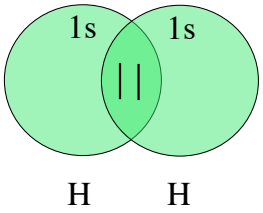
5.111 Lecture Summary #14 Wednesday, October 8, 2014

Readings for today: Sections 3.4, 3.5, 3.6 and 3.7 (Same sections in 4th and 5th ed) – Valence Bond Theory.
Read for Lecture #16: Sections 6.13, 6.15, 6.16, 6.17, 6.18, and 6.20 (Same sections in 4th and 5th ed) – The Enthalpy of Chemical Change.

Topics: I. Valence bond theory and hybridization
- **A.** Sigma and pi bonds
- **B.** Hybridization of atomic orbitals
  - **i.** sp^3 hybridization
  - **ii.** sp^2 hybridization
  - **iii.** sp hybridization

I. VALENCE BOND THEORY AND HYBRIDIZATION

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



A. 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.

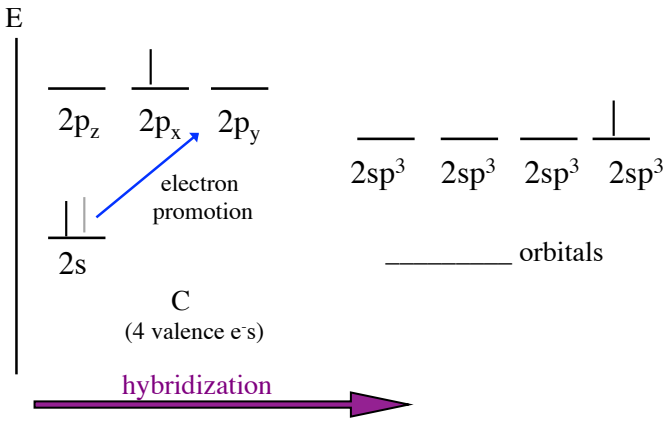
We can describe multiple bonds according to valence-bond theory.

- single bond: _____
- double bond: one **σ**-bond plus one _____
- triple bond: one **σ**-bond plus _____ π-bonds

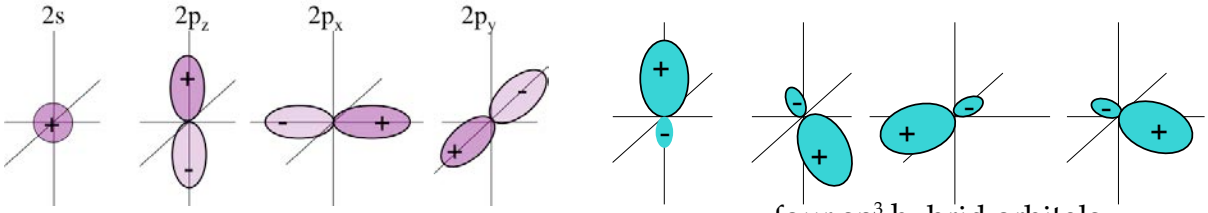
B. HYBRIDIZATION OF ATOMIC ORBITALS

i) sp^3 hybridization

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

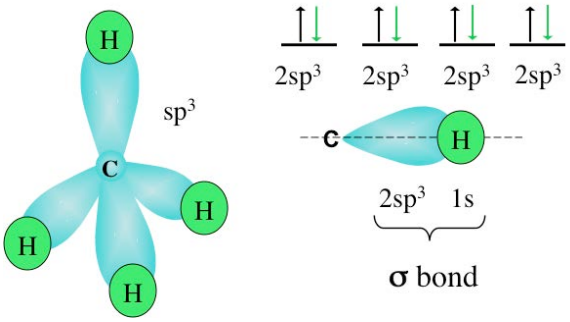


The sp^3 hybrid orbitals are equivalent and degenerate. They differ only in their _____ in space.



four sp^3 hybrid orbitals

For carbon, each sp^3 orbital contains a single electron, allowing four bonds.

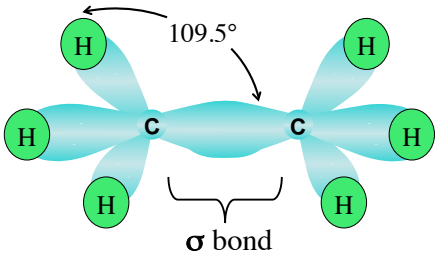


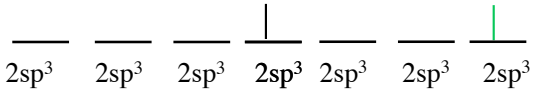
What provides the energy for the initial electron promotion?

_____!

Each bond is labeled based on the bond type (σ or π) and atomic orbital composition: _____(C _____ , H_____)

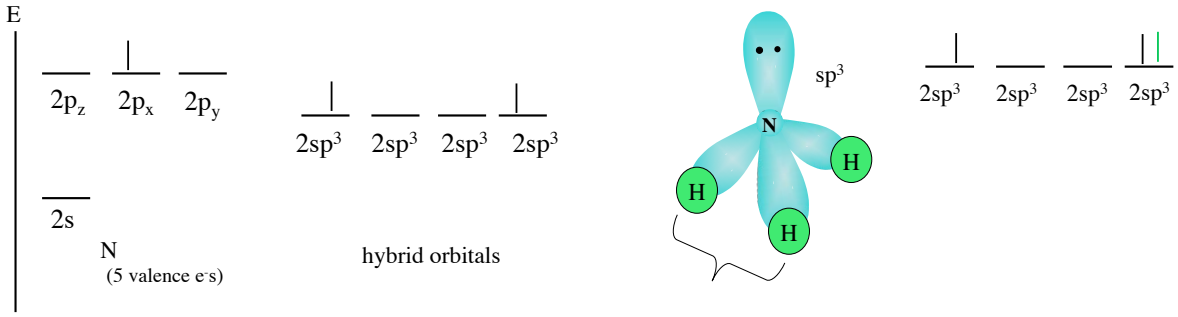
Consider ethane, C_2H_6.





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.

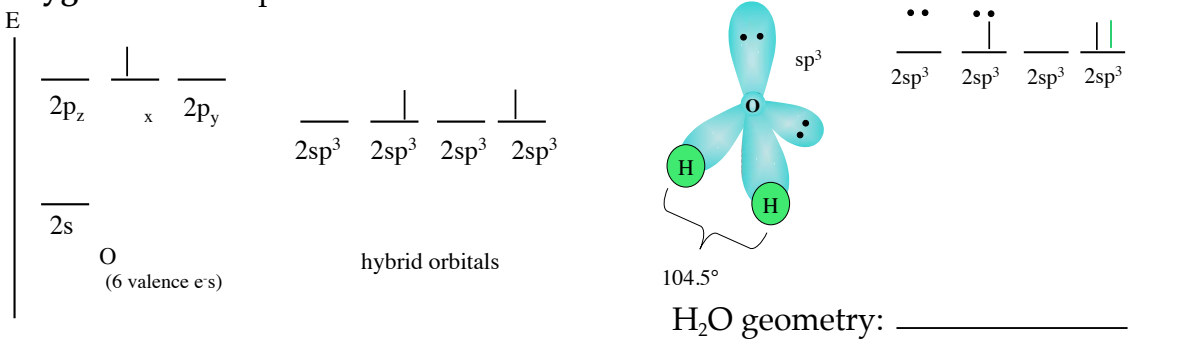


H-N-H bond angle _____

N-atom geometry: _____

N-H bond description: _____

Oxygen: Electron promotion does not occur.

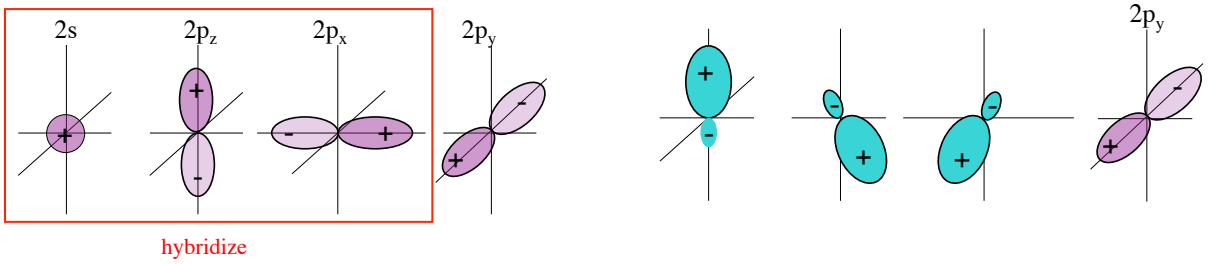


H_2O geometry: _____

O-H bond description: _____

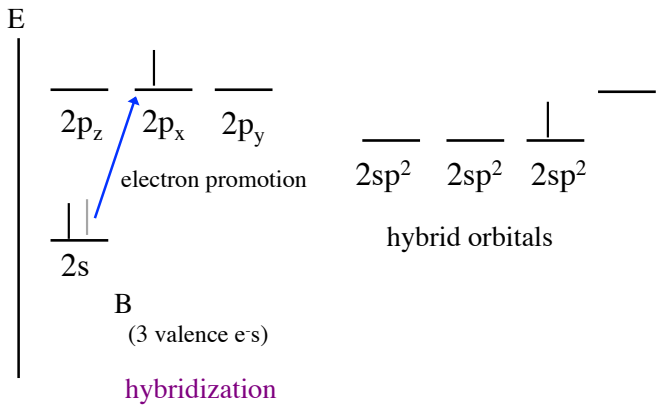
ii) sp^2 hybridization

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



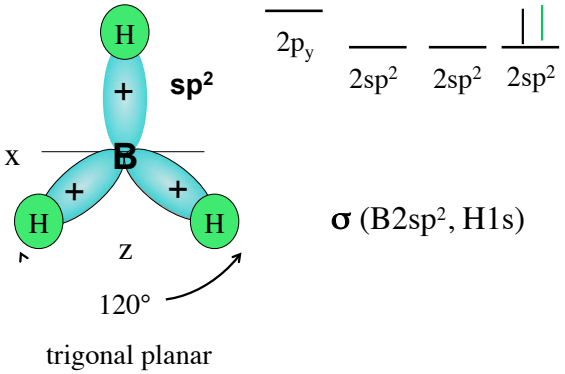
3 hybrid orbitals 1 p-orbital

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

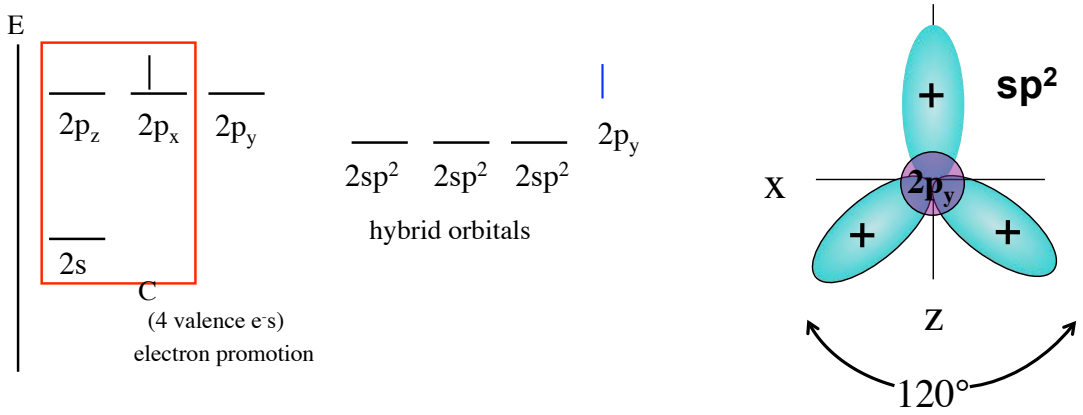


The s-orbital and two of the p-orbitals hybridize to form _____ sp^2 orbitals.

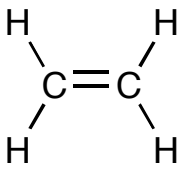
The three sp^2-orbitals lie in a _____ to minimize electron repulsion.

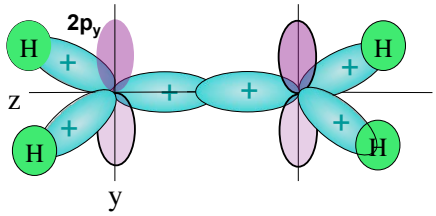


Carbon: Carbon can also form sp^2 hybrid orbitals, such as in the case of ethylene C_2H_4.

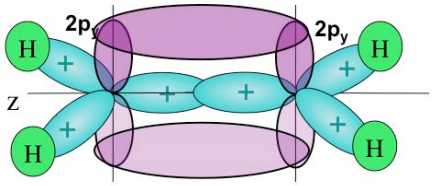


Ethylene (C_2H_4) has a C-C double bond, meaning 1 _____ -bond and 1 _____ -bond.





looking down the x-axis



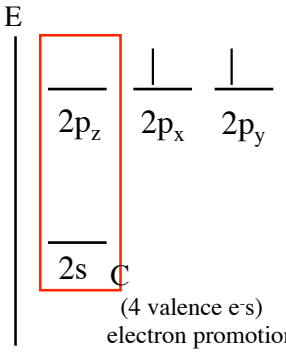
σ(_____ , _____) π(_____ , _____)

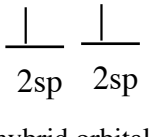
In addition to the C-C double bond, there are four C-H bonds: σ(_____, _____)

Molecules _____ rotate around a double bond. Rotation would require breaking the pi (π) bond.

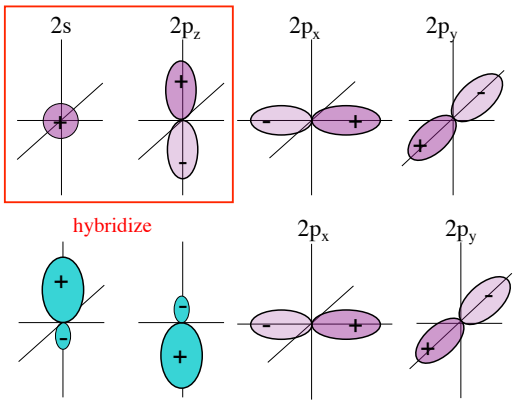
iii) sp hybridization

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

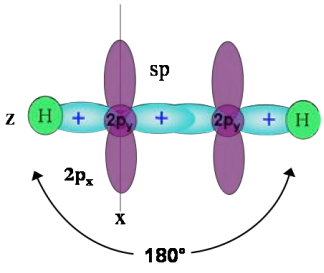


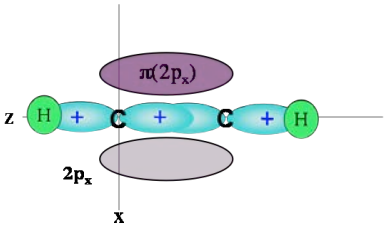


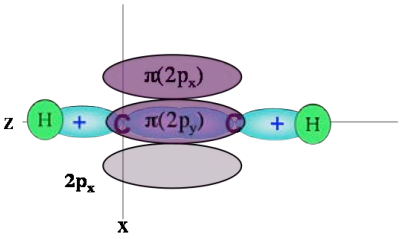
hybrid orbitals



Carbon can also form sp hybrid orbitals. Acetylene (C_2H_2) with C-C triple bond.







σ(_____ , _____) π(_____ , _____) π(_____ , _____)

Summary for hydrocarbon molecules that contain two-carbons:

Carbons in C_2H_6 are _____ hybridized, have a _____ C-C bond, and **tetrahedral** geometry

Carbons in C_2H_4 are **sp^2** hybridized, have a _____ C-C bond, and _____ geometry

Carbons in C_2H_2 are _____ hybridized, have a **triple** C-C bond, and _____ geometry

DETERMINING HYBIDIZATION IN COMPLEX MOLECULES

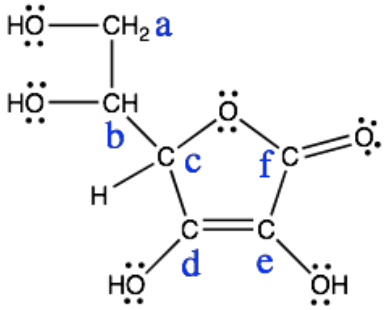
To determine the hybridization of a given atom in a molecule,

(# of bonded atoms) + (# of lone pairs) = # of hybrid orbitals

2 hybrid orbitals- _____, 3 hybrid orbitals - _____, 4 hybrid orbitals- sp^3

Exception: single-bonded, _____ atoms. For the purposes of this course, do NOT hybridize single-bonded, terminal atoms.

Try an example: ascorbic acid (vitamin C)



Identify the hybridization and geometry of each C atom:

C_a: C_d:

C_b: C_e:

C_c: C_f:

Identify the symmetry and name the hybrid or atomic orbitals that constitute the bonds below:

Bonds to carbon b:

C_b-H:

C_b- C_a: $\sigma(C2sp^3, C2sp^3)$

C_b-C_c: $\sigma(C2sp^3, C2sp^3)$

C_b-O:

Bonds to carbon d:

C_d-O:

C_d- C_c: $\sigma(C2sp^2, C2sp^3)$

C_d-C_e:

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Fall 2014