Hybridization

Reading: Gray: (4-7)
OGN: (16.2)
The Story so far:

MO-LCAO works great for diatomic molecules! We can use hybridization of the central atom and MO-LCAO together to describe small polyatomic molecules.

But...

What about larger molecules? Does hybridization / MO-LCAO enable us to describe more complicated molecules?
Watson and Crick’s Original DNA Model
We’ll take the challenge:

C₂H₆

From VSEPR and Lewis dot structures, we know it looks like this:
Let’s analyze one C at a time.

Look at the left C.

Notice it has a steric number of four:

What other molecule had a steric number of four? CH₄

This suggests we should hybridize our current C the same way.
C\textsubscript{2}H\textsubscript{6}

\textit{sp}^3 hybridize the carbon:

Add 3 hydrogens (using MO-LCAO)

Notice the tetrahedral shape.
Do the same to the other side:

Bring the two halves together:

Success!
Notice that all the bonds formed are $\sigma$ bonds. Each is rotationally symmetrical about its axis.
Let’s try another:

\[ \text{C}_2\text{H}_4 \]

From VSEPR and Lewis dot structures, we know it looks like this:

\[ \begin{align*}
\text{H} & \quad \text{C} = \text{C} \\
\text{H} & \quad \text{H}
\end{align*} \]
Look at the left C.

Notice it has a steric number of three:

What other molecule had a steric number of three? BH$_3$

This suggests we should hybridize our current C the same way.
sp² hybridize the carbon:

Notice there is an extra p orbital that is not involved in hybridization:
For now, we will de-emphasize the p orbital.

Add hydrogen:

Do the same for the other C:
Now bond the two C together:

Notice that the two sp\(^2\) orbitals form a \(\sigma\) orbital that is rotationally symmetric.
Count the bonding e\textsuperscript{-} around each carbon:

\[ \text{left C} \]
\[ \text{right C} \]

left over: 1 left over: 1

left over: 1

But each C has 4 e\textsuperscript{-}! What do we do with the extras?
Let’s re-emphasize the p orbitals:

The p orbitals can combine, forming a $\pi$ bond:
Notice that \( \pi \) bonds are not rotationally symmetric.

The orbital changes sign every 180°
Notice that $\pi$ bonds do not allow rotation. When rotated around the axis, the bond is broken:
Notice that $\pi$ bonds do **not** allow rotation. When rotated around the axis, the bond is broken:
Notice that $\pi$ bonds do not allow rotation.
When rotated around the axis, the bond is broken:
Notice that π bonds do **not** allow rotation.

When rotated around the axis, the bond is broken:

**Orientation of orbitals**

[Diagram showing the orientation of orbitals and the π bond breaking when rotated around the axis.]
π bonds

Notice that π bonds do **not** allow rotation.
When rotated around the axis, the bond is broken:

Orientation of orbitals

Bond
Notice that π bonds do not allow rotation. When rotated around the axis, the bond is broken:

Orientation of orbitals

No Bond
Notice that π bonds do not allow rotation. When rotated around the axis, the bond is broken:

Orientation of orbitals

No Bond
Notice that π bonds do **not** allow rotation.

When rotated around the axis, the bond is broken:

Orientation of orbitals

---

No Bond
Notice that \( \pi \) bonds do not allow rotation.

When rotated around the axis, the bond is broken:

Orientation of orbitals

Bond
Because of the extra energy required to rotate the $\pi$ bond, the H’s are constrained to lie in a plane.
Let’s try another:

\[ \text{C}_2\text{H}_2 \]

From VSEPR and Lewis dot structures, we know it looks like this:

\[ \text{H} \equiv \text{C} \equiv \text{C} \equiv \text{H} \]
Let's analyze one C at a time.

Look at the left C.

Notice it has a steric number of two:

What other molecule had a steric number of two? \( \text{BeH}_2 \)

This suggests we should hybridize our current C the same way.
sp hybridize the carbon:

Notice there are two extra p orbitals that are not involved in hybridization.
For now, we will de-emphasize the p orbitals.

Add hydrogen: Do the same for the other C:
Bond the two C together:

Notice that the two sp orbitals form a $\sigma$ orbital that is rotationally symmetric.
Count the e\textsuperscript{-} around each carbon:

But each C has 4 e\textsuperscript{-}! What do we do with the extras?
Let’s re-emphasize the $p$ orbitals:

The $p$ orbitals combine, forming $\pi$ bonds:
Unlike a double bond (one $\pi$), a triple bond (two $\pi$) allows rotation.

Because the $\pi$ bonds occupy almost all the space around the carbons, the transition between a $p_y$-$p_y$ $\pi$ bond and a $p_y$-$p_x$ $\pi$ bond is fairly smooth.
Unlike a double bond (one $\pi$), a triple bond (two $\pi$) allows rotation.
Let’s try another: \( \text{C}_6\text{H}_6 \)

From VSEPR and Lewis dot structures, we know it looks like this:
Let’s analyze one C at a time.

Since they are all the same, pick any C.

Notice it has a steric number of three: BH$_3$

What other molecule had a steric number of three?

This suggests we should hybridize our current C the same way.
Just as in $\text{C}_2\text{H}_4$, there is an extra $\text{p}$ orbital that is not involved in hybridization:
For now, we will de-emphasize the p orbital.

Since all the C’s are in the same plane, we will switch to a top view:

Add hydrogen:
Bond the six C together:

\[ \text{C}_6\text{H}_6 \]
(C_{16}H_{33})_2O

CH_3(CH_2)_3O(CH_2)_3CH_3

43.0 Å

43.4 Å
Benzene in 1914
Faraday’s sample of benzene

Benzene $\text{C}_6\text{H}_6$
labelled bicarburet of hydrogen

Perchloroethane $\text{C}_2\text{Cl}_6$
labelled sub-chloride of carbon
Let’s re-emphasize the p orbitals:

The p orbitals act as a single, delocalized π bond.
The p orbitals act as a single, delocalized π bond. Thus, the nodes in the antibonding orbitals also act over the entire molecule.
Instead of 2 atomic orbitals combining to form 2 MO’s, we have **6 atomic orbitals** combining to form **6 MO’s**.
Napthalene Phenanthrene

Benzene

Benzo(a)pyrene (tar) Graphite (all sp$^2$)
Non-Resonance in Cyclooctatetraene

“COT”

Anti-Bonding

Non-Bonding

Bonding

COT goes non-planar!
but...COT$^{2-}$ and COT$^{2+}$ are planar!
Another Look at Ethylene

These are non-identical \textit{isomers}

Light can promote interconversion

Excited State is Free to Rotate
Bonding and Polymer Properties

Acetylene

Ethylene

A Conducting Polymer

An Insulating Polymer
Bonding and Polymer Properties

Acetylene

A Conducting Polymer
Bonding and Polymer Properties

\[ \pi^* \]

\[ \pi_b \]
Bonding and Polymer Properties

$\pi^*$

$\pi_n$

$\pi_b$
Band Structure of Conducting Polymers

\[ \pi^* \]
\[ \pi_n \]
\[ \pi_b \]

Antibonding MO’s

Bonding MO’s
Band Structure of Conducting Polymers

- Bonding MO's: \( \pi_b \) and \( \pi_n \)
- Antibonding MO's: \( \pi^* \)

- \( n \) p-orbitals
- \( n \) electrons
Energy Difference in Ethylene

\[ \pi^* \]

\[ E = \alpha - \beta \]

\[ 2\beta \]

\[ \pi_b \]

\[ E = \alpha + \beta \]
Bandwidth of Infinite Conjugated $\pi$ System

$E = \alpha - 2\beta$

$E = \alpha + 2\beta$

$n\ p$-orbitals
$n$ electrons

$\pi_b$

$n$ electrons

$\pi^*$

Antibonding MO’s

Bonding MO’s
2000 Nobel Prize

Alan MacDiarmid
“For the Discovery of Conducting Organic Polymers”, 1977

Alan Heeger
Aspects of Chemical Bonds

- Atomic Structure
- Explain Atomic Line Spectra, Galaxies, etc.
- Shapes of Orbitals in Atoms for Bonding
- Ionization Energies and Trends in Chemical Reactivity (e.g., Li\(^+\) vs Li)
- Which Molecules are Likely to Exist and Their Shapes and Reactivities (Ozone, Glo. Warm.)
- Magnetic and Bonding Properties of Molecules (Magnetic Tapes, Disks, etc.)
- Special Properties of Resonance Stabilization
- Directionality of Covalent Chemical Bonds
- Hydrogen Bonds
Nobel Prize in Physiology/Medicine, 1962

Francis Crick
Cambridge

Competed with Pauling and Corey for alpha-helix structure of peptides

James Watson
Harvard

1951-1953 Proposes double helix Of DNA
1954-1956 Caltech with A. Rich Structure of RNA

Maurice Wilkins
King’s College
London

Demonstrates X-ray Diffraction Of DNA
Purines

Adenine

Pyrimidines

Thymine

Cytosine

Guanine

O&N p. 872
Watson and Crick’s Original DNA Model
Peptide Bonds

The peptide bond

\[ \text{Gly–Gly–Gly} \]
Beta Sheets from Peptides

Average length is 6 residues
Most sheets contain <6 strands

Secondary structure
Antiparallel Beta Sheets

Thioredoxin

Antiparallel is intrinsically more stable due to optimal H-bond orientation
Overall macrodipole leaving an effective charge of
$\sim +1/15$ unit elemental charge at the N-terminus and $-1/15$
charge at the C-terminus of each strand of average length
Peptides form Alpha Helices

White dots indicate the hydrogen bond.

The hydrogen bond forms a cycle of 10 main chain atoms including the hydrogen itself. There are three residues per turn.