

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 (σ , σ^* , π , π^*)

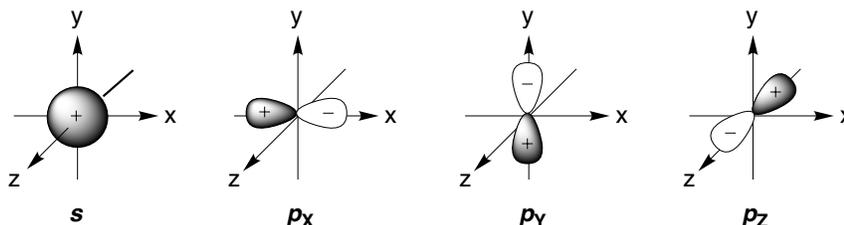
Hybrid Atomic Orbital: Combination of atomic orbitals from the **same** atom

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

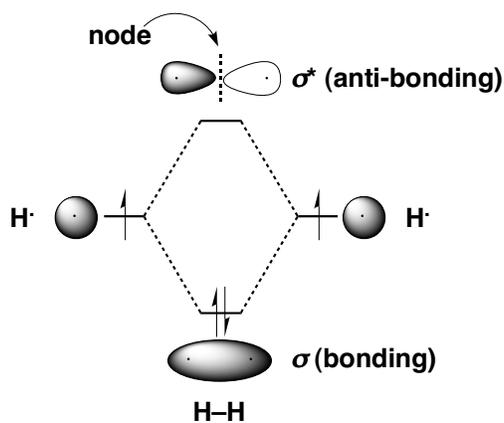
p-orbitals: two lobes with opposite signs, electrons further from nucleus

- **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 (σ)

- 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



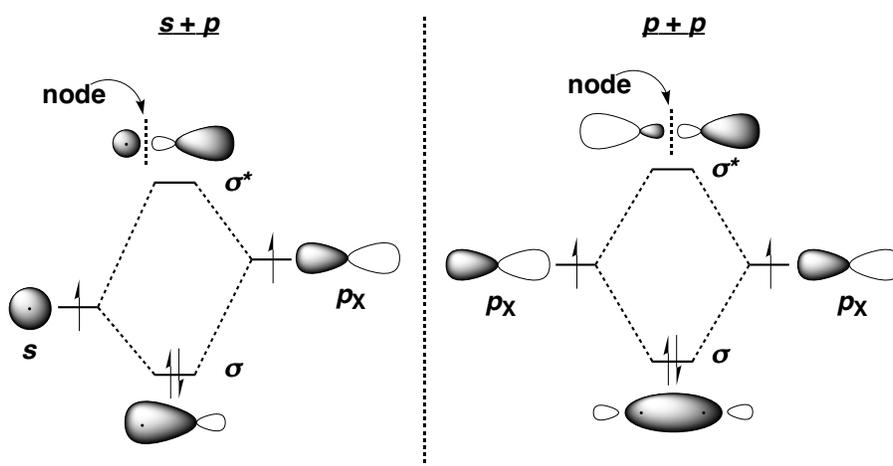
bonding: (+/+ or -/-) electron density centered between nuclei

anti-bonding: (+/-) generally has a node between nuclei

node: area of zero electron density

- In stable bonding situations, usually only the bonding orbitals (σ , π) are occupied.

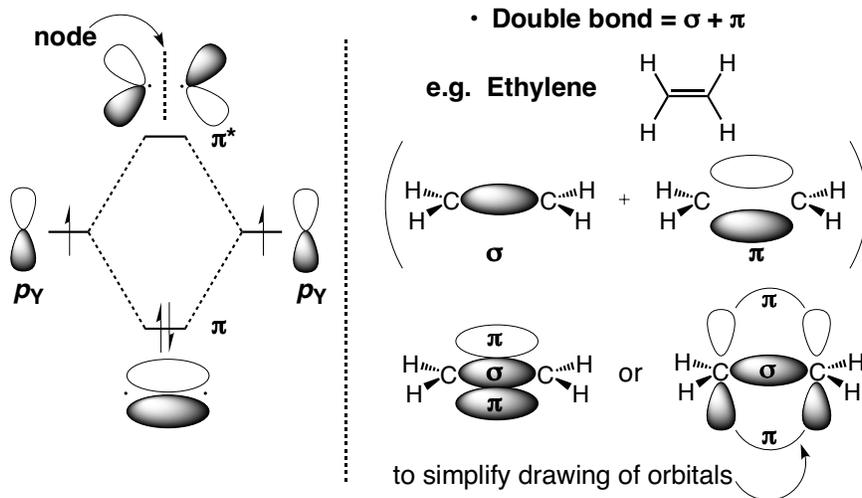
- Sigma bonds aren't necessarily between two s-orbitals.



- These are all examples of single bonds.

C. Pi-Bonding (π)

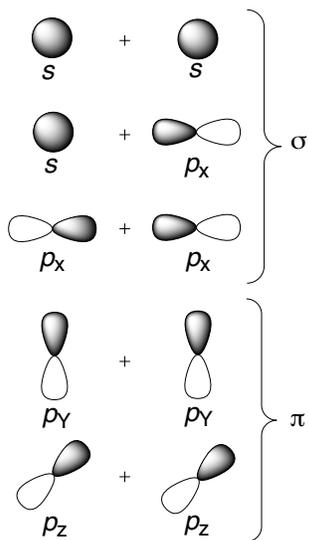
- Pi-bonding orbitals are **not** cylindrically symmetrical.
- Electron density is located above and below the axis of the bond.
- Double and triple bonds are pi-bonds.



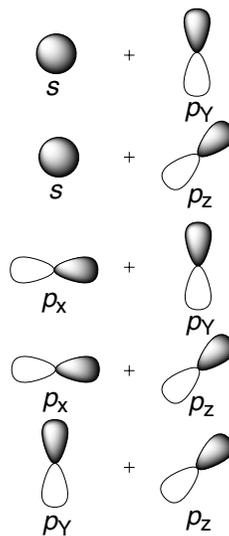
Orbital Overlap

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

Good Overlap



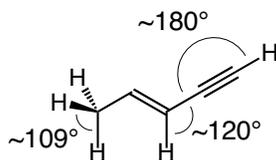
Orthogonal: No Overlap



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 $\sim 109^\circ$, $\sim 120^\circ$ and $\sim 180^\circ$.



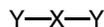
How do we account for this?

D. Valence Shell Electron Pair Repulsion (VSEPR)

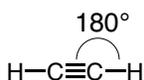
- Electrons repel each other!
- Lone pairs and bonds want to be as far apart as possible.

Simply...

Di-substituted
linear (180°)



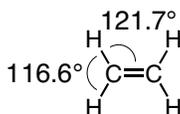
e.g. acetylene



Tri-substituted
trigonal planar (120°)



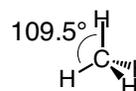
e.g. ethylene



Tetra-substituted
tetrahedral (109°)



e.g. methane



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/rnb/>

IV. Hybridization (Linear Combination of Atomic Orbitals)

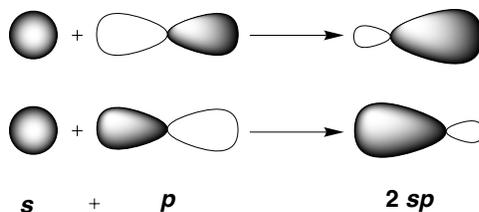
- Atomic orbitals on the **same** atom combine to form **hybrid atomic orbitals**.

Why?

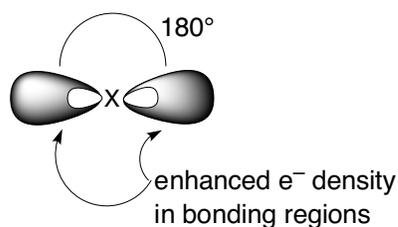
- Hybrid orbitals are more directional, so they have more effective bonding interactions.
- Second row elements hybridize using their *s*- and *p*-orbitals (*sp*, *sp*², *sp*³).

Remember conservation of orbitals!

A. *sp* Hybridization (Linear)

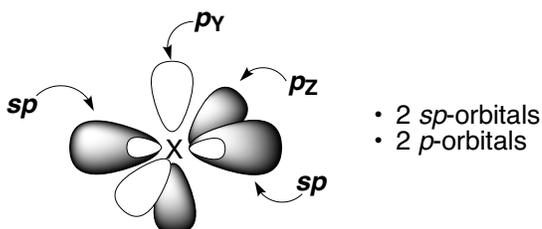


- two *sp*-orbitals



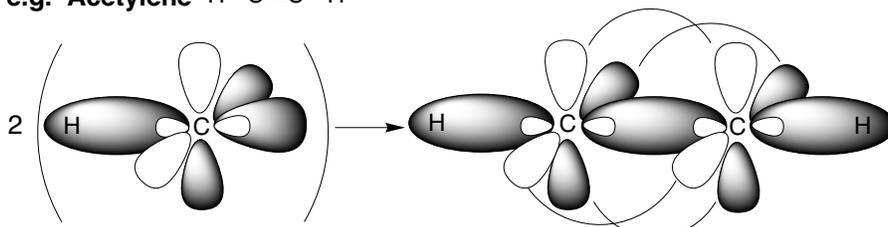
**But, we only used one *s*- and one *p*-orbital!
There are two more *p*-orbitals.**

Complete Orbital Picture of an *sp* Hybridized Atom



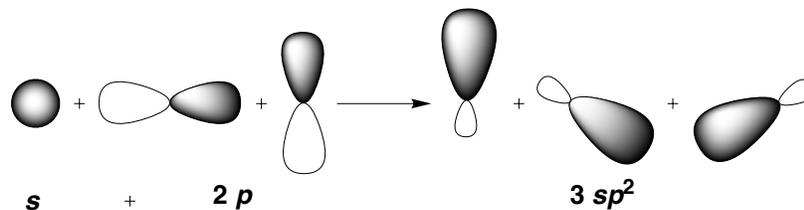
How about a molecule?

e.g. Acetylene H-C#C-H

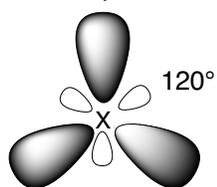


- For simplicity, draw lines connecting *p*-orbitals to represent π -bonds.

B. sp^2 Hybridization (Trigonal Planar)

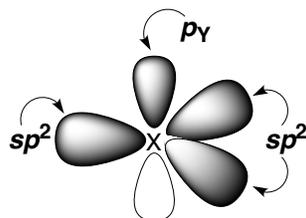


- three sp^2 -orbitals



- enhanced e^- density in bonding regions

Complete Orbital Picture

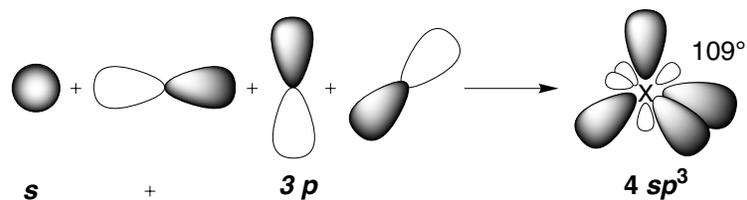


- 3 sp^2 -orbitals
- 1 p -orbital

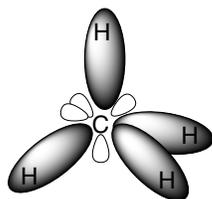
• For practice, draw the orbitals for ethylene ($H_2C=CH_2$).

- For simplicity, can leave out small back lobes.

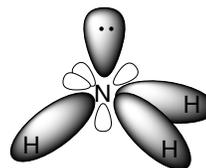
B. sp^3 Hybridization (Tetrahedral)



e.g. Methane (CH_4)



e.g. Ammonia (NH_3)



- Sigma-bonds and lone pairs involve **hybrid orbitals**.
- Pi-bonds involve **unhybridized p -orbitals**.

Assigning Hybridization to Atoms in a Molecule

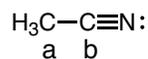
(You need to be able to do this!)

Count the hybrid atomic orbitals.

of hybrid orbitals = # of σ -bonds + # of lone pairs

# hybrid orbitals	hybridization	geometry	approx. bond angles
4	sp^3	tetrahedral	109°
3	sp^2	trigonal planar	120°
2	sp	linear	180°

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

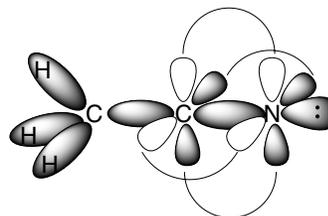


a b

C_a : sp^3 (4 σ -bonds)

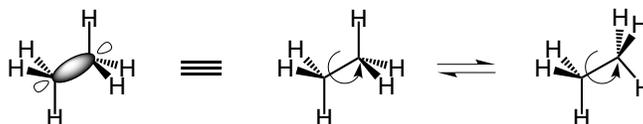
C_b : sp (2 σ -bonds)

N: sp (1 σ -bond, 1 lone pair)



1. Rotation of Ethane versus Ethylene

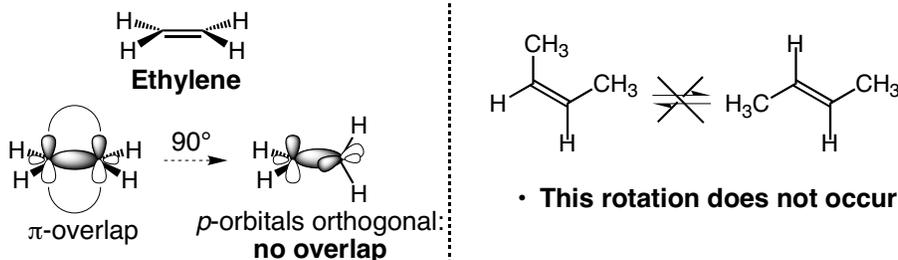
- Sigma-bonds are cylindrically symmetrical: rotation does not disrupt bonding.
- **Sigma-bonds rotate freely.**



Ethane

(much more on the energetics of this rotation later!)

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



- **This rotation does not occur!**