Chapter 1
Electronic Structure and Bonding

Ch. 1: Important topics/concepts

Covalent Bonds: **polar, or nonpolar** (electronegativity)
compare polarity of bonds, such as H-C vs H-N vs H-O vs H-F

Structures: **Lewis structures** (Kekule, condensed, skeletal)
properly placing lone pairs of e, **formal** charges

\[
\begin{align*}
\text{H}_2\text{O}\text{BF}_3 & = & \text{H} & \text{F} \\
\text{H} & \text{F} & \text{F} & \text{H} \\
\text{condensed} & & \text{skeletal} & \text{Lewis}
\end{align*}
\]

Bonds: **\(\sigma\) and \(\pi\) bonds** (single bonds, double bonds, triple bonds)
\(\sigma\) formed by orbital overlap, s+s, s+p, p+s, or hybridized
\(\pi\) formed by overlap between p orbitals
double bond = 1 \(\sigma\) bond + 1 \(\pi\) bond
triple bond = 1 \(\sigma\) bond + 2 \(\pi\) bonds
Ch. 1: Important topics/concepts

Hybrid orbitals: s and p orbitals mix to form new hybrid orbitals (comes from valence-shell electron-pair repulsion (VSEPR) theory explains geometry of CH₄ and many other molecules)

Geometry (shape of molecules):
CH₄: tetrahedral, four sp³ orbitals, bond angle 109°,
H₂C=CH₂, ethylene, three sp² orbitals, one p orbital, bond angle ~120°
HC≡CH, acetylene, two sp bonds, 2 p orbitals, bond angle 180°
Bond length and strength: shorter bonds are stronger.

The Distribution of Electrons in an Atom

Table 1.1 Distribution of Electrons in the First Four Shells

<table>
<thead>
<tr>
<th>Atomic orbitals</th>
<th>First shell</th>
<th>Second shell</th>
<th>Third shell</th>
<th>Fourth shell</th>
</tr>
</thead>
<tbody>
<tr>
<td>Number of atomic orbitals</td>
<td>1, 1, 3</td>
<td>8</td>
<td>18</td>
<td>32</td>
</tr>
<tr>
<td>Maximum number of electrons</td>
<td>2</td>
<td>s, p, d</td>
<td>s, p, d, f</td>
<td></td>
</tr>
</tbody>
</table>

- The first shell is closest to the nucleus.
- The closer the atomic orbital is to the nucleus, the lower its energy.
- Within a shell, s lower in energy than p.
Side-to-Side Overlap of In-Phase $p$ Orbitals Forms a $\pi$ Bond

Methane ($\text{CH}_4$)

- the 4 C-H bonds have the same length (~1.1 Å).
- all the bond angles are the same (109.5°)
Methane (CH₄)

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- all the bond angles are the same (109.5°)

1) **hybridization**

2) valence shell electron pair repulsion (VSEPR) theory:
   - σ bonds and lone pairs (**) as far apart as possible

In Order to Form Four Bonds, Carbon Must Promote an Electron

- An electron in the s orbital is promoted to the empty p orbital
- Carbon's valence electrons before promotion
- Carbon's valence electrons after promotion
In Order to Form Four Bonds, Carbon Must Promote an Electron

Four Orbitals are Mixed to Form Four Hybrid Orbitals

The Carbon in Methane is $sp^3$

Note, it is 1 s orbital mixing with 3 p orbitals (3:1 ratio)

$sp^3$ carbon is tetrahedral.
The tetrahedral bond angle is 109.5°.
The Bonding in Ethane

another type of $\sigma$ bond: by overlap of two $sp^3$ orbitals

End-on Overlap of Orbitals
Forms a $\sigma$ Bond
Ammonia (NH$_3$)

Nitrogen has 3 unpaired valence electrons and forms 3 bonds.
Nitrogen does not have to promote an electron.

The Bonds in Ammonia (NH$_3$)

If N used $p$ orbitals to form bonds, the bond angles would be 90°.

The observed bond angles are 107.3°, so nitrogen must used hybridized orbitals.
Ammonia

Representations of Ammonia

The Ammonium Ion (\(^+\text{NH}_4\))

Representations of the Ammonium Ion
Water (H₂O)

Oxygen has 2 unpaired valence electrons and forms 2 bonds. Oxygen does not have to promote an electron.

The Bonds in Water (H₂O)

The observed bond angles are 104.5°, so oxygen must use hybridized orbitals.
Water

The Bond in a Hydrogen Halide

A halogen has 1 unpaired valence electron and forms 1 bond.

A halogen uses hybrid orbitals.  
- The 3 lone pairs are energetically identical.  
- Lone pairs position themselves to minimize electron repulsion.
Overlap of an s Orbital with an sp³ Orbital

- H—F: overlap of the s orbital of hydrogen with a 2p orbital
- H—Cl: overlap of the s orbital of hydrogen with a 3p orbital
- H—Br: overlap of the s orbital of hydrogen with a 4p orbital
- H—I: overlap of the s orbital of hydrogen with a 5p³ orbital

- Decreasing electron density in the region of orbital overlap
- Decreasing bond strength
- Increasing bond length
The Length and Strength of a Hydrogen Halide Bond

Table 1.6 Hydrogen–Halogen Bond Lengths and Bond Strengths

<table>
<thead>
<tr>
<th>Hydrogen halide</th>
<th>Bond length (Å)</th>
<th>Bond strength (kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H—F</td>
<td>0.917</td>
<td>136</td>
</tr>
<tr>
<td>H—Cl</td>
<td>1.275</td>
<td>103</td>
</tr>
<tr>
<td>H—Br</td>
<td>1.415</td>
<td>87</td>
</tr>
<tr>
<td>H—I</td>
<td>1.609</td>
<td>71</td>
</tr>
</tbody>
</table>

Ethene (Ethylene): double bond

\[
\text{double bond} = \sigma \text{ bond} + \pi \text{ bond}
\]

Carbon bonds to 3 atoms, so it needs to hybridize 3 atomic orbitals.

\[1s + 2p = 3sp^2 \text{ orbitals}\]
An $sp^2$ Carbon Has Three $sp^2$ Orbitals and One $p$ Orbital

The Bonding in Ethene
Ethene

A double bond consists of one \( \sigma \) bond and one \( \pi \) bond.

\[
\text{Ethene} \quad \text{Perspective formula}
\]

\[
\text{Ethene} \quad \text{Ball-and-stick model}
\]

\[
\text{Ethene} \quad \text{Space-filling model}
\]

\[
\text{Ethene} \quad \text{Electrostatic potential map}
\]

Carbon bonds to 2 atoms, so it needs to hybridize 2 atomic orbitals.

\[
1s + 1p = 2 \text{ sp orbitals}
\]

Ethyne (Acetylene)

**triple bond** =  \( \sigma \) bond + 2\( \pi \) bond

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

Need 2 \( p \) orbitals!

Carbon bonds to 2 atoms, so it needs to hybridize 2 atomic orbitals.

\[
1s + 1p = 2 \text{ sp orbitals}
\]
The Two \textit{sp} Orbitals Point in Opposite Directions; 
The Two \textit{p} Orbitals are Perpendicular

The Bonding in Ethyne

\begin{itemize}
\item[a.] \textit{\sigma} bond formed by \textit{sp}-\textit{s} overlap
\item[b.] the purple \textit{p} orbitals are perpendicular to the blue \textit{p} orbitals
\end{itemize}
Ethylene

The Carbon in the Methyl Cation and in the Methyl Radical are $sp^2$
The Carbon in the Methyl Anion is $sp^3$

Quick generalizations:

1) lone pairs (••) and $\sigma$ bonds will be on hybridized orbitals
2) •• + $\sigma$ bonds = number of hybridized orbitals (made of 1 s and p orbitals)
3) everything else (a radical $e$, $\pi$ bond, positive charge) – non-hybridized
   (usually on a $p$ orbital)
Quick generalizations:

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what is the hybridization of each C and N atom in nicotine?:

[Chemical structure image]

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[Chemical structure image]
Hybridization and Molecular Geometry

The orbitals used in bond formation determine the bond angle for each atom in a molecule.

Do the sp² and the indicated sp³ carbons lie in the same plane?
Bond Strength and Bond Length

The more bonds holding 2 atoms together, the stronger and shorter it is.

The greater the electron density in the region of overlap, the stronger and shorter the bond.

Hybridization Affects Bond Length and Bond Strength

The more s character in the orbital, the stronger and shorter is the bond.
Hybridization Affects the Bond Angle

The more $s$ character, the greater the bond angle.

Bond angle increases as $s$ character in the orbital increases.

Hybridization, Bond Angle, Bond Length, Bond Strength

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<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethane</td>
<td>$sp^3$</td>
<td>109.5°</td>
<td>1.54</td>
<td>90.2</td>
<td>1.10</td>
<td>101.1</td>
</tr>
<tr>
<td>Ethene</td>
<td>$sp^2$</td>
<td>120°</td>
<td>1.33</td>
<td>174.5</td>
<td>1.08</td>
<td>110.7</td>
</tr>
<tr>
<td>Ethyne</td>
<td>$sp$</td>
<td>180°</td>
<td>1.20</td>
<td>230.4</td>
<td>1.06</td>
<td>133.3</td>
</tr>
</tbody>
</table>
Summary

• The shorter the bond, the stronger it is.
• The greater the electron density in the region of orbital overlap, the stronger the bond.
• The more s character, the shorter and stronger the bond.
• The more s character, the larger the bond angle.

A \pi Bond is Weaker Than a \sigma Bond

\[
\begin{align*}
\text{C} &= \text{C} \\
\text{strength of the double bond} &= 174 \text{ kcal/mol} \\
\text{strength of the } sp^2 - sp^2 \text{ } \sigma \text{ bond} &= -112 \text{ kcal/mol} \\
\text{strength of the } \pi \text{ bond} &= 62 \text{ kcal/mol}
\end{align*}
\]

a \pi bond is weaker than a \sigma bond
Dipole Moments of Molecules

- Carbon dioxide: \( \mu = 0 \text{ D} \)
  - The 2 bond dipole moments cancel because they are identical and point in opposite directions.

- Carbon tetrachloride: \( \mu = 0 \text{ D} \)
  - The bond dipole moments cancel because all 4 are identical and project symmetrically out from carbon.

Dipole Moments of Molecules

- Chloromethane: \( \mu = 1.87 \text{ D} \)
  - The 4 bond dipole moments point in the same general direction.

- Water: \( \mu = 1.85 \text{ D} \)

- Ammonia: \( \mu = 1.47 \text{ D} \)
Differences in electronegativity between atoms lead to polar bonds. The bigger the difference, the more polar the bond.