Chemistry 5.12, Lecture #3, 2/10/03

Outline

III. Review of Molecular Orbital Theory (Read Chapter 2)
   A. Atomic Orbitals (2-1)
   B. Sigma-Bonding (2-2A)
   C. Pi-Bonding (2-2B)
   D. VSEPR Theory (2-4)

IV. Hybridization/LCAO
   A. $sp$ Hybridization (2-4A)
   B. $sp^2$ Hybridization (2-4B)
   C. $sp^3$ Hybridization (2-4C)
      1. Rotation of Ethane versus Ethylene (2-3,7,8)

Problem Set #1 Due Today by 4pm
Problem Set #2 Posted: Due Tuesday (2/18/03)

Suggested Problems: 2-28,29,31,33

* Read 2-12,13: Survey of Organic Molecules

III. Molecular Orbital Theory

Electrons Are Waves!
They exist as 3-D Standing Waves (Orbitals).

atomic orbitals: unhybridized orbitals on an atom ($s$, $p$, $d$)

Linear Combination of Atomic Orbitals (LCAO): Individual wave
functions (orbitals) combine to form hybrid atomic orbitals ($sp$, $sp^2$, $sp^3$)
and molecular orbitals ($\sigma$, $\sigma^*$, $\pi$, $\pi^*$)

Hybrid Atomic Orbital: Combination of atomic orbitals from the same
atom

Molecular Orbital: Combination of atomic orbitals from different atoms

Conservation of Orbitals: When you add orbitals together, you always
end up with the same number of orbitals that you started with.
A. Atomic Orbitals

- The s- and p-orbitals are the most important in organic compounds.
- Orbital pictures are actually electron probability clouds.

- **s-orbitals**: spherical, electrons held close to nucleus, one sign
- **p-orbitals**: two lobes with opposite signs, electrons further from nucleus

- Remember, the sign of the orbital does not indicate charge. It represents the sign of the wavefunction and lets us think qualitatively about whether orbital interactions are constructive (bonding) or destructive (anti-bonding).

B. Sigma-Bonding ($\sigma$)

- Sigma-bonding orbitals are cylindrically symmetrical molecular orbitals.
- Electron density is centered along the axis of the bond.
- Single bonds are sigma-bonds.

**e.g. H$_2$ is the simplest sigma-bond**

- **bonding**: $(+/+ \text{ or } --)$ electron density centered between nuclei
- **anti-bonding**: $(+/-)$ generally has a node between nuclei
- **node**: area of zero electron density

- In stable bonding situations, usually only the bonding orbitals ($\sigma$, $\pi$) are occupied.
• Sigma bonds aren't necessarily between two s-orbitals.

\[ s + p \]

\[ p + p \]

• These are all examples of single bonds.

C. Pi-Bonding (\(\pi\))

• Pi-bonding orbitals are **not** cylindrically symmetrical.
• Electron density is located above and below the axis of the bond.
• Double and triple bonds are pi-bonds.

\[ \pi^* \]

\[ \pi \]

\[ p\gamma \]

\[ p\gamma \]

\[ \sigma \]

\[ \sigma^* \]

• Double bond = \(\sigma + \pi\)

\[ \text{e.g. Ethylene} \]

\[ \text{or} \]

\[ \text{to simplify drawing of orbitals} \]
Orbital Overlap

- Orbitals must have the correct symmetry to overlap.
- Orthogonal orbitals do not overlap.

**Good Overlap**

- S + S
- S + px
- px + px
- py + py
- pz + pz

**Orthogonal: No Overlap**

- S + py
- S + pz
- px + px
- py + py
- pz + pz

- If all bonding occurred between simple s- and p-orbitals, then all bond angles would be approximately 90°.

  We know that isn't true!

- Most bond angles in organic molecules are ~109°, ~120° and ~180°.

  ![Bond Angles Diagram](image)

  How do we account for this?

  **D. Valence Shell Electron Pair Repulsion (VSEPR)**

  - Electrons repel each other!
  - Lone pairs and bonds want to be as far apart as possible.
Simply...

<table>
<thead>
<tr>
<th></th>
<th>Di-substituted</th>
<th>Tri-substituted</th>
<th>Tetra-substituted</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>linear (180°)</td>
<td>trigonal planar (120°)</td>
<td>tetrahedral (109°)</td>
</tr>
<tr>
<td></td>
<td>Y—X—Y</td>
<td>Y—X—Y</td>
<td>Y—X—Y</td>
</tr>
<tr>
<td>e.g. acetylene</td>
<td>180°</td>
<td>121.7°</td>
<td>109.5°</td>
</tr>
<tr>
<td></td>
<td>H—C≡C—H</td>
<td>116.6°</td>
<td></td>
</tr>
</tbody>
</table>

But, how do we think about this in terms of orbitals?

- In 1930, Linus Pauling introduced a theory that combines VSEPR with quantum mechanics (orbitals).

**HYBRIDIZATION!**

Linus Pauling’s Journals: [http://osulibrary.orst.edu/specialcollections/mb/](http://osulibrary.orst.edu/specialcollections/mb/)

---

**IV. Hybridization (Linear Combination of Atomic Orbitals)**

- Atomic orbitals on the same atom combine to form **hybrid atomic orbitals**.

  **Why?**

  - Hybrid orbitals are more directional, so they have more effective bonding interactions.
  - Second row elements hybridize using their s- and p-orbitals (sp, sp², sp³).

  Remember conservation of orbitals!
A. *sp* Hybridization (Linear)

- *s* + *p* → *2 sp*

  - two *sp*-orbitals
  - 180°
  - enhanced e⁻ density in bonding regions

  But, we only used one *s*- and one *p*-orbital! There are two more *p*-orbitals.

Complete Orbital Picture of an *sp* Hybridized Atom

- 2 *sp*-orbitals
- 2 *p*-orbitals

How about a molecule?

e.g. Acetylene **H—C≡C—H**

- For simplicity, draw lines connecting *p*-orbitals to represent π-bonds.
B. \( sp^2 \) Hybridization (Trigonal Planar)

- Three \( sp^2 \)-orbitals
- Enhanced \( e^- \) density in bonding regions
- Complete Orbital Picture
  - 3 \( sp^2 \)-orbitals
  - 1 \( p \)-orbital

- For simplicity, can leave out small back lobes.

- For practice, draw the orbitals for ethylene (\( H_2C=CH_2 \)).

B. \( sp^3 \) Hybridization (Tetrahedral)

- Sigma-bonds and lone pairs involve hybrid orbitals.
- Pi-bonds involve unhybridized \( p \)-orbitals.

- E.g. Methane (\( CH_4 \))
- E.g. Ammonia (\( NH_3 \))
Assigning Hybridization to Atoms in a Molecule
(You need to be able to do this!)

Count the hybrid atomic orbitals.
# of hybrid orbitals = # of $\sigma$-bonds + # of lone pairs

<table>
<thead>
<tr>
<th># hybrid orbitals</th>
<th>hybridization</th>
<th>geometry</th>
<th>approx. bond angles</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>$sp^3$</td>
<td>tetrahedral</td>
<td>109°</td>
</tr>
<tr>
<td>3</td>
<td>$sp^2$</td>
<td>trigonal planar</td>
<td>120°</td>
</tr>
<tr>
<td>2</td>
<td>$sp$</td>
<td>linear</td>
<td>180°</td>
</tr>
</tbody>
</table>

e.g. What is the hybridization of each non-hydrogen atom in acetonitrile? Draw the bonding orbitals (leaving out the small back lobes).

H$_3$C–C≡N:

a: $sp^3$ (4 $\sigma$-bonds)
b: $sp^3$ (2 $\sigma$-bonds)
N: $sp$ (1 $\sigma$-bond, 1 lone pair)

1. Rotation of Ethane versus Ethylene

- Sigma-bonds are cylindrically symmetrical: rotation does not disrupt bonding.
- Sigma-bonds rotate freely.

- Pi-bonds require overlap of the $p$-orbitals: rotation disrupts overlap.
- Pi-bonds do not rotate.

- This rotation does not occur!