in Alkynes.

The same logic that told us that the C atoms in ethylene cannot be sp³-hybridized tells us that the C atoms in ethyne (acetylene, HCC=CH) cannot be sp³- or sp²-hybridized. Instead, each C atom is sp-hybridized. The s orbital is averaged with just one p orbital to make two new hybrid sp orbitals that are pointing 180° from one another. The energy of the sp orbital is halfway between that of an s orbital and that of a p orbital. One of the sp orbitals is used to make a σ bond with the other C, and the other is used to make a σ bond with H. The two remaining, unhybridized p orbitals are used to overlap with two p orbitals on the other C atoms to make two π bonds.

Whenever you have a triple bond between two atoms, there are one filled σ MO and two filled π MOs (and the corresponding empty anti-bonding MOs). Again, there are anti-bonding orbitals associated with the C(sp)–C(sp) σ bond and the C(p)–C(p) π bonds. A C atom that makes one triple bond and one single bond is sp-hybridized.

Even though it's hard to tell, the π electrons around the C≡C bond form a hollow cylinder of electron density.
3.5 Hybridization in Heteroatoms.

Heteroatoms also hybridize. We treat most lone pairs as if they were groups to which the heteroatom was bound; usually they reside in hybrid orbitals. If a heteroatom has only σ bonds to its neighbors, it is sp³-hybridized. (Examples: dimethyl ether, ammonia.) If a heteroatom has one π bond to one neighbor, it is sp²-hybridized. (Examples: pyridine, acetone, protonated acetone.) If a heteroatom has two π bonds to its neighbors, it is sp-hybridized. (Acetonitrile.) These hybridizations have consequences for both structure (bond angles and lengths) and reactivity (lone pairs with certain energies).

To summarize: Hybrid orbitals are used to form σ bonds and to contain lone pairs. Unhybridized p orbitals are used to form π bonds or are empty. To determine the hybridization of an atom, count the number of σ bonds and lone pairs not used in resonance; you need that many hybrid orbitals.

We said that lone pairs are put in hybrid orbitals. If the lone pair can be used in resonance, however, it must be in a p orbital for maximum overlap to occur. Therefore: Hybrid orbitals are used to form σ bonds and to contain lone pairs not used in resonance. Unhybridized p orbitals are used to form π bonds, hold lone pairs used in resonance, or are empty.

Be careful when determining hybridization of heteroatoms in cyclic compounds. Pyridine, pyrrole, furan all have sp²-hybridized heteroatoms. In pyrrole and furan one lone pair is involved in resonance; in pyridine the lone pair is not involved in resonance.

3.6 Hybridization and energy.

An sp orbital of a particular element is lower in energy than an sp² orbital of the same element, which is lower in energy than an sp³ orbital of the same element. A pair of electrons residing in, say, an N(sp) orbital will therefore be less reactive than a pair of electrons in an N(sp²) orbital, which will be less reactive than a pair of electrons in an N(sp³) orbital. So already, just by looking at hybridization, we can predict that the N atom in CH₃CN will be less basic than the N in pyridine, which will be less basic than the N in NH₃. And our prediction would be true.

Hybridization also affects energy by affecting geometry. If the shape of a compound forces an atom to assume bond angles or shapes that diverge from the optimum bond angles or shapes as determined by that atom’s hybridization, then the compound is higher in energy than one might expect. Small-ring compounds such as cyclopropane are much higher in energy than their
acyclic congeners because the bond angles in cyclopropane are forced to be 60°, not 109° as is optimum for sp\(^3\)-hybridized atoms. The smallest cyclic alkyne that can be isolated is cyclooctyne; smaller alkynes such as cyclohexyne are very high in energy because the bond angles of the two C(sp) atoms are forced to diverge from their optimum 180°. You have seen that amides are generally much lower in energy than ketones because amides have a low-energy \( \overset{\cdot}{N} = C - \overset{-}{O} \) resonance structure open to them, but the amide shown below is higher in energy than your average ketone because the lone pair of N is contained in an sp\(^3\) orbital that is perpendicular to the p orbitals that make up the C=O single bond, so resonance is not possible, and the greater electronegativity of N compared to C raises the energy of this amide compared to the corresponding ketone.

3.7 Conjugation and hyperconjugation.
We’ve seen that an AO on one atom can overlap with an AO on another atom to make a MO. We’ve also seen that the concept of “overlap” is simply a mathematical process of addition and subtraction of equations that represent orbitals. An MO, therefore, is just another equation describing where in space you can find an electron of a particular energy. Given that the MO, just like an AO, is an equation, is it possible for an MO to overlap with an AO to make new orbitals in the same way that AOs overlap to make new orbitals? The answer is a resounding YES! Let’s look at some specific examples.

3.7.1 Ketone vs. aldehyde stabilization.
When we discussed the energy of carbonyl compounds, we mentioned that ketones were lower in energy than aldehydes. In both ketones and aldehydes, we can draw the \( \overset{\cdot}{C} - \overset{-}{O} \) resonance structure in which the C atom is electron-deficient. Any nearby orbitals that can overlap with the empty p orbital on the C atom will help ameliorate the electron-deficiency of the C atom. In aldehydes, there is always one neighboring C–H σ bond available that has the right symmetry and the right spatial positioning to overlap with the empty C(p) orbital, producing two new orbitals, one of which is lower in energy than either of the starting orbitals. The two electrons of the C–H σ bond find themselves in this lower energy orbital, lowering the energy of the compound overall.
And because the carbonyl C contributes to this lower energy orbital, the electrons in the orbital are residing part of the time near the carbonyl C atom.

In ketones, there are two C–H orbitals at any one time that can overlap in this way with the carbonyl C atom. The more overlap, the lower in energy the compound is. That’s why ketones are lower in energy than aldehydes.

The phenomenon in which C–H σ bonds stabilize an electron-deficient C atom by sharing electron density is one example of hyperconjugation. In general, hyperconjugation occurs whenever σ MOs overlap with AOs or other MOs.

3.7.2 Allylic resonance.

We’ve already seen that \( \overset{\bullet}{C} = C = C \) compounds have a resonance form \( C = C - \overset{\bullet}{C} \). In reality, both of the terminal C atoms are partially charged, and both are electron-deficient. Another way to think about this compound is to imagine that it consists of three AOs, each overlapping with a neighbor, that together contain two electrons. When we combine two AOs we always get two
MOs back, and when we combine three AOs we must likewise get three MOs back. The three MOs are called $\psi_0$, $\psi_1$, and $\psi_2$, respectively, because they have zero, 1, and two nodes (places where the negative and positive lobes meet). The $\psi_0$ orbital is lower in energy than any of the starting C(p) orbitals, the $\psi_1$ orbital is the same energy as the starting C(p) orbitals, and the $\psi_2$ orbital is higher in energy than any of the starting C(p) orbitals. The two electrons that we began with go into the $\psi_0$ orbital, leaving the nonbonding $\psi_1$ orbital as the LUMO of this compound. You can see that the LUMO is localized on both of the terminal C atoms, meaning both these C atoms are the ones that bear the lack of electron density induced by the absence of a third electron or an octet.

The interaction of the three orbitals all at once is called conjugation. In general, conjugation involves p or $\pi$ orbitals overlapping with one another.

3.7.3 1,3-Dienes.

Consider 1,3-butadiene, CH$_2$=CH–CH=CH$_2$. It contains two double bonds. The p orbital on C(1) overlaps with the p orbital on C(2) to make a $\pi$ orbital and a $\pi^*$ orbital, and the p orbital on C(3) overlaps with the p orbital on C(4) to make another $\pi$ orbital and another $\pi^*$ orbital.
The problem with this picture is that it is incomplete, because it is also true that the p orbital on C(2) overlaps with the p orbital on C(3). Indeed, it is more accurate to treat all four p orbitals at the same time. The four AOs can overlap to form four new MOs of different energy. We call these MOs $\psi_{0-3}$. The four electrons contributed by the four AOs go into the two lower energy orbitals, $\psi_0$ and $\psi_1$, which have zero nodes and one node, respectively, and are bonding orbitals, both lower in energy than the starting p orbitals. The remaining two orbitals, $\psi_2$ and $\psi_3$, are empty antibonding orbitals, having two and three nodes, respectively.
What are the consequences of conjugation?

1. The total energy of the diene electrons is *lower* than it would have been if there were no conjugation. As a result, a conjugated diene is lower in energy than an unconjugated diene.

2. The energy gap between the highest occupied MO (HOMO) of the diene and its lowest unoccupied MO (LUMO) is smaller than it would have been if there were no conjugation. As a result, the diene can absorb light of longer wavelength (lower energy) than a simple alkene. In fact, the more conjugation, the smaller the HOMO–LUMO gap, and the longer the wavelength of light that can be absorbed. Because simple alkenes absorb UV light, enough conjugation brings the wavelength of absorbed light into the visible region. For example, beta-carotene, which contains 11 conjugated double bonds, absorbs blue light, making it bright orange.

3.8 *Aromaticity.*

If we look at benzene, we can see that it has six p orbitals, all overlapping with the next. We can expect six MOs from these six AOs. What do they look like, and what are their energies? The lowest energy orbital, in which all the orbitals are in the same phase, has no nodes, and the highest energy orbital, in which all the orbitals are in alternating phases, has *three* nodes, not six, because the ring shape joins each pair of opposite nodes into single nodes. That means that two of the remaining four orbitals must have one node and two must have two nodes. The two $\psi_1$ orbitals have the same energy, as do the two $\psi_2$ orbitals. The orbital energy diagram we obtain is as follows:
Because of the cyclic nature of the orbitals, it happens that when you do the math, the energy of $\psi_0$ of benzene is much lower than the energy of $\psi_0$ of the acyclic analog, 1,3,5-hexatriene. As a result, benzene is a much lower energy compound than 1,3,5-hexatriene. Benzene’s particularly low energy is an example of what we now call **aromaticity**. (The word “aromatic” was originally used to describe benzene’s sickly sweet odor, but it eventually came to refer to all benzene-like compounds, and then to refer to their unusually low energy.)
Benzene is aromatic because it has a *continuously overlapping cyclic array of p orbitals*. The continuously overlapping cyclic array of p orbitals is an absolute requirement for a compound to be aromatic. However, the atoms in the ring do not have to be C atoms for a compound to be aromatic. That’s why pyridine and pyrimidine are aromatic. At first blush it seems that 2-pyridone is nonaromatic because it lacks a continuously overlapping cyclic array of six p orbitals, but if you draw its $\text{N}^{+}=\text{C}–\text{O}$ resonance form, you’ll see that it does indeed have one.

Pyrrole, furan, and thiophene are five-membered aromatic compounds. They also have a continuously overlapping cyclic array of p orbitals, although in their case there are *five* p orbitals, not six. Nevertheless, five p orbitals in a ring make five MOs, of which the one lowest in energy has no nodes and the four remaining have either one node or two nodes. The six electrons (four from the two C=C $\pi$ bonds, and two from the N lone pair) go into $\psi_0$ and the two $\psi_1$, all of which are bonding orbitals, and the overall energy of the electrons is lower than it would have been had the compound not been cyclic.

Note that the six orbitals of benzene form a hexagon shape standing on a vertex, and the five orbitals of furan/pyrrole/thiphene form a pentagon shape standing on a vertex. It turns out that no matter how many atoms are in the ring, if you have a continuously overlapping cyclic array of p orbitals, the energy levels of the orbitals is given by standing the polygon on its vertex and putting orbitals at each vertex. This trick is called the *Frost mnemonic*. 
So far we’ve considered only compounds with six electrons in the continuously overlapping cyclic array of p orbitals. What happens if we have more or fewer electrons? Let’s consider cyclobutadiene. According to the Frost mnemonic, it has one $\psi_0$, two $\psi_1$, and one $\psi_2$. Putting the four electrons from the four C atoms into the orbitals, we see that we end up with two half-filled $\psi_1$ orbitals. That can’t be good. In fact, it gets even worse. Those two half-filled orbitals are at the same energy level as a nonbonding C(p) orbital. It’s as if two of the C atoms weren’t even participating in a $\pi$ bond. As a result, cyclobutadiene is particularly high in energy compared to its acyclic congener (1,3-butadiene). In fact, cyclobutadiene is so high in energy that it’s been isolated only at very, very low temperatures in a frozen matrix. We call it antiaromatic.

\[
\begin{align*}
\text{ψ}_2 \\
\begin{array}{c}
\text{ψ}_1 \\
\text{ψ}_0
\end{array}
\end{align*}
\]

So are all compounds with fewer than six electrons in a continuously overlapping cyclic array of p orbitals antiaromatic? Consider the cyclopropenium ion, which has two electrons in a continuously overlapping cyclic array of three p orbitals. It’s aromatic.

\[
\begin{align*}
\text{ψ}_1 \\
\begin{array}{c}
\text{ψ}_0
\end{array}
\end{align*}
\]
So one pair of electrons in a continuously overlapping cyclic array of p orbitals is aromatic, two pairs is antiaromatic, and three pairs is aromatic. What about four pairs? As you might have guessed, these compounds tend to be antiaromatic. An important example of an antiaromatic compound is the coenzyme FADH (vitamin B$_2$). Its central ring contains eight electrons in a continuously overlapping array of six p orbitals. FADH bends into a butterfly shape to try to disrupt the overlap of the p orbitals, but it can’t completely avoid them. Because it is antiaromatic, FADH is particularly prone to undergo reactions that would cause the antiaromatic ring to become nonaromatic or aromatic. In particular, deprotonation of FADH and expulsion of H$^-$ gives FAD, which is an aromatic compound. As a result, FADH is a common source of H$_2$, or a reducing agent, in biological compounds.

The artificial compound 1,3,5,7-cyclooctatetraene avoids being antiaromatic by bending into a tub shape in which continuous overlap of p orbitals is disrupted. In fact, cyclooctatetraene behaves more like a compound with four isolated $\pi$ bonds than it does a conjugated tetraene.

_Hückel’s rule_ is as follows: A compound that has an _odd_ number of electron _pairs_ in a continuously overlapping cyclic array of p orbitals is _aromatic_. A compound that has an _even_ number of electron _pairs_ in a continuously overlapping cyclic array of p orbitals is _antiaromatic_. A compound that _lacks_ a continuously overlapping cyclic array of p orbitals or that has one that contains an _odd_ number of _electrons_ is _nonaromatic_.

Let’s go back to the heteroatom-containing aromatic compounds we discussed previously.
• The N atom of pyridine has a lone pair. How does one know whether the lone pair is part of the continuously overlapping array of p orbitals? It comes back to hybridization. The N atom is already making one \( \pi \) bond to a C atom, so it needs at least one p orbital in its set of AOs. If it puts the lone pair in a p orbital as well, then it will need to be sp-hybridized, which means 180° bond angles, which is not possible in this cyclic compound. As a result, the N atom can only be sp\(^2\)-hybridized, so its lone pair must be in a hybrid sp\(^2\) orbital, which places it in the plane of the aromatic ring, where it cannot overlap with any of the C(p) orbitals.

\[ \text{N} \quad \text{H} \]

• In pyrrole, the N atom only makes single bonds to its two neighboring C atoms. If the lone pair is placed in a p orbital, the N atom will be sp\(^2\)-hybridized, giving it bond angles (120°) that do not put undue strain on the ring. Because placing the lone pair in a p orbital produces a compound that has a continuously overlapping array of p orbitals containing an odd number of electron pairs, it is an energetically favorable arrangement, and the N assumes sp\(^2\) hybridization.

• In furan, the O atom has two lone pairs. If both of these lone pairs were put in p orbitals, the O atom would have sp hybridization, which would force 180° bond angles on the atom. As a result, the O atom assumes sp\(^2\) hybridization, which puts one of the lone pairs in a p orbital, where it can contribute to the continuously overlapping array of p orbitals containing an odd number of electron pairs, and the other lone pair in a hybrid sp\(^2\) orbital, which is situated in the plane of the ring where it cannot interact with any of the C(p) orbitals.

How much energy does aromaticity provide? It depends on the compound, but the short answer is, a lot. 1,3-Cyclopentadiene is a nonaromatic compound. When it is deprotonated, the product is an aromatic compound. 1,3-Cyclopentadiene is about 20 orders of magnitude more acidic than the acyclic analog 1,4-pentadiene, whose conjugate base is nonaromatic. That’s a lot of energy. The aromatic energy of benzene is worth about 30 kcal/mol, depending on whom you ask. A typical C–C bond has an energy of about 85 kcal/mol.