

CHEM 221 section 01

LECTURE #02

Thurs., Sept.8, 2005

ASSIGNED READINGS:

TODAY'S CLASS:

1.6	Introduction to molecular orbital theory
1.7-1.9	Bonding: single, double, triple bonds
1.10	Bonding in cations, anions, radicals
1.11-1.13	Bonding in simple compounds
1.14	Summary: Bond lengths, strengths & angles

NEXT CLASS: 1.16-1.19, 7.2-7.5

<http://artsandscience.concordia.ca/facstaff/P-R/rogers>

Typical ways to draw organic structures

- Kekulé structures: show all bonds but not lone pairs
- Condensed structures: formulas that show connectivity

Table 1.5 Kekulé and Condensed Structures

Kekulé structure

Condensed structures

Groups bonded to a carbon can be shown (in parentheses) to the right of the carbon, or hanging from the carbon.



Groups bonded to the far-right carbon are not put in parentheses.

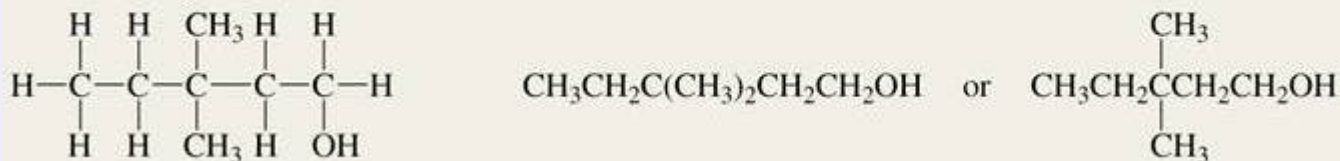
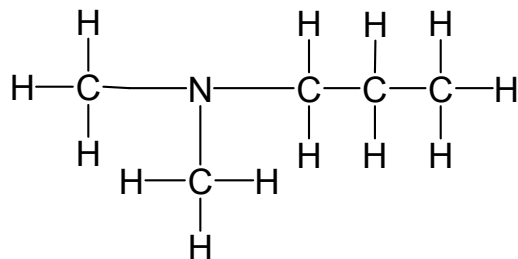


Table 1.5 Kekulé and Condensed Structures

Kekulé structure

Condensed structures

Two or more identical groups considered bonded to the first atom on the left can be shown (in parentheses) to the left of that atom, or hanging from the atom.



or

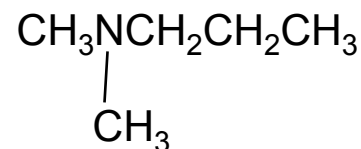
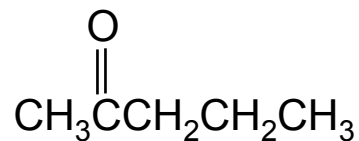
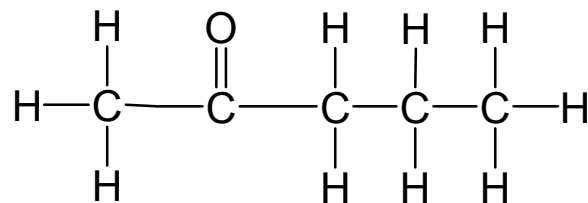


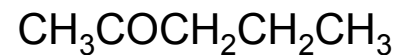
Table 1.5 Kekulé and Condensed Structures

Kekulé structure**Condensed structures**

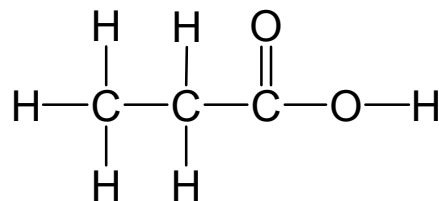
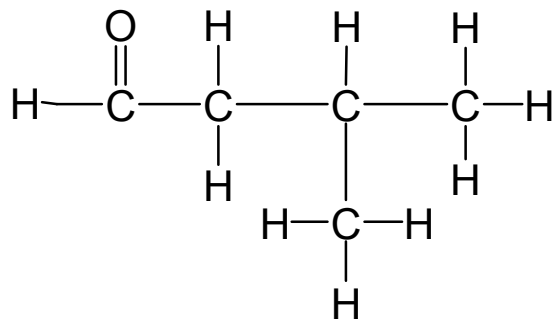
An oxygen doubly bonded to a carbon can be shown hanging off the carbon or to the right of the carbon.



or



or

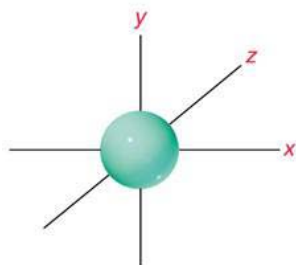


1.5 REVIEW: Atomic orbitals

The 1s & 2s Orbitals

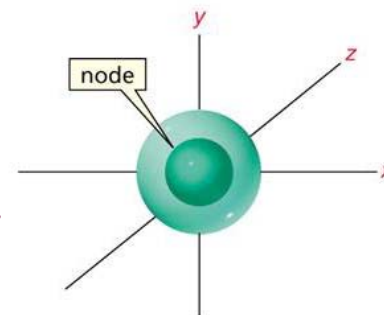
- Spherical

where
C's core
e⁻s reside



1s atomic orbital

Part of
C's valence

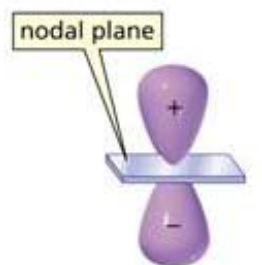


2s atomic orbital
node shown

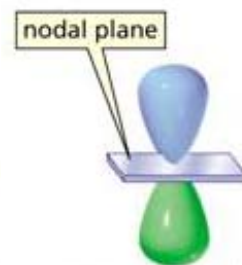
1.5 REVIEW: Atomic orbitals

The $2p$ Orbitals

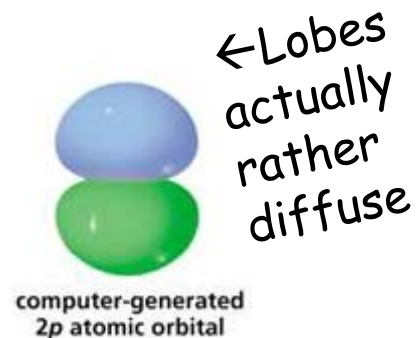
- Dumbbell-shaped
- Opposite mathematical sign on either side of node
(shown as +/- or colours)



$2p$ atomic orbital

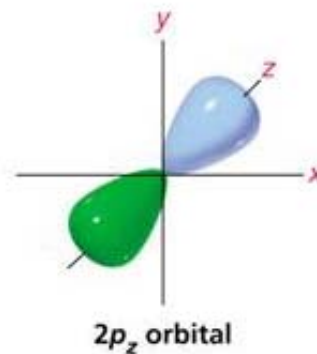
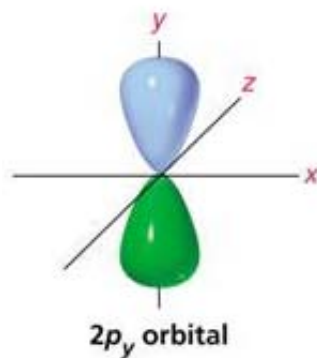
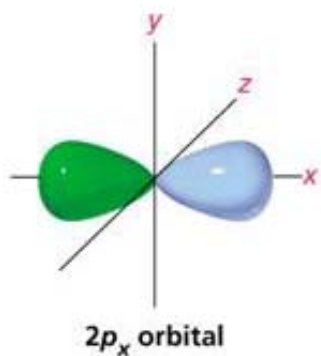


$2p$ atomic orbital



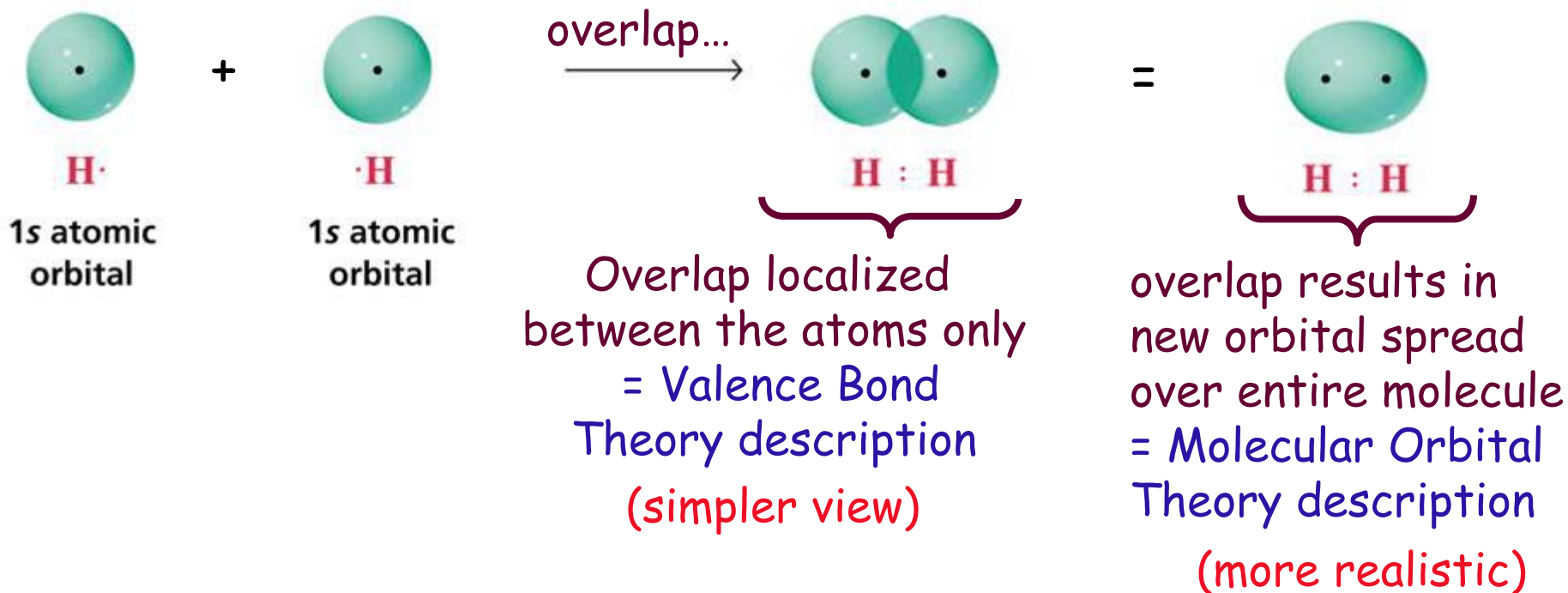
computer-generated $2p$ atomic orbital

- 3 degenerate orbitals in 3 orientations:



1.6 Molecular Orbital ("M.O.") Theory

[Note: Gen. Chem. texts also helpful - Kotz & Treichel 10.3; Zumdahl 9.2-5]



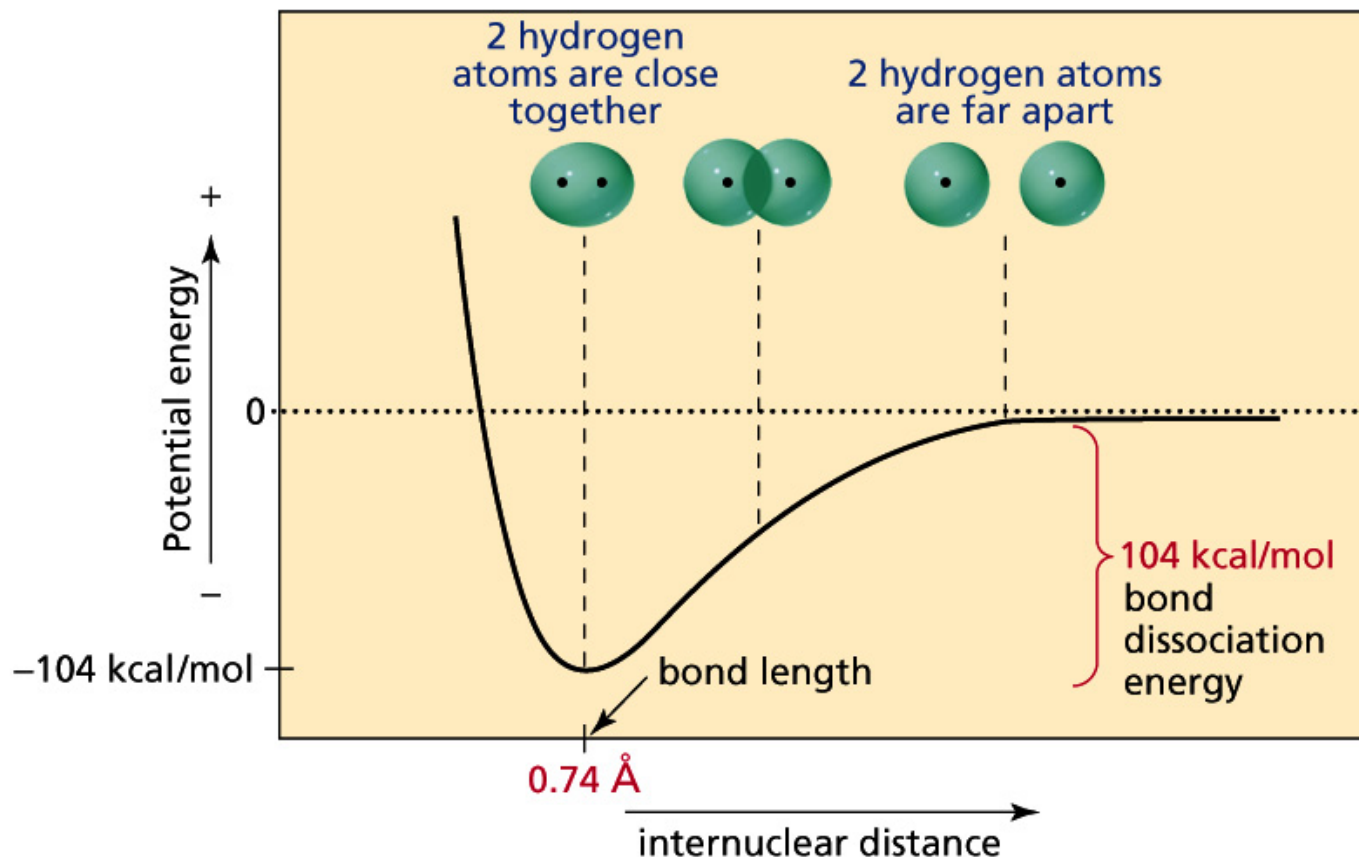
- a σ -bond: formed by the overlap of two s orbitals

Bond strength described by **bond dissociation energy**

= energy required to break a bond (always endothermic!)

= energy released when a bond forms (always exothermic!)

Bruice
Figure 1.2



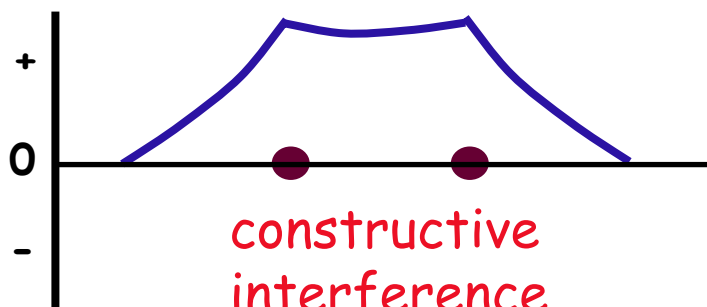
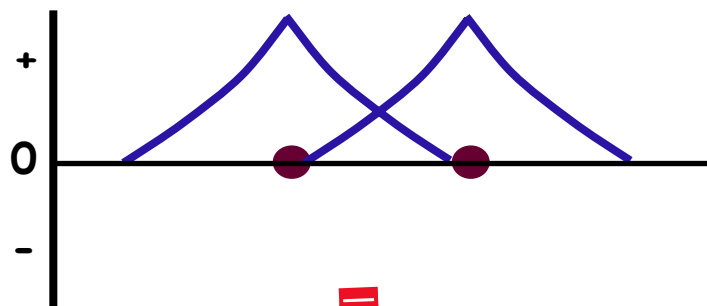
Remember that orbitals are WAVES...

Like waves: orbitals have *phase* & *interfere* if overlapped

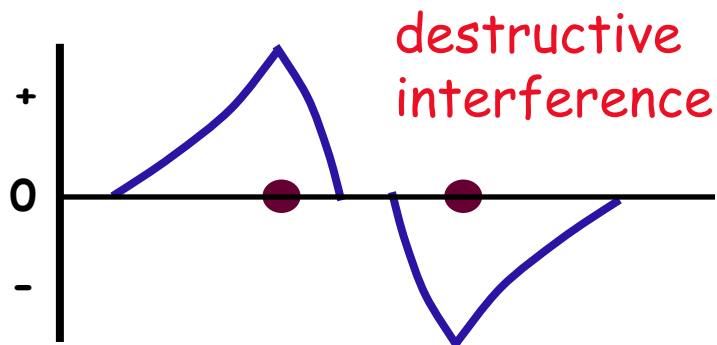
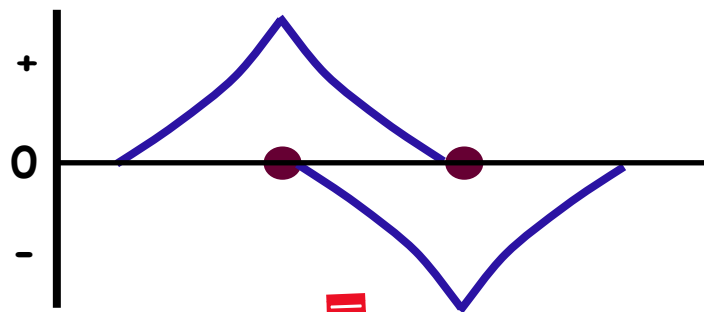
Consider a simplified view of 2 s-orbitals:

See Fig.1.3

In-phase overlap:

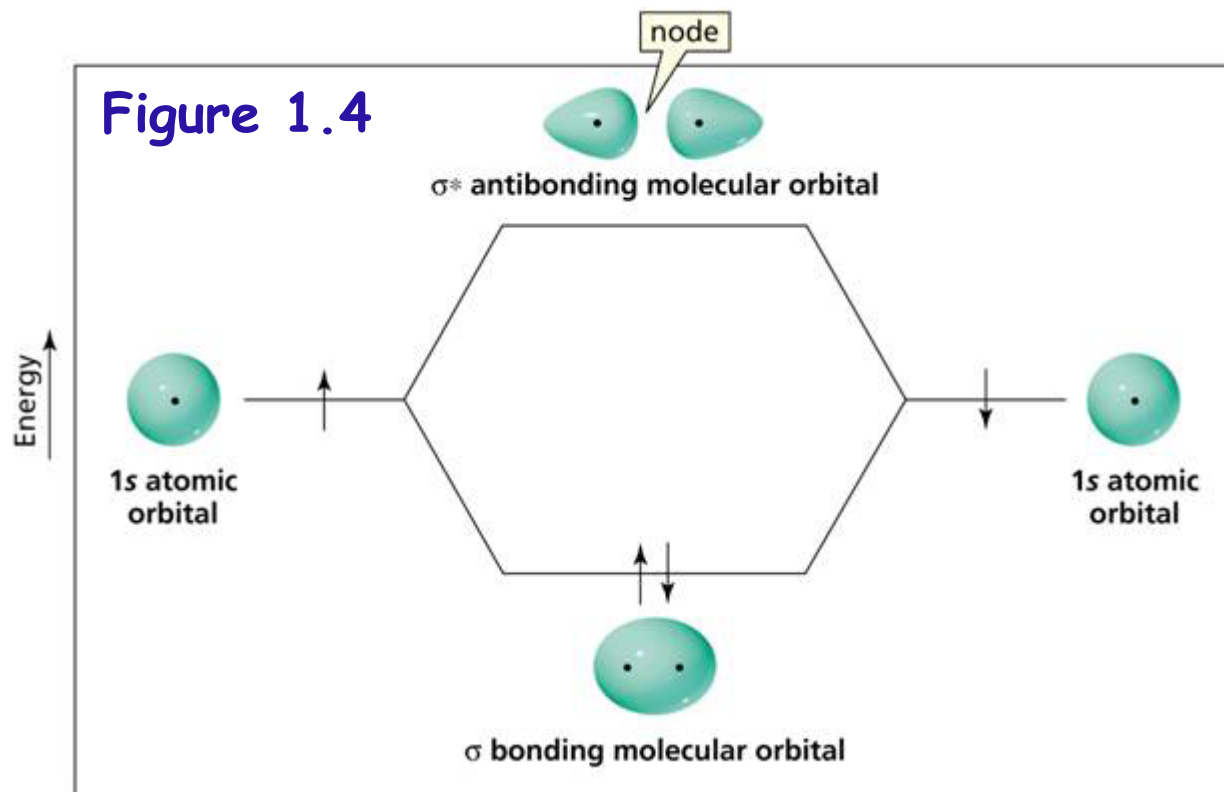


Out-of-phase overlap:



In-phase overlap forms a **bonding MO**
out-of-phase overlap forms an **antibonding MO**

Important: BOTH types of overlap occur every time 2 orbitals overlap!



← An "MO diagram"

ON OUTSIDES:
relative energies,
names & occupancies
of the orbitals of
the 2 atoms coming
together

& ON INSIDE:
the resulting MO's

Note: both e^- s will occupy the bonding orbital (since lower in E!)

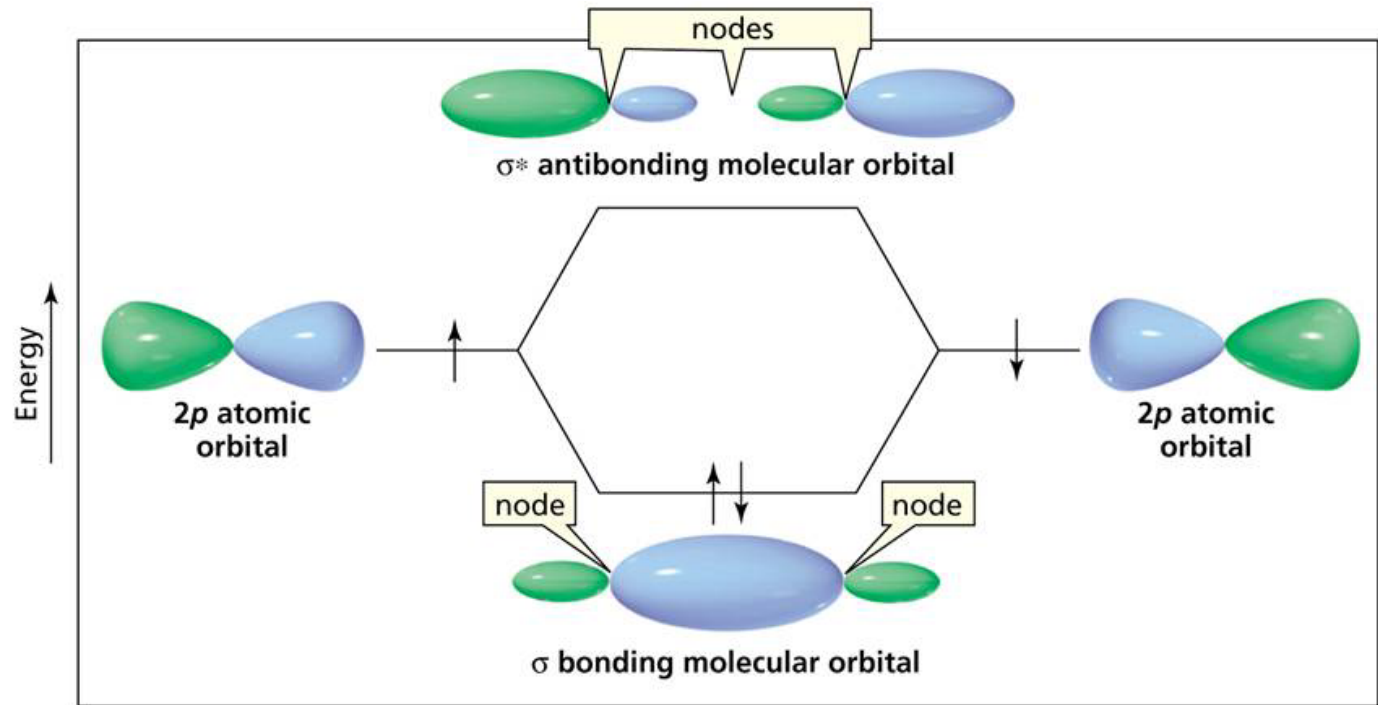
IMPORTANT:

Bonding occurs if it is energetically favourable

If a bond's σ AND σ^* orbital are simultaneously filled:
the bond will not actually exist.

Example on board: Justify why He_2 does not form.

A sigma bond (σ) can also be formed by end-on overlap of two p orbitals:



So, what makes a bond a sigma-bond?

- if the lobes of the orbitals that are overlapping are *pointing at each other along the "bond axis"* (i.e., the space between the nuclei)
- the bond can rotate without diminishing the overlap

A pi bond (π) is formed by side-on overlap of 2 p orbitals:

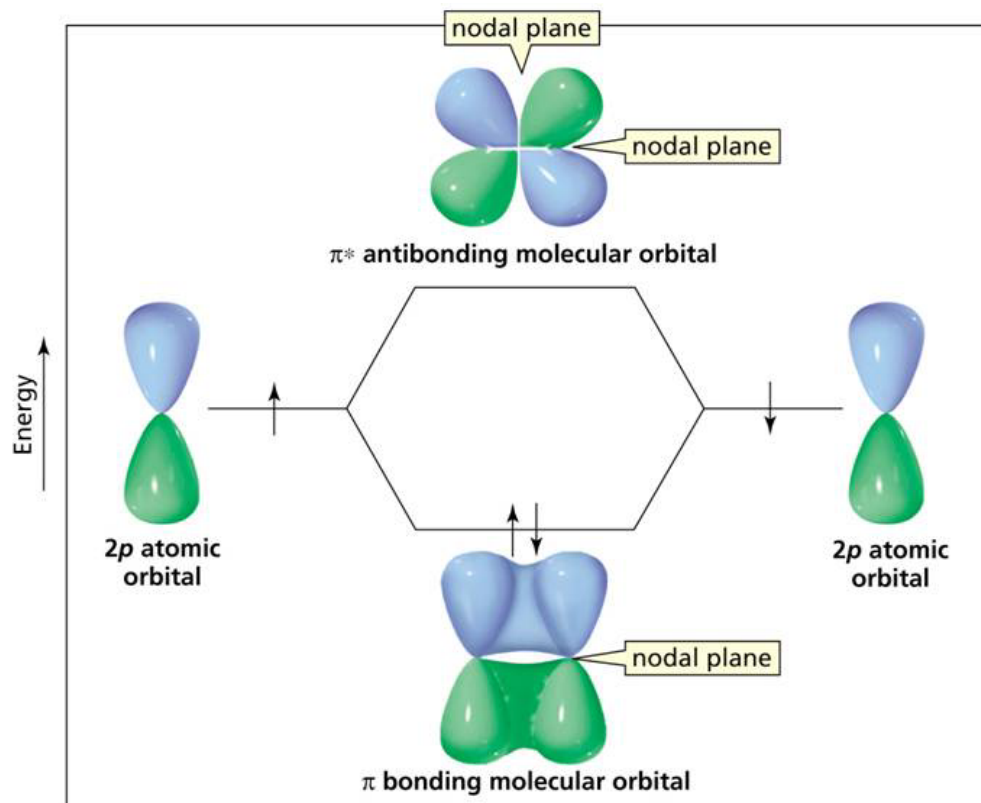
So, what defines a π -bond?

- the overlapping lobes are *parallel* to each other
- the bond **cannot rotate** without diminishing the overlap

Note: A σ bond is stronger than a π bond.

WHY?

- Larger parts of the orbitals actually overlap when end-on *vs.* when oriented side-on.
- *i.e.*, higher e^- density in region of overlap



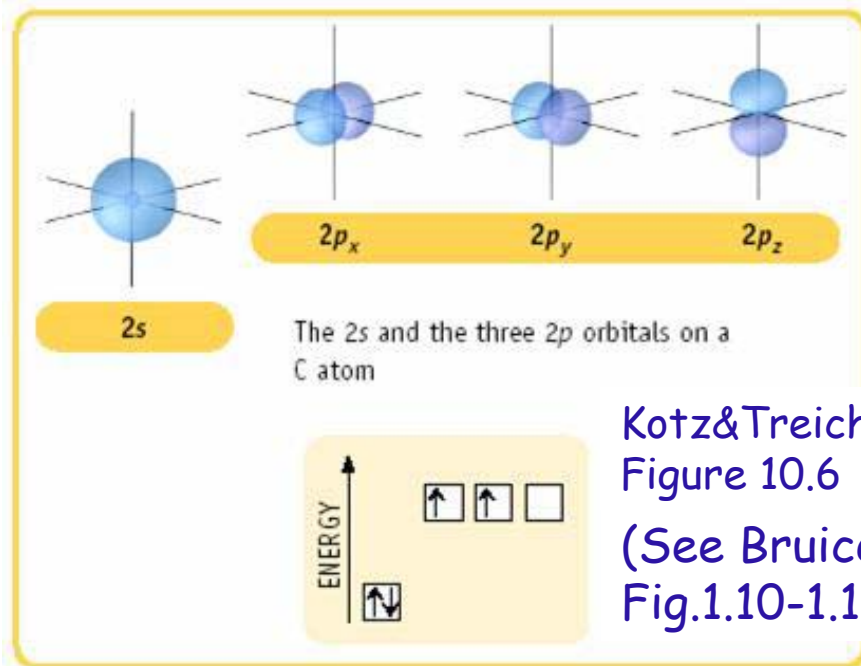
1.7 Bonding in Methane & Ethane: Single Bonds

Recall VSEPR model for predicting geometries:

- draw Lewis structure: determine # of single bonds & lone pairs
- electron pairs (bonding & lone) will spread themselves out in space as far from each other as possible

- Atomic orbitals *hybridize* to achieve necessary geometries

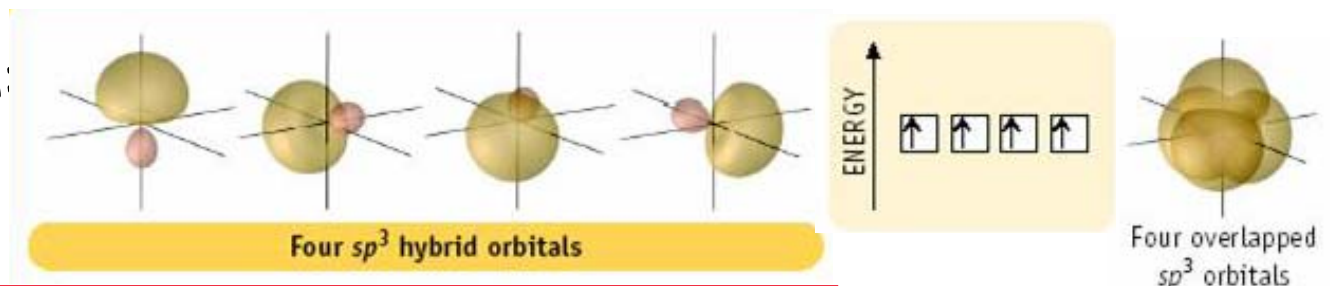
Valence shell of C:



Hybridization of atomic orbitals

IF MIX THESE ATOMIC ORBITALS	GET BACK THESE HYBRID ORBITALS	ANGLE b/w HYBRIDS	GEOMETRY
One <i>s</i> & one <i>p</i>	2 " <i>sp</i> " hybrids	180°	Linear
One <i>s</i> & two <i>p</i> 's	3 " <i>sp</i> ² " hybrids	120°	Trig. planar
One <i>s</i> & three <i>p</i> 's	4 " <i>sp</i> ³ " hybrids	109.5°	Tetrahedral

To make a Td carbon:
One *s* & three *p*'s



Fat lobes of hybrids used for bonding...

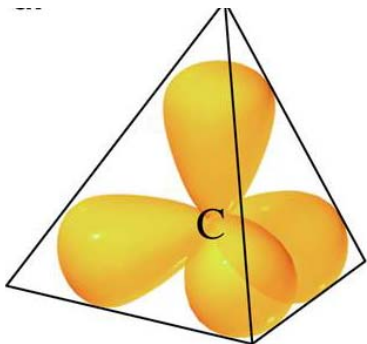
Kotz & Treichel Figure 10.6
(Compare to Bruice Fig.1.10-1.12)

Orbital description of the bonding in Methane, CH_4

CH_4 : requires 4 bonds to C \Rightarrow tetrahedral geometry

sp^3 hybrid set:

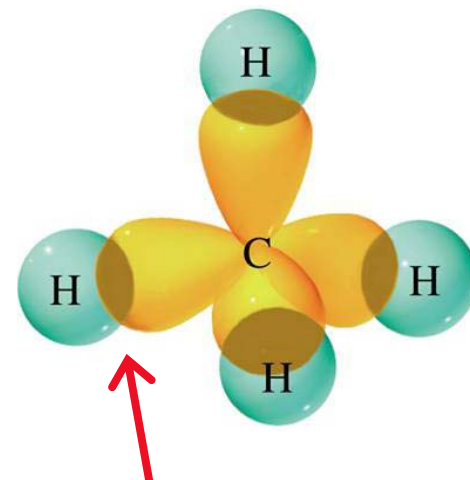
- Tetrahedral
- bond angle 109.5°



Each σ -bond formed by
one C sp^3 hybrid
overlapping with
one H $1s$ orbital

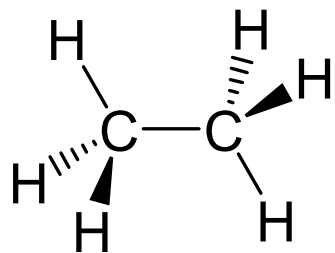
Summary:

4 σ -bonds produced by
C $2sp^3$ - H $1s$ overlap



*Valence Bond view
(easier to see)
of the BONDING
 σ -orbitals
...but reality is MO*

Orbital description of the bonding in Ethane, CH_3CH_3



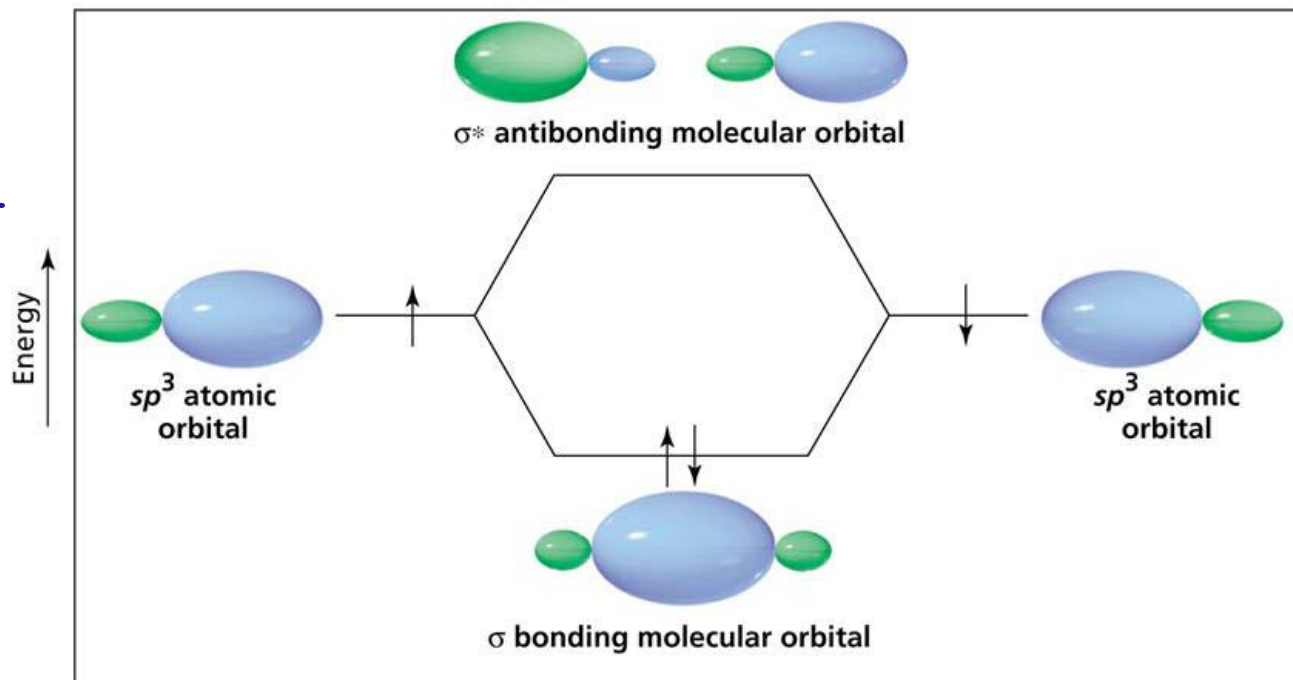
Requires 4 bonds to each C \Rightarrow each C has Td geometry

6 C-H σ -bonds: C $2sp^3$ - H $1s$ overlap

& 1 C-C σ -bond: C $2sp^3$ - C $2sp^3$ overlap

Bruice Figure 1.14

MO diagram for
a C-C σ -bond

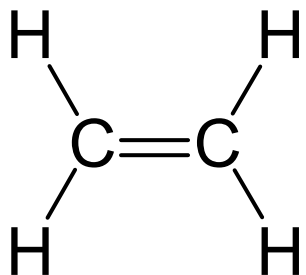


A simple organic reaction: $\text{CH}_3\text{I} + \text{F}^- \rightarrow \text{CH}_3\text{F} + \text{I}^-$

Draw the orbitals involved in the C-H & C-I bonds of methyl iodide
(both bonding & antibonding):

What would happen if a lone pair on F^- entered the C-I σ^* orbital?

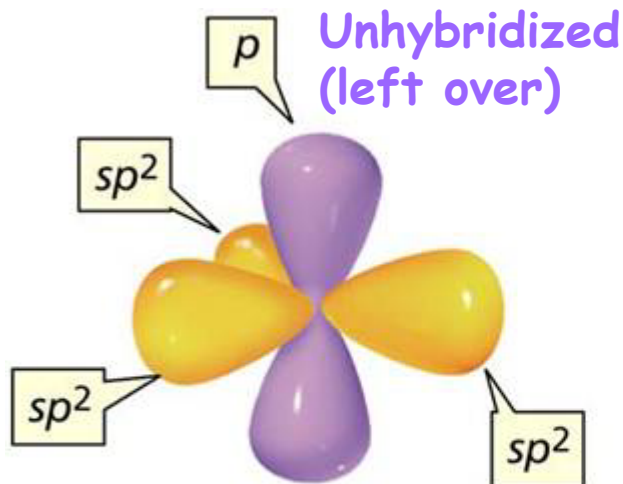
1.8 Bonding in Ethene: A Double Bond ($=1\sigma+1\pi$)



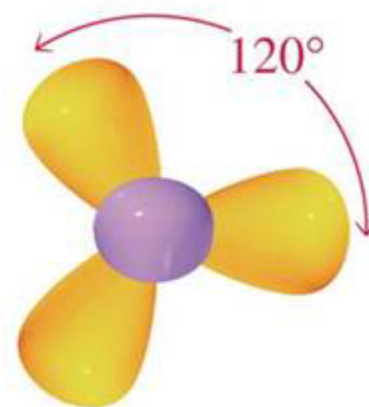
Requires 3 bonds to each C
 \Rightarrow each C is \therefore trigonal
 \Rightarrow sp^2 hybridized

Bruice Fig.1.15

sp^2 -hybridized
carbon atom:



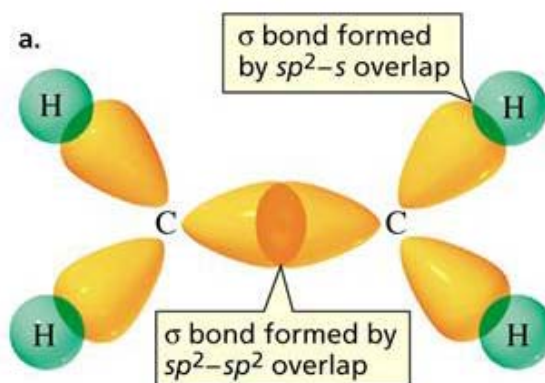
side view



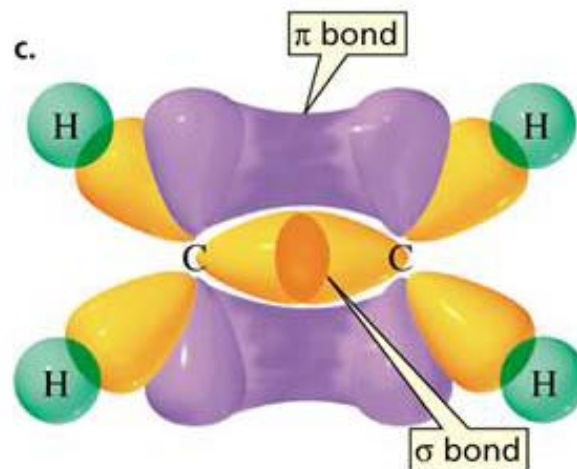
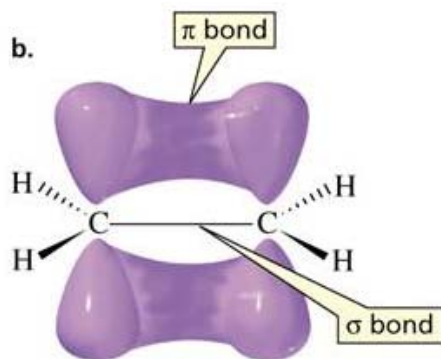
top view

1.8 Bonding in Ethene: A Double Bond ($=1\sigma+1\pi$)

σ -framework:



π -bond forms
between parallel
unhybridized
p-orbitals:



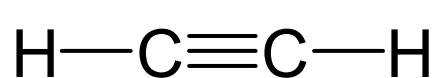
1 C-C σ -bond:
C $2sp^2$ - C $2sp^2$

1 C-C π -bond:
C $2p$ - C $2p$

4 C-H σ -bonds:
C $2sp^2$ - H $1s$

THE
DOUBLE
BOND

1.9 Bonding in Ethyne: A Triple Bond ($=1\sigma+2\pi$)

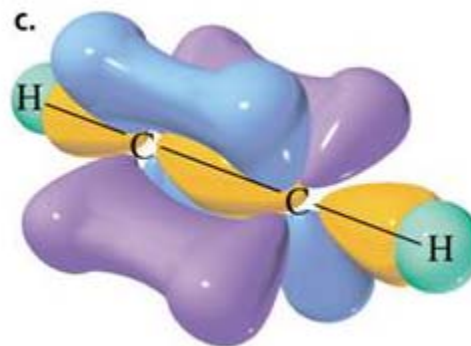
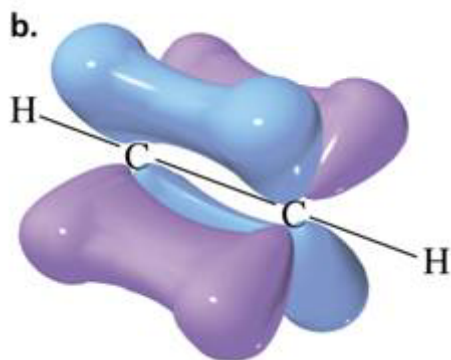
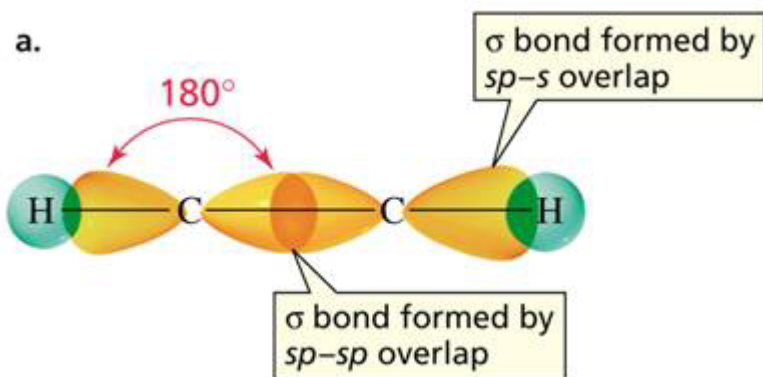


Requires 2 bonds to each C \Rightarrow linear

\therefore sp hybridized

\therefore 2 unhybridized p-orbitals

see Bruice Fig.1.17



1 C-C σ -bond:

C $2sp$ - C $2sp$

2 C-C π -bonds:

C $2p$ - C $2p$

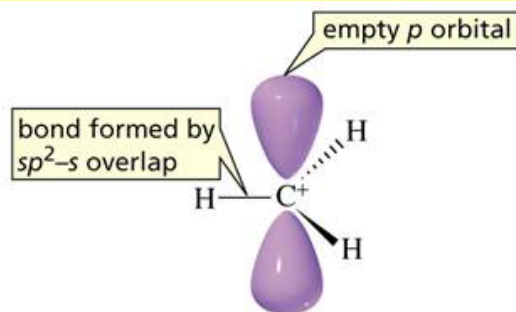
2 C-H σ -bonds:

C $2sp$ - H $1s$

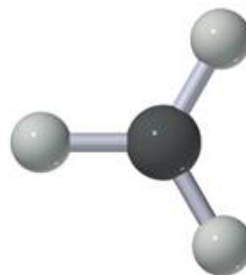
THE
TRIPLE
BOND

1.10 Bonding in methyl cation, radical & anion

Methyl cation
 CH_3^+
(3 pairs of valence e^- s)



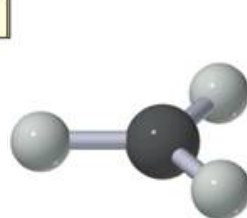
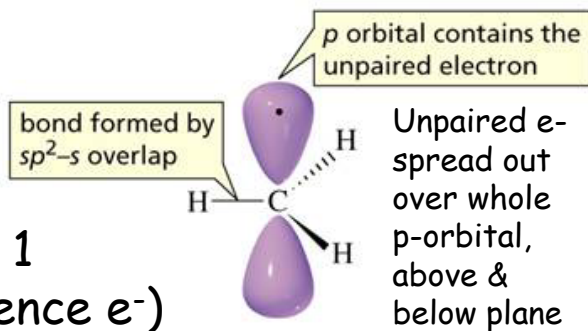
angled side view



top view



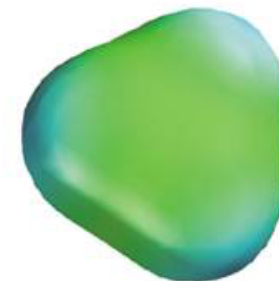
Methyl radical
 CH_3^\cdot
(3 pairs + 1 extra valence e^-)



angled side view

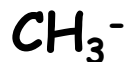


top view

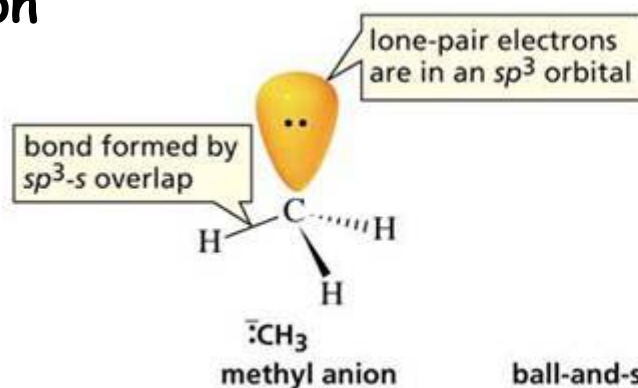


1. Carbocations are planar at their open-shell (e^- -deficient) centre.
2. Carbon radicals are planar at the radical centre: an unpaired e^- does NOT exert enough repulsion to make C atom rehybridize

Methyl Anion



4 pairs of
valence e⁻s



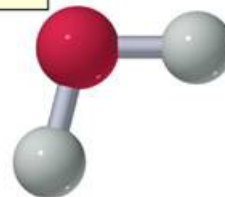
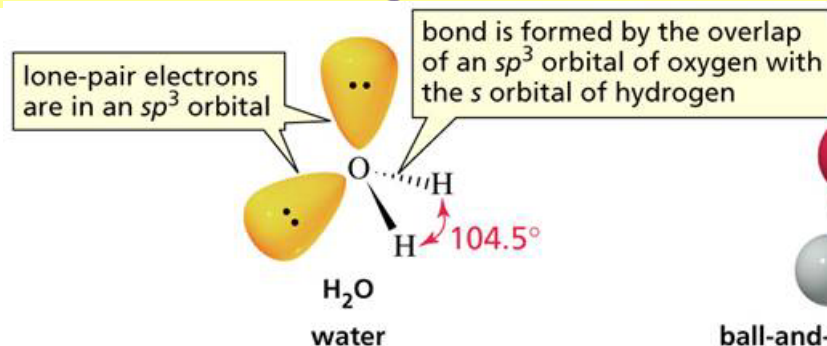
ball-and-stick model of the methyl anion



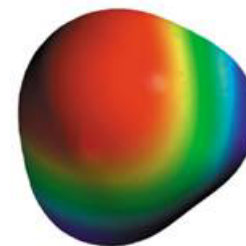
electrostatic potential map
for the methyl anion

3. Carbanions are tetrahedral at the anionic centre:
→ another pair of electrons DOES exert enough repulsion to make the C atom rehybridize
→ just like we see for NH_3 , H_2O , *etc...* based on VSEPR model

1.11 Bonding in water

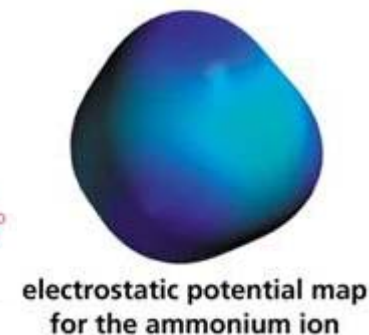
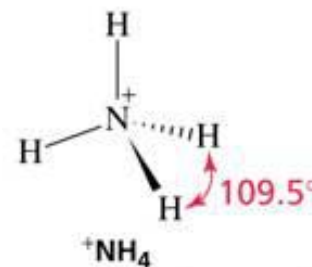
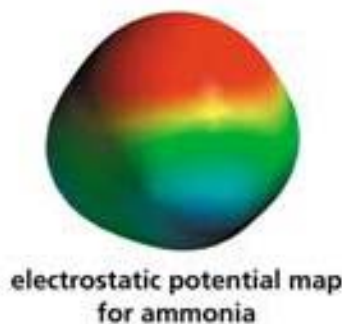
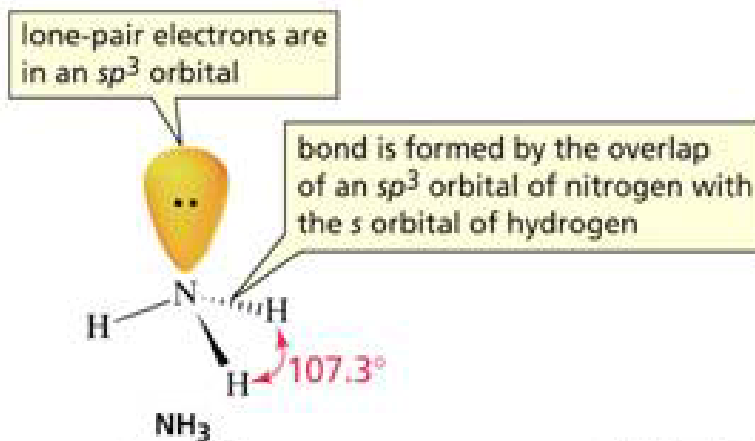


ball-and-stick model of water



electrostatic potential map for water

1.12 Bonding in ammonia & ammonium cation



1.13 Bonding in the hydrogen halides



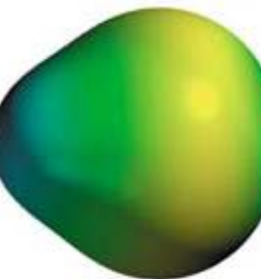
HF



HCl



HBr



HI

Table 1.6 Hydrogen–Halogen Bond Lengths and Bond Strengths

Hydrogen halide		Bond length (Å)	Bond strength	
			kcal/mol	kJ/mol
H—F		0.917	136	571
H—Cl		1.2746	103	432
H—Br		1.4145	87	366
H—I		1.6090	71	298

weakest
acid...

strongest
acid...

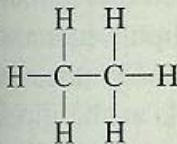
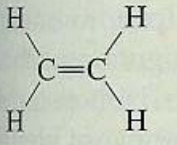
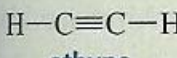
- H-X bonds involve H 1s - X np overlap
- larger value of "n" → larger orbital (higher energy)

SO WHAT?

- mismatch in orbital sizes results in less efficient overlap
 - weaker bond
 - reflected in bond energy & bond length

1.14 Summary of important bonding principles

Table 1.7 Comparison of the Bond Angles and the Lengths and Strengths of the Carbon–Carbon and Carbon–Hydrogen Bonds in Ethane, Ethene, and Ethyne

Molecule	Hybridization of carbon	Bond angles	Length of C—C bond (Å)	Strength of C—C bond (kcal/mol) (kJ/mol)	Length of C—H bond (Å)	Strength of C—H bond (kcal/mol) (kJ/mol)
 ethane	sp^3	109.5°	1.54	sp^3-sp^3 377	1.10	sp^3-s 423
 ethene	sp^2	120°	1.33	sp^2-sp^2 & p-p 720	1.08	sp^2-s 466
 ethyne	sp	180°	1.20	$sp-sp$ & 2x p-p 967	1.06	$sp-s$ 548

1.) Higher bond order \rightarrow stronger bond (for same atom types)

2.) The greater the "s-character", the stronger the bond.

WHY?

\rightarrow s-orbitals are closer to nucleus than p's (or hybrids)

\rightarrow thus: stronger nucleus-to-electron attraction

Summary: important bonding principles

- When a bonding / antibonding orbital pair are filled, the bond will break (or never form)
- A π bond is weaker than a σ bond
- The greater the electron density in the region of orbital overlap, the stronger is the bond
- The more s character:
the shorter and stronger is the bond

ASSIGNED READINGS

BEFORE NEXT LECTURE:

Read: rest of Bruice Ch.1

Review: Chem206: acids & bases

- conjugate pairs
- pH, pK_a , pK_b
- reactions of acids & bases
- effect of structure on acidity

Note:

supplementary orbital figures were taken from
Kotz & Treichel's *Chemistry & Chemical Reactivity* 5th Ed.

On reserve at Vanier library for Chem 205/206