Organic chemistry is the study of carbon and its compounds. Because of carbon’s unique position in the periodic table (second period, group IV), it is able to form a very large number of stable compounds due to its size and ability to form single, double, and triple bonds with other elements. Organic molecules and functionalized organic molecules span an enormous range of types and functionalities. These include familiar compounds such as simple hydrocarbons that underly the oil-based economy, conjugated systems, which are currently being studied extensively for their potential use in molecular electronics and organic semiconductors, fullerenes, for their ability to confine molecules and molecular wires, and a whole host of other fascinating yet relatively simple systems.

In this chapter, we will apply the quantum mechanical concepts we have introduced for chemical bonding to study how chemical bonding in organic molecules and their derivatives works. Generally, this requires combining ideas from the valence bond theory and the LCAO theories, as we will demonstrate below.

**Alkanes**

The simplest class of molecules is the simple straight-chain alkanes, which are the most prevalent in petroleum. The general formula for a linear alkane chain \( C_nH_{2n+2} \). That is, linear alkanes contain \( n \) carbons and \( 2n+2 \) hydrogens and nothing else. Some examples are methane \( CH_4 \), ethane \( C_2H_6 \), propane \( C_3H_8 \), butane \( C_4H_{10} \), etc. In a general alkane chain, each carbon is bonded to two other carbons and two hydrogens, except for the carbons at the ends of the chain, which are bonded to one other carbon and three hydrogens. Thus, butane is \( CH_3CH_2CH_2CH_3 \), for example.

In order to understand the bonding orbitals, we can apply the valence bond theory directly. Because each carbon is bonded to four other atoms, each carbon is \( sp^3 \) hybridized. In the CH bonds, an \( sp^3 \) hybrid orbital from carbon combines with the orbital of H to form \( \sigma \) bonds. Recognizing that a hybrid orbital is just another type of atomic orbital and that each bond contains two electrons, the form of the two-particle valence-bond wave function is:

\[
\Psi(\mathbf{x}_1,\mathbf{x}_2) = C\left[\psi_{1s}^{\text{H}}(\mathbf{r}_1)\psi_{sp^3}^{\text{C}}(\mathbf{r}_2) + \psi_{1s}^{\text{H}}(\mathbf{r}_2)\psi_{sp^3}^{\text{C}}(\mathbf{r}_1)\right]\left[\psi_\uparrow(s_1)\psi_\downarrow(s_2) - \psi_\uparrow(s_2)\psi_\downarrow(s_1)\right]
\]

for a hydrogen H bonding to a carbon C. Here, \( \psi_{sp^3} \) is one of the \( \psi_{sp^3} \) hybrids of the carbon, and for a hydrogen H bonding to a carbon C. Here, \( \psi_{1s} \) is one of the \( \psi_{1s} \) orbitals of \( \text{H} \). For the CC bond, two \( sp^3 \) hybrids on the two different carbons combine to form another \( \sigma \) bond whose wave function is:

\[
\Psi(\mathbf{x}_1,\mathbf{x}_2) = C\left[\psi_{sp^3}(\mathbf{r}_1)\psi_{sp^3}(\mathbf{r}_2) + \psi_{sp^3}(\mathbf{r}_2)\psi_{sp^3}(\mathbf{r}_1)\right]\left[\psi_\uparrow(s_1)\psi_\downarrow(s_2) - \psi_\uparrow(s_2)\psi_\downarrow(s_1)\right]
\]

Here, we have to remember to choose among the \( sp^3 \) orbitals for each atom that will overlap substantially with the \( sp^3 \) orbitals of the bonding partners as the figure below illustrates for methane and ethane:
Figure: Overlapping $1s$ and $(sp^3)$ orbitals in methane or two $(sp^3)$ orbitals in ethane.

We could also combine the sp

$^3$

$(sp^3)$ orbitals using LCAO theory to form $(\sigma)$ and $(\sigma^*)$ molecular orbitals. The appropriate combinations would be

$$\sigma_{sp^3} = \frac{1}{\sqrt{2(1-S)}} [\psi_{sp^3}^{C_1}(r) - \psi_{sp^3}^{C_2}(r)]$$

$$\sigma_{sp^3} = \frac{1}{\sqrt{2(1+S)}} [\psi_{sp^3}^{C_1}(r) + \psi_{sp^3}^{C_2}(r)]$$
The $\sigma_{sp^3}$ contains the bonding electron pair between the two carbons.

Because all of the $\sigma$ bonds are single bonds, alkanes are quite flexible. In ethane, for example, the two $\sigma$ groups (called methyl groups) can rotate about the $\sigma$ bond axis. This type of rotation is known as **torsion** (see figure below):

**Figure:** Rotation of the methyl group about the C-C bond axis.

Torsional motion depends on the so-called dihedral angle, which is the angle between the planes formed by four atoms. That is, we use the angle between the plane defined by the atoms 1, 2, and 3 and the plane defined by the atoms 2, 3, and 4, as the figure below illustrates:
Interestingly, if the bond axis between atoms 2 and 3 coincides with the $z$-axis, and the bond axis between atoms 1 and 2 coincides with the $x$-axis, then the spherical coordinates for the bond between atoms 3 and 4 can be used to define the dihedral angle; it will simply be the azimuthal angle. As a result of this flexibility, a long alkane chain can assume a compact structure as the figure below illustrates for $\text{C}_{400}\text{H}_{802}$:

**Figure:** Example conformation of $\text{C}_{400}\text{H}_{802}$.

**Cyclic alkanes**

In a cyclic alkane, we remove one of the hydrogens in each of the terminating methyl groups of a linear alkane chain and
then use the dangling \( \text{sp}^3 \) orbitals that result to form an additional \( \sigma \) bond between the ends to form a cyclic molecule. The general formula is \( \text{C}_{2n}\text{H}_{2n} \). Examples of cyclopropane, cyclobutane and cyclohexane are shown in figure below:

**Figure:** cyclopropane, cyclobutane, cyclohexane.

Although the bonding is based on the \( \text{sp}^3 \) hybrid orbitals as in the linear alkanes, the fact that the angle between the different \( \text{sp}^3 \) hybrids is \( 109.5^\circ \) is somewhat at odds with the cyclic geometry of the cyclic alkanes. As a result, the ring possesses some amount of strain energy that needs to be minimized. This fact determines the stable conformations of cyclic alkanes, which are not generally planar like benzene. Consider, for example, cyclohexane. Two stable conformations of this molecule, known as the "chair" and "boat" conformations exist and are shown in the figure below (or as an animated gif in the html version of the lecture):

**Figure:** Chair and boat conformations of cyclohexane.

Such conformations exist because of the conformational flexibility of the molecule combined with the need to minimize strain energy. In the chair and boat conformations of cyclohexane, the chair is lower in energy. However, there is only a small barrier to convert from the chair to the boat, and at room temperature, the molecule undergoes an isomerization process, in which the chair and boat conformations interconvert (see animated gif in the html version of the lecture).

**Branched-chain alkanes**

Branched-chain alkanes are alkanes that contain only \( \text{C} \) and \( \text{H} \) (with only \( \text{C}-\text{C} \) single bonds) but are not linear. They contain branches with groups such as methyl, ethyl,... coming off the main branch of the molecule. Consider the branched molecule below:
which, for comparison, is shown together with butane (top panel). The molecule in the bottom panel is known as 2-methylpropane. It has the same number of carbons and hydrogens as butane but the bonding pattern is completely different. These two molecules are known as geometric isomers because they have the same number of carbons, hydrogens, and electrons but differ in the geometric arrangement and chemical bonding pattern between the atoms.

The name of the molecule is derived from the fact that the main chain of the molecule, i.e. the longest carbon chain, is that of propane. However, on the central carbon, one of the hydrogens is replaced by a methyl group. In general, the procedure for naming such compounds follows the IUPAC (International Union of Pure and Applied Chemistry) procedure, which is given below:

1. Find the longest continuous carbon chain in the molecule. The molecule is named for this chain and will be a derivative of whatever this longest chain is.
2. The hydrocarbon groups attached to the chain are called alkyl groups, such as methyl, ethyl, propyl, etc. The group name is determined by the number of carbons in the chain usually minus one hydrogen where it attaches to the main chain.
3. Number the carbons along the main chain identified in step 1 and identify the attached groups. The carbon number where the group is attached appears in the name of the molecule. By convention, the numbering should start so as to give the shortest possible length of the main chain before the first group is encountered.
4. If more than one alkyl group is attached to the main chain, use the prefixes di-, tri-, tetra- etc. for the number of times a given alkyl group appears.

5. If several groups appear, then list them in alphabetical order in the name of the molecule.

The figure below provides a series of examples, showing how the geometric isomers of octane are named. Noting just the first group for now, which are all alkanes, one can see how the rules are applied.

![Figure: Naming the geometric isomers of octane.](image)

With branched alkanes and other organic molecules comes the intriguing possibility of having two molecules that are mirror images of each other (see figure below):

When two isomers of a molecule are mirror images, one cannot be converted into the other without breaking chemical bonds. These are called optical isomers or chiral isomers. These are of great interest to the pharmaceutical industry as it often happens that one of the isomers will have therapeutic activity in blocking the catalytic mechanism of an enzyme while the other isomer will be inactive and can even be toxic.

**Alkenes and alkynes**

Hydrocarbons with only $\text{CC}$ single bonds are known as saturated hydrocarbons. If a hydrocarbon contains double and/or triple bonds, it is known as unsaturated. The molecule ethylene $(\text{C}_2\text{H}_4)$ contains a carbon double bond and is officially referred to as ethene, although the name “ethylene” is more commonly used. Similarly, the molecule acetylene $(\text{C}_2\text{H}_2)$ contains a carbon triple bond and has the official name ethyne. In general, alkenes contain double bonds and alkynes contain triple bonds. If the main carbon chain contains more than three carbons, it is necessary to specify where on the chain the double or triple bond occurs. Here, we follow the same IUPAC rules as specified above. The molecule $(\text{H}_2\text{C}=\text{C}-\text{CH}_2 -\text{CH}_3)$ is known as 1-butene while $(\text{CH}_3 - \text{CH} = \text{CH}-\text{CH}_3)$ is known as 2-butene.

In order to describe bonding in alkenes, we need a combination of the valence bond theory and LCAO. Let us consider ethylene (ethene). The two carbons are $\text{sp}^2$ hybridized, and there is one $\text{2p}_z$ orbital that is not hybridized. The book uses the convention that the unhybridized orbital is a $\text{p}_z$ orbital and combines it with another $\text{p}_z$ orbital to form a $\text{2p}_z$ orbital, which contradicts the definition of a $\text{p}_z$ orbital as having $m=1$ as the angular momentum quantum number (recall the exact treatment of $\text{H}_2^+$!). However, this is all just a matter of how the coordinate system is defined, so as along as one is consistent, is does not matter which $\text{p}$ orbitals are hybridized and which are combined to give $\text{p}_z$ orbitals. In this case, if the bond axis between the carbon atoms is the $x$-axis, then $\text{L}_x$ would be conserved, and the $\text{p}_z$ orbital would be an $m=1$ orbital! In any case, adopting the book's convention, the $\text{sp}^2$ orbitals all lie in the $xy$-plane and the $\text{p}_z$ orbital points out of the plane as shown in the figure below:
The $\text{CH}$ bonds form in the same way as they do in alkanes. An $\text{(sp}^2\text{)}$ hybrid orbital from a carbon combines with the $\text{(1s)}$ orbital of $\text{H}$, and the two-electron wave function is:

$$\Psi(x_1, x_2) = C [\psi_{1s}^H(r_1)\psi_{sp^2}^C(r_2) + \psi_{1s}^H(r_2)\psi_{sp^2}^C(r_1)]\psi_{\uparrow}(s_1)\psi_{\downarrow}(s_2) - \psi_{\uparrow}(s_2)\psi_{\downarrow}(s_1)$$

For the double bond, however, something rather interesting happens. Two of the $\text{(sp}^2\text{)}$ hybrids on the carbons combine to give a $\text{(\sigma)}$ molecular orbital via the LCAO procedure. However, this $\text{(\sigma)}$ bond only describes one of the electron pairs in the bond. The other electron pair ends up in a $\text{(\pi)}$ bond that forms by applying the LCAO procedure to the two unhybridized $\text{(p}_z\text{)}$ orbitals on the carbons. We will not write down the full four-electron wave function (it contains too many terms), however, it is worth noting that a double bond contains both $\text{(\sigma)}$ and $\text{(\pi)}$ character. This is something that is completely hidden when writing down the Lewis structures. The orbitals for ethylene can be visualized as below:
Figure: Bonding orbitals in ethene (ethylene).

In alkynes, the hybridization is simply \( \text{sp} \). Thus, in acetylene (ethyne), there are two unhybridized orbitals, which, by convention are \( \text{p}_x \) and \( \text{p}_y \) (see figure below):

Figure: Illustrating the sp orbitals.

The \( \text{CH} \) bonds in acetylene are formed by combining the \( \text{1s} \) orbital in \( \text{H} \) with one of the \( \text{sp} \) orbitals in carbon to form a \( \sigma \) bond. The other \( \text{sp} \) combines with an \( \text{sp} \) from the other carbon to form another \( \sigma \) bond that contains two of the 6 electrons in the triple bond. The remaining 4 electrons are placed in the MOs formed by mixing the \( \text{p}_x \) and \( \text{p}_y \) unhybridized orbitals. These orbitals combine via the LCAO procedure to form two \( \pi \) bonds, each of which contains a pair of electrons. Thus, a triple bond contains both \( \sigma \) and \( \pi \) character. The bonding in acetylene is pictured below:

Figure: Bonding in ethyne (acetylene).

Rotation around double and triple bonds is energetically unfavorable. Thus, ethylene prefers to be planar while acetylene prefers to be linear. Moreover, alkynes tend to be less stable than alkenes because of the larger number of \( \pi \) electrons. The energetic spacing between the degenerate pair of \( \pi \) orbitals and the corresponding \( \pi^* \) orbitals is smaller than the spacing between the nondegenerate \( \pi \) and \( \pi^* \) orbitals in alkenes.
If we consider a molecule like 2-butene, which is \( \text{CH}_3 - \text{CH} = \text{CH} - \text{CH}_3 \), the outer electrons are clearly \( \text{sp}^3 \) hybridized, while the inner carbons forming the double bond are \( \text{sp}^2 \) hybridized. Hence, while there can be rotation of the outer methyl groups, but not rotation about the C=C bond axis. This means that the four carbons tend to lie in a single plane. However, within this configuration two isomers are possible, which are the *cis* and *trans* conformers shown in the figure below (cis-top, trans-bottom):

**Figure:** Isomers of 2-butene.

![cis-2-butene](image)

*cis-2-butene*

![trans-2-butene](image)

*trans-2-butene*

Because rotation about the \( \text{C} = \text{C} \) double bond is energetically unfavorable, interconversion between these isomers at room temperature is very slow.

Compounds that contain more than one double bond are called *polyenes*. As with alkenes, if the backbone contains four or more carbons, we need to specify where on the chain the double bonds occur. Thus, the molecule \( \text{CH}_2 = \text{CH} - \text{CH} = \text{CH}_2 \) is known as 1,3-butadiene (see Figure below):
The di is used here because the molecule contains two double bonds. 1,3-butadiene is particularly interesting because all of the carbons are \(sp^2\) hybridized. Because of this, each of the four carbons has an unhybridized \(p_z\) orbital, and these four \(p_z\) orbitals can be combined to give four new MOs for carbons A, B, C, D:

\[
\begin{align*}
\psi_1 (r) &\propto \psi_{2p_z}^A(r)+\psi_{2p_z}^B(r)+\psi_{2p_z}^C(r)+\psi_{2p_z}^D(r) \\
\psi_2 (r) &\propto \psi_{2p_z}^A(r)+\psi_{2p_z}^B(r)-\psi_{2p_z}^C(r)-\psi_{2p_z}^D(r) \\
\psi_3 (r) &\propto \psi_{2p_z}^A(r)-\psi_{2p_z}^B(r)-\psi_{2p_z}^C(r)+\psi_{2p_z}^D(r) \\
\psi_4 (r) &\propto \psi_{2p_z}^A(r)-\psi_{2p_z}^B(r)+\psi_{2p_z}^C(r)-\psi_{2p_z}^D(r)
\end{align*}
\]

For \(\psi_1\), the four \(p_z\) orbitals have the positive lobes above the plane of the carbons and the negative lobes below the plane, so the resulting MO has a single nodal plane, which is the plane of the carbons. This is the lowest energy MO. For \(\psi_2\), the leftmost pair of \(p_z\) orbitals have their positive lobes above the plane and negative lobes below the plane, but the rightmost pair of \(p_z\) orbitals is oriented in the opposite sense, with the positive lobes below and plane and the negative lobes above the plane. This MO will have an additional nodal plane cutting the \(\text{C-C}\) single bond in the middle of the molecule. For \(\psi_3\), the central pair of \(p_z\) orbitals is oriented so that both positive lobes are below the plane, while for the outer \(p_z\) orbitals, the positive lobes are above the plane. This MO will, therefore, have two additional nodal planes cutting through the two double bonds. Finally, for \(\psi_4\), the highest energy orbital, the \(p_z\) orbitals alternate in their orientation with respect to the carbon plane. The resulting MO has three additional nodal planes cutting through each of the carbon-carbon bonds. The MOs are shown in the figure below:
Thus, 1,3-butadiene has two short CC bonds and one long bond between the two short bonds. When short and long bonds alternate in this way, the molecule is known as a *conjugated \( \pi \) system*. Note that the lowest energy MO is an extended orbital that is delocalized over the entire molecule. This is typical of conjugated \( \pi \) systems and indicates that the electrons in such an orbital are really delocalized over the entire molecule. This type of electron delocalization makes such systems ideal in molecular electronics, as it is possible to pass an electrical current through the molecule, with electrons passing through the delocalized \( \pi \) system between two electrodes.
Aromatic hydrocarbons

The last class of hydrocarbons we will consider are known as aromatic compounds, so named originally because of the aromas they gave off. Aromatic compounds are generally cyclic conjugated systems. The simplest example of such a system is 1,3,5-cyclohexatriene also known as benzene, whose formula is \( \text{C}_6\text{H}_6 \). Although the classical picture of this molecule is of a resonance structure:

**Figure**: Resonance in benzene.

However, quantum mechanics gives us a more accurate picture of the electronic structure of benzene. Each of the 6 carbons is \( \text{sp}^2 \) hybridized. Hence, the remaining unhybridized \( 2p_z \) orbitals can be combined in much the same way as was done for 1,3-butadiene. Here, we expect 6 new MOs, which are shown in the figure below:

**Figure**: Molecular orbitals that result in combining the \( 2p_z \) orbitals in benzene.

Note that, for each orbital, the plane of the 6 carbons is a nodal plane!! Unlike with 1,3-butadiene, however, each of the carbon-carbon bonds in benzene has the same length. This means that the bonds are really neither single nor double bonds but something intermediate between single and double. This is the origin of the third panel in the benzene
resonance picture above. In fact, we can represent any organic molecule in this abstract fashion. We would eliminate the hydrogens and just show the bonding pattern between the carbons.

### Fullerenes

Fullerenes, which were discovered in 1985 by Kroto, Curl and Smalley (and for which the Nobel prize was awarded in 1996). The archetypal fullerene \( \text{C}_{60} \), also known as buckminsterfullerene, \( \text{C}_{60} \) is composed entirely of carbon (no hydrogens), and each of the 60 carbon atoms is \( sp^2 \) hybridized. The molecule is also nearly perfectly spherical as shown in the picture below:

The pattern of carbon bonding is exactly the same as the pattern on the surface of a soccer ball. There are 20 hexagonal carbon rings and 12 pentagonal carbon rings. In order to accommodate this structure, some of the bond angles are distorted from the ideal \( 120^\circ \) corresponding to \( sp^2 \) hybridization, with a value of \( 108^\circ \). Combining the 60 \( p_z \) orbitals gives MOs that are spread over the entire molecule.
Another type of fullerene is known as the carbon nanotube, which is obtained by taking a sheet of graphene (a single layer of carbon in the structure of graphite) and rolling it into a cylinder. Depending on how the sheet is rolled, carbon nanotubes can be either metallic or semiconducting. The picture below shows a graphene sheet and a typical carbon nanotube:

Some interesting uses of carbon nanotubes are as nanowires, which exploit their high conductivity, nanoropes, which exploit their high tensile strength, and confinement agents for molecular wires.

It has also been proposed that closed fullerenes, such as \( \text{C}_{60} \) or carbon nanotubes capped at both ends (also known as nanohorns) could be used to encapsulate drug molecules. The fullerene could then be coated with protein so as to make it soluble and specific to a particular biological environment. In this way, such fullerenes could serve as drug-delivery agents. This proposal has yet to be realized in practice.
The Diels-Alder reaction and frontier molecular orbitals

One of the most powerful and important reactions in organic chemistry is a ring-closing reaction, an example of which is the reaction between 1,3-butadiene and ethylene, shown in the figure below:

![Figure: The Diels-Alder reaction.](image)

This reaction, first discovered by O. Diels and K. Alder in 1928, is now known as the Diels-Alder reaction, and the ethylene is referred to as a dieneophile. The previous figure of the $\pi$ molecular orbitals for 1,3-butadiene show the HOMO and LUMO orbitals. The frontier molecular orbital approach requires that an electron pair in the HOMO of one of the molecules occupies the LUMO of the other. The tricky part here is deciding which molecule supplies the HOMO and which the LUMO. The general rule is the more $\pi$ electrons there are, the higher in energy is the HOMO. Thus, in the Diels-Alder reaction, it is the diene that supplies the HOMO to donate an electron pair to the LUMO of ethylene. Since ethylene has two electrons in a $\pi$ orbital, when an electron pair enters the LUMO, which is a $\pi^*$ orbital, the bond order in ethylene is reduced to a single $\sigma$ bond, and hence the double bond becomes a single bond. The terminal $2p$ orbitals now become involved in a rehybridization of the $sp^2$ orbitals to $sp^3$ orbitals. The $\pi$ orbital structure for both molecules is shown in the figure below:

![Figure: $\pi$ orbitals in 1,3-butadiene and ethylene.](image)
The interaction between these orbitals is shown in the figure below. The figure illustrates that they must be combined so as to lead to constructive interference between the lobes:

**Figure:** Interaction between the HOMO of 1,3-butadiene and LUMO of ethylene.

The mechanism of the reaction is generally considered to be *concerted*, meaning that the two new CC bonds form "in concert" rather than sequentially. The requirement of arranging the orbitals such that they add constructively or "in phase" in concerted reactions is part of a system of rules known as the Woodward-Hoffmann rules. These are useful guidelines for many organic reactions, however, there are cases in which they fail as in, for example, Diels-Alder type reactions of dienes on a silicon surface for the formation of molecular devices. See, for example, *J. Am. Chem. Soc.* **126**, 13920 (2004) for a study of 1,3-butadiene on the \(\text{Si(100)-2*1}\) surface shown below:

**Figure:** Idealized \(\text{Si(100)-2*1}\) surface.

In this figure, the Si-Si dimers on this surface play a role similar to that of ethylene in the traditional Diels-Alder reaction, however, the addition of 1,3-butadiene to this surface violates the Woodward-Hoffmann rules.

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