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:

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. sp³ hybridization

A carbon atom has four unpaired electrons available for bonding once a 2s-electron is _______________ to an empty 2-p orbital.

The sp³ hybrid orbitals are equivalent and degenerate. They differ only in their _______________ in space.

four sp³ 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.

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.

\[
\begin{align*}
2s & \quad 2p_x \quad 2p_y \quad 2p_z \\
\uparrow & \quad \uparrow & \quad \uparrow & \quad \uparrow \\
\text{O} & \quad \text{(6 valence e's)} & \quad \text{hybrid orbitals} & \quad \text{sp}^3
\end{align*}
\]

H₂O geometry: ____________

**B. sp² hybridization**

sp² hybrid orbitals form from the combination of one s-orbital and two p-orbitals.

**Boron:** Boron has 3 unpaired electrons available for bonding once a 2s-electron is promoted to an empty 2-p orbital.

\[
\begin{align*}
2s & \quad 2p_x \quad 2p_y \quad 2p_z \\
\uparrow & \quad \uparrow & \quad \uparrow & \quad \uparrow \\
\text{B} & \quad \text{(3 valence e's)} & \quad \text{hybrid orbitals} & \quad \text{2sp}^2 \quad \text{2sp}^2 \quad \text{2sp}^2
\end{align*}
\]

The s-orbital and two of the p-orbitals hybridize to form ______________ sp² orbitals.

The three sp²-orbitals lie in a ______________ to minimize electron repulsion.
**Carbon:** Carbon can also form sp² hybrid orbitals.

Ethylene ($C_2H_4$) has a C-C double bond, meaning one _______-bond and 1 _______-bond.

Ethylene ($C_2H_4$) has a C-C double bond, meaning one _______-bond and 1 _______-bond.
In addition to the C-C double bond, there are four C-H bonds: $\sigma(\ldots, \ldots)$

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

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

$\ldots\sigma(\text{C}_2\text{sp}^2, \text{C}_2\text{sp}^2)\text{ bonds}\ldots$

$\ldots\pi(\text{C}_2\text{py}, \text{C}_2\text{py})\text{ bonds}\ldots$

$\ldots\sigma(\text{C}_2\text{sp}^2, \text{H}_1\text{s})\text{ bonds}\ldots$

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.

\[
\begin{align*}
&\text{E} \\
&\text{2s} \quad \text{2p}_x \quad \text{2p}_y \\
&\text{C} \\
&\text{(4 valence e's)} \\
&\text{electron promotion}
\end{align*}
\]

\[
\begin{align*}
&\sigma(_____,_____) \\
&\pi(_____,_____) \\
&\pi(_____,_____) 
\end{align*}
\]