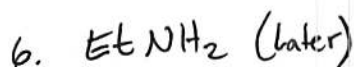
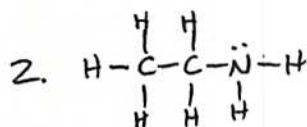
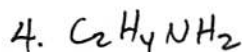
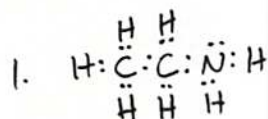


## Lecture 2: Orbitals & Bonding

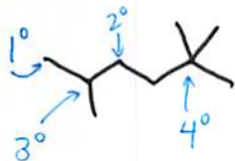
①

### Drawing Molecules:



Identifying carbon bonds, relative to the number of ~~carbon~~ carbon atoms that are bonded.

Consider



then

$1^\circ$  = Primary = C bonded to 1 non-H atom

$2^\circ$  = Secondary = C bonded to 2 non-H atoms

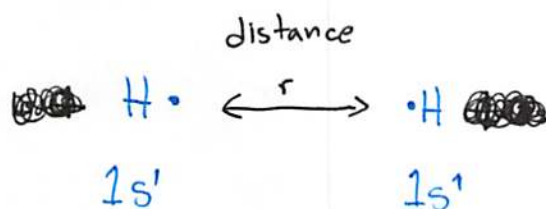
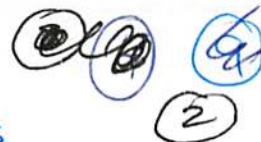
$3^\circ$  = Tertiary = C " " 3 " "

$4^\circ$  = Quaternary = " " " 4 " "

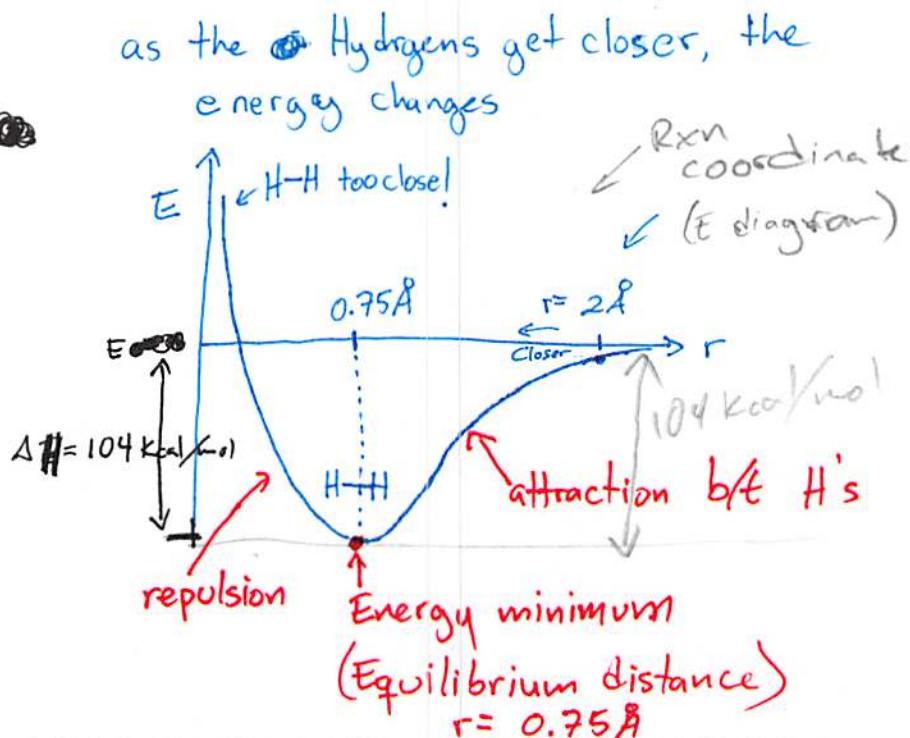
Chemical Structures are not flat!

How do bonding interactions occur?

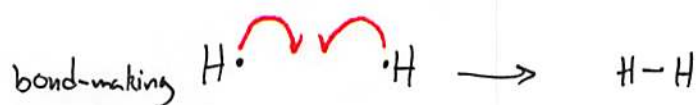
To better understand <sup>Orbitals and</sup> chemical bonding, let's consider the simplest molecule:  $H_2$



To make a bond,  $e^-$  have opposite spins

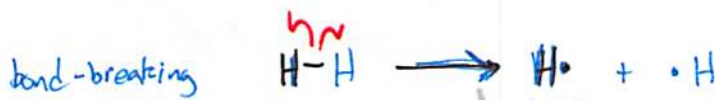


Therefore:



$\Delta H = -104 \text{ Kcal/mol}$   
Exothermic

~~Energy~~ given off  
← Amt of E ~~off~~



$\Delta H = +104 \text{ Kcal/mol}$   
Endothermic

← Bond dissociation Energy.

(Amount of energy req'd to break a bond)

Homolytic cleavage

Note arrow formalism  $\curvearrowright = 1e^-$  moves

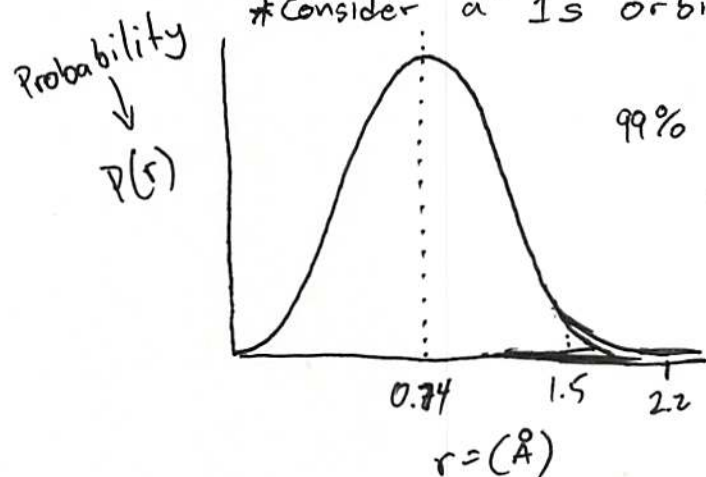
**VERY IMPORTANT!**

$\rightarrow = 2e^-$  move

WHAT ABOUT THE ORBITAL INTERACTIONS?

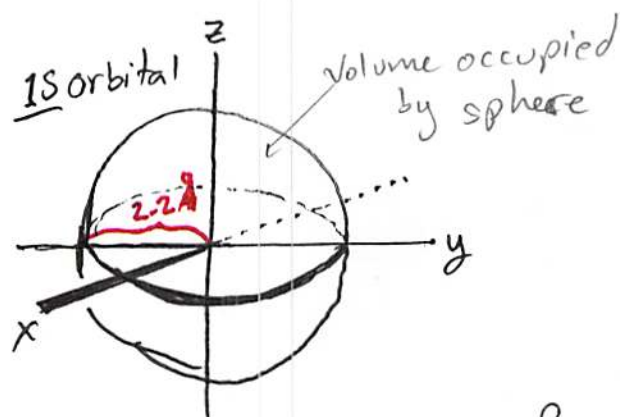
Atomic orbitals  $\Rightarrow$  E. Schrödinger formulated an eqn that describes molecular & atomic systems.

From the solution to Schrödinger's eqn, one can plot the probability ( $P(r)$ ) of finding an  $e^-$  @ a given point.  
\*Consider a 1s orbital.



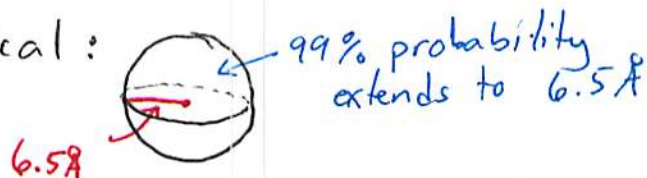
99% Probability of finding an  $e^- \leq 2.2 \text{\AA}$

Shape plotted in 3D  $\Rightarrow \psi_{1s}$   
wavefunction

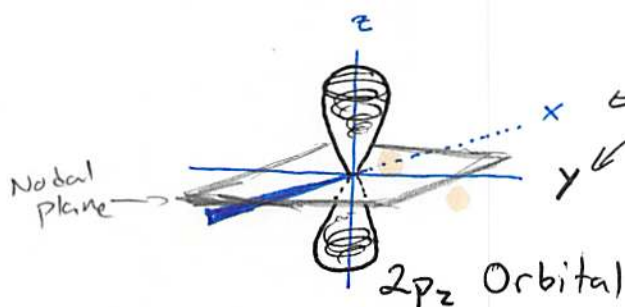


99% of the  $e^-$  density is found within the sphere.

Similarly a 2s orbital is also spherical:



A higher energy 2p orbital displays a nodal plane:



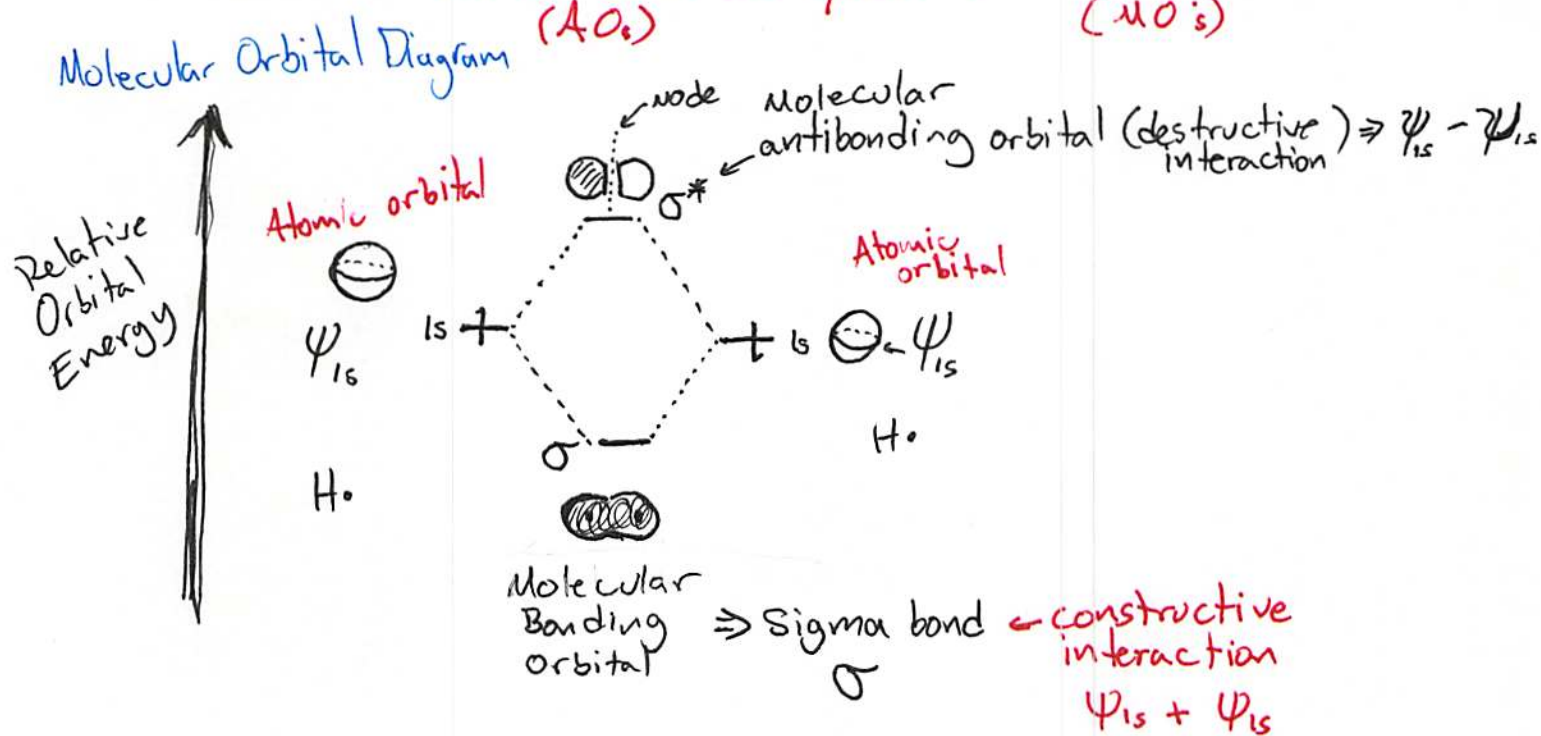
orbitals can also be found along x- & y-axes ( $2p_x$  &  $2p_y$ )

There are 3 p-orbitals

## Orbital interactions in $H_2$

The molecular orbital results from  
a Linear Combination of Atomic Orbitals

ex. 2 atomic orbitals yield 2 molecular orbitals  
(AOs) (MOs)

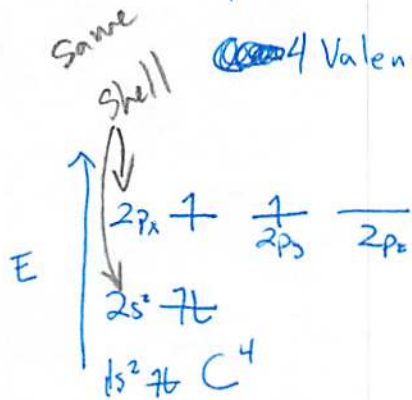


What about bigger systems, like  $CH_4$ ?



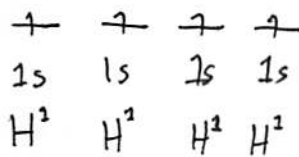
# Orbital Hybridization: Methane (CH<sub>4</sub>)

- consider the e<sup>-</sup> configuration of C and the way that e<sup>-</sup>s fill up the orbitals.



4 Valence e<sup>-</sup>s of C. = 2s<sup>2</sup>, 2p<sub>x</sub><sup>1</sup>, 2p<sub>y</sub><sup>1</sup>, 2p<sub>z</sub><sup>0</sup>

4 hydrogens:



How can you form covalent bonds?

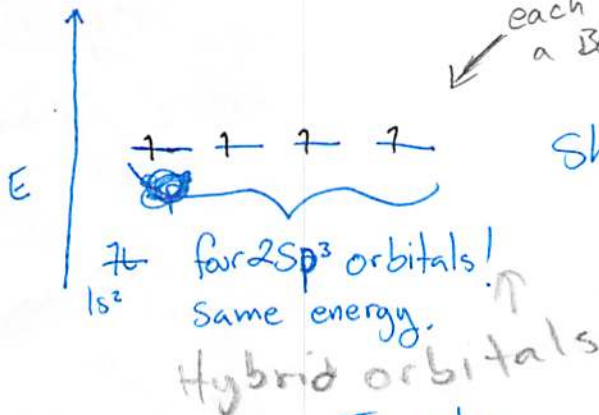


on board

In 1950, Linus Pauling (~~Nobel~~ Nobel Laureate in Chemistry) had a solution to this problem. He proposed that orbitals "Hybridize" (re-arrange to lower energy conformations). The 4 AO's in C become new orbitals.

That is:

mix subshells  
s + p → sp

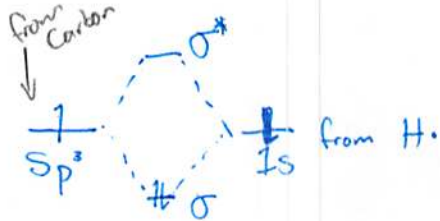


each forms a Bonding MO w/ Hydrogen

Shape has 25% s-character  
75% p- "



To make a C-H bond

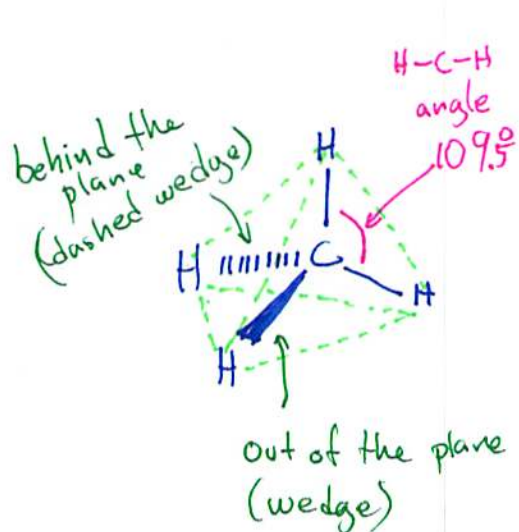


\* How do we arrange all 4 bonds in space?

From VSEPR Theory (Valence Shell Electron Pair Repulsion)

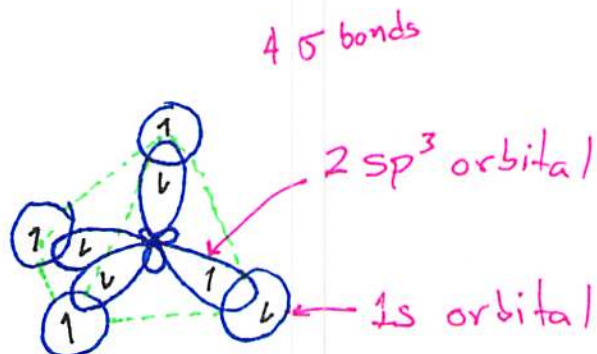
- Geometry is determined by V.S.E. pairs both bonded and non-bonded, arranging to minimize electrostatic repulsion.

for  $\text{CH}_4$  (methane)  $\Rightarrow \text{AX}_4$  Type  $\Rightarrow$  Tetrahedral

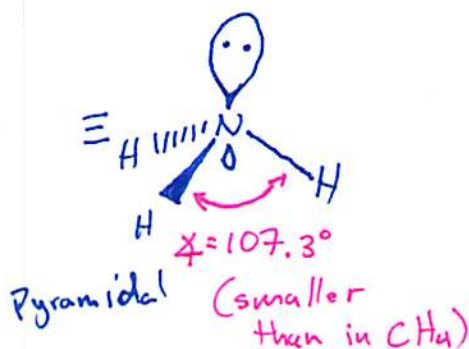
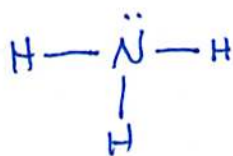


similarity symbol

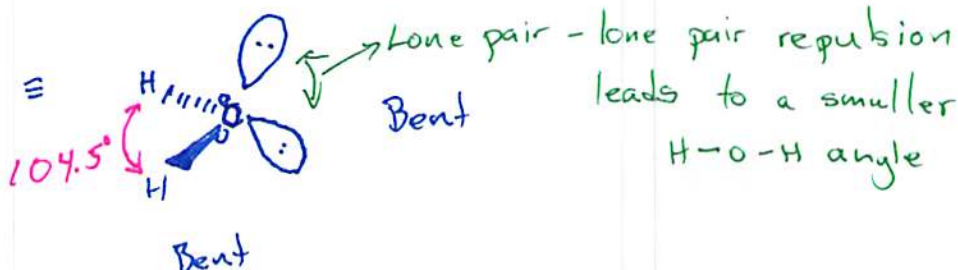
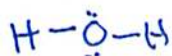
$\equiv$



Shape is important!



on your own:  
- draw the orbital picture  
(similar to the example above)



# Bonding in Alkenes:

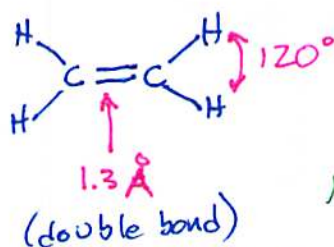
recitation

Alkenes are "unsaturated" hydrocarbons (aka olefins)

$C_nH_{2n}$  - contain a carbon-carbon double bond.

\* Consider  $C_2H_4$  (Ethylene, or Ethene)

From VSEPR Theory:



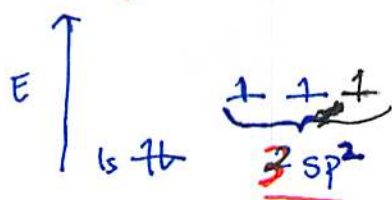
All flat

(all atoms are on the same plane)

Note: can not rotate about the double bond.

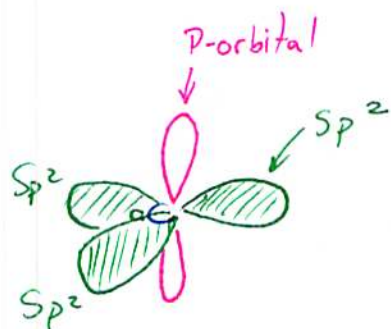
the carbons are  $sp^2$  hybridized.

Hybrid orbital diagram for one Carbon.



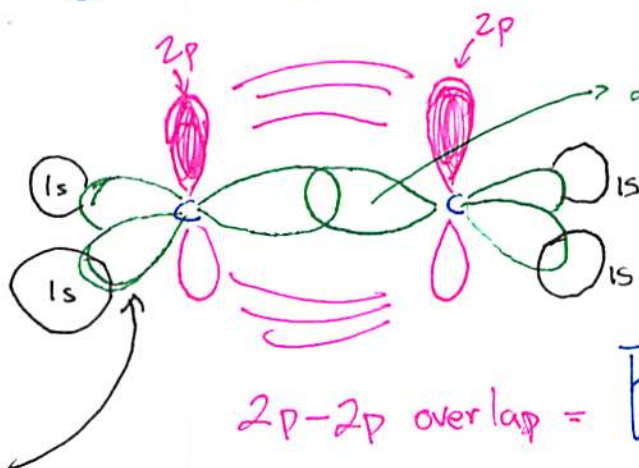
$\frac{1}{2p}$

$\Rightarrow$  looks like:



Atomic orbitals

## Bonding in Ethylene:



$2sp^2 - 2sp^2$  overlap =  $\sigma$  bond

Note: a  $\sigma$ -bond is stronger than a  $\pi$ -bond.

$2p - 2p$  overlap =  $\pi$ -bond

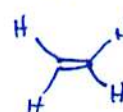
$1s - 2sp^2$  overlap =  $\sigma$ -bond



Top view

side view

Drawing Alkenes:



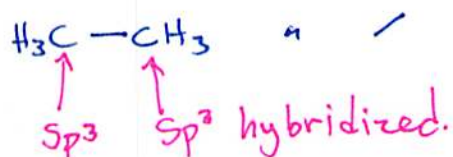


## Bonding in Alkanes:

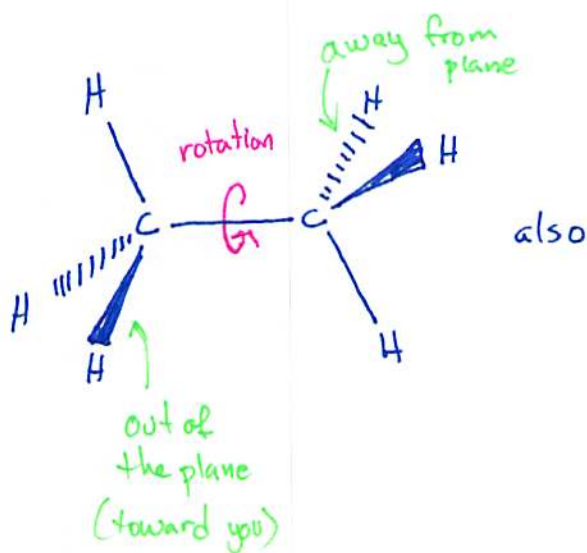
Alkanes are "saturated" hydrocarbons

molec. formula:  $C_n H_{2n+2}$

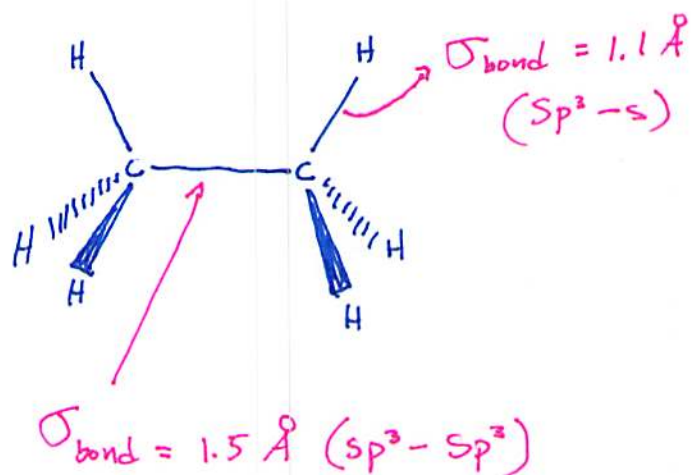
Consider  $C_2H_6$  (Ethane)



$= 7 \sigma$  bonds



also



Single bonds can rotate.

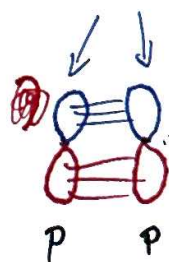
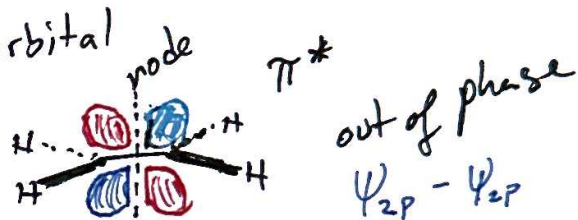
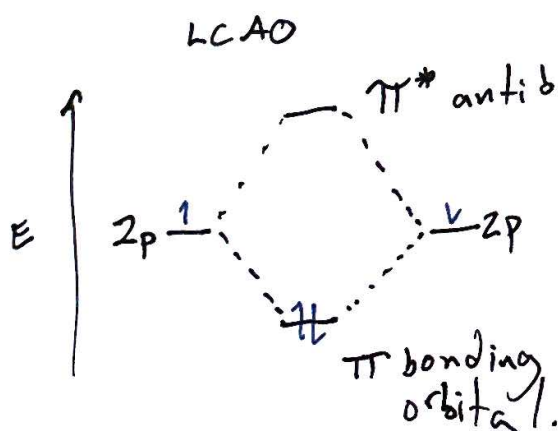
The two molecules above are called "rotational isomers"  
 or "rotamers"  
 or "conformational isomers"  
 or "conformers"



# Alkenes, cont.

## M.O. Diagram of the $\pi$ bond.

$\pi$  bonds are generally higher in energy than  $\sigma$ -bonds.  
i.e. more reactive.  
→ composed of the two higher energy p-orbitals that are not hybridized.



in phase  $\psi_{2p} + \psi_{2p}$

