5.111 Lecture Summary #15

Readings for today: Sections 3.4, 3.5, 3.6 and 3.7 (Sections 3.4, 3.5, 3.6, 3.7, and 3.8 in 3rd ed) – Valence Bond Theory.


Assignment: Problem set #5 (due Friday, October 17th at noon)

Topics: Valence bond theory and hybridization

I. Sigma and pi bonds

II. Hybridization of atomic orbitals

A. sp³ hybridization

B. sp² hybridization

C. sp hybridization

VALENCE BOND THEORY AND HYBRIDIZATION

In valence bond theory, bonds result from the pairing of unpaired electrons in atomic orbitals.

I. SIGMA AND PI BONDS

σ (sigma) bond: cylindrically symmetric with ____ nodal plane across the bond axis.

π (pi) bond: a bond with e⁻ density in two lobes, one on each side of the bond axis.

A pi bond has a ______________ nodal plane along the bond axis.

We can describe multiple bonds according to valence-bond theory.

• single bond: ______________

• double bond: one σ-bond plus one ______________

• triple bond: one σ-bond plus _________ π-bonds
Applying simple VB theory results in the following prediction for methane bonding:

\[
\begin{align*}
\uparrow & \quad \uparrow \\
2p_z & \quad 2p_x & \quad 2p_y \\
\uparrow & \quad \downarrow \\
2s & \\
\end{align*}
\]

According to this model, the C is bonded to only two H-atoms with an H-C-H bond of _______°. This is NOT what is observed for methane!

II. HYBRIDIZATION OF ATOMIC ORBITALS

A. \(\text{sp}^3\) hybridization

A carbon atom has four unpaired electrons available for bonding once a 2s-electron is \(\text{promoted}\) to an empty 2-p orbital.

The \(\text{sp}^3\) hybrid orbitals are equivalent and degenerate. They differ only in their \(\text{symmetry}\) in space.

four \(\text{sp}^3\) hybrid orbitals
In carbon, each sp³ orbital contains a single electron, allowing four bonds.

What provides the energy for the initial electron promotion? ____________!

Each bond is labeled based on the bond type (σ or π) and atomic orbital composition. ____ (C______, H______)

Consider ethane, C₂H₆.

Two bond types in ethane: ____________________ and ____________________.

**Nitrogen:** Electron promotion ____________ occur with nitrogen because promotion would not increase the number of unpaired electrons available for bonding.

N-H bond description: ________________
N-atom geometry: ________________
**Oxygen:** Electron promotion does not occur.

- **E**
  - \( 2p_z \) \( 2p_x \) \( 2p_y \) \( 2s \)

- (6 valence e's)

- \( \text{hybrid orbitals} \)

- \( \text{H}_2\text{O geometry: } \)

**B. sp\(^3\) hybridization**

- sp\(^2\) hybrid orbitals form from the combination of one s-orbital and two p-orbitals.

- \( \text{Boron: } \text{Boron has 3 unpaired electrons available for bonding once a 2s-electron is promoted to an empty 2-p orbital.} \)

- \( \text{E} \)
  - \( 2p_z \) \( 2p_x \) \( 2p_y \) \( 2s \)

- electron promotion

\( \text{B} \)

- (3 valence e's)

- \( \text{hybrid orbitals} \)

- 3 hybrid orbitals

- 1 p-orbital

The s-orbital and two of the p-orbitals hybridize to form \_______________ sp\(^2\) orbitals.

The three sp\(^2\)-orbitals lie in a \_______________ to minimize electron repulsion.
**Carbon:** Carbon can also form sp$^2$ hybrid orbitals.

Ethylene (C$_2$H$_4$) has a C-C double bond, meaning one ______-bond and 1 ______-bond.

$$\sigma(\ldots, \text{H}1\text{s})$$
In addition to the C-C double bond, there are four C-H bonds: \( \sigma(\text{_______, _______}) \)

Note: molecules cannot rotate around a double bond. Rotation would require breaking the pi bond.

Benzene \((\text{C}_6\text{H}_6)\)

\[\sigma(\text{C}2\text{sp}^2, \text{C}2\text{sp}^2) \text{ bonds} \quad \pi(\text{C}2\text{p}_y, \text{C}2\text{p}_y) \text{ bonds} \quad \sigma(\text{C}2\text{sp}^2, \text{H}1\text{s}) \text{ bonds} \]

In reality, the 6 pi-electrons are ________________ over all six carbon atoms in the benzene molecule. Each C-C bond is a ________ bond.
C. sp hybridization

sp hybrid orbitals form from the combination of one s-orbital and 1 p-orbital.

Electron promotion

\[ \text{2s} \quad \text{2p}_z \quad \text{2p}_x \quad \text{2p}_y \]

\[ \text{hybrid orbitals} \]

(4 valence e's)

\[ \text{C} \]

\[ \text{2sp} \quad \text{2sp} \quad \text{2p}_x \quad \text{2p}_y \]

\[ \text{σ(______,______)} \quad \text{π(______,______)} \quad \text{π(______,______)} \]