

Recipe for MO's  
General Chemistry, Boston University  
December 10, 2008

<http://quantum.bu.edu/notes/GeneralChemistry/MORecipe.pdf>

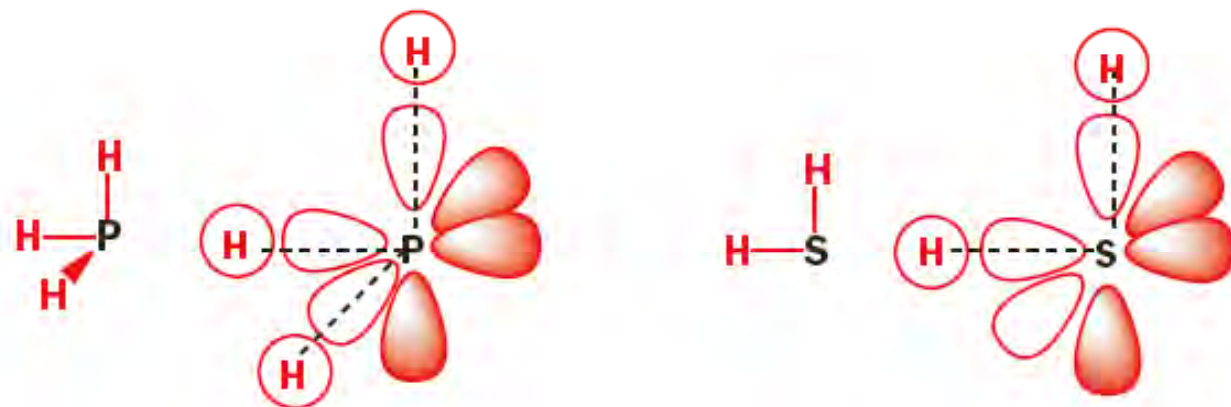
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# Polyatomic MO recipe review

1. Use the Lewis structure to get
  - the *number of electron pairs*
  - *hybrid AO's* on each atom (except H)
2. Sketch the  *$\sigma$  framework* and *place pairs*
  - in each *bonding  $\sigma$  MO*
  - in each *nonbonding hybrid AO*
3. Sketch the  *$\pi$  framework MO's*,
  - mark as *bonding, nonbonding, antibonding*
  - place *remaining pairs* (Auf Bau)
  - get the  *$\pi$  bond order*

# Central atom AO mixing: Hybrid AO's

*Unmixed* AO's have the *wrong* central atom geometry

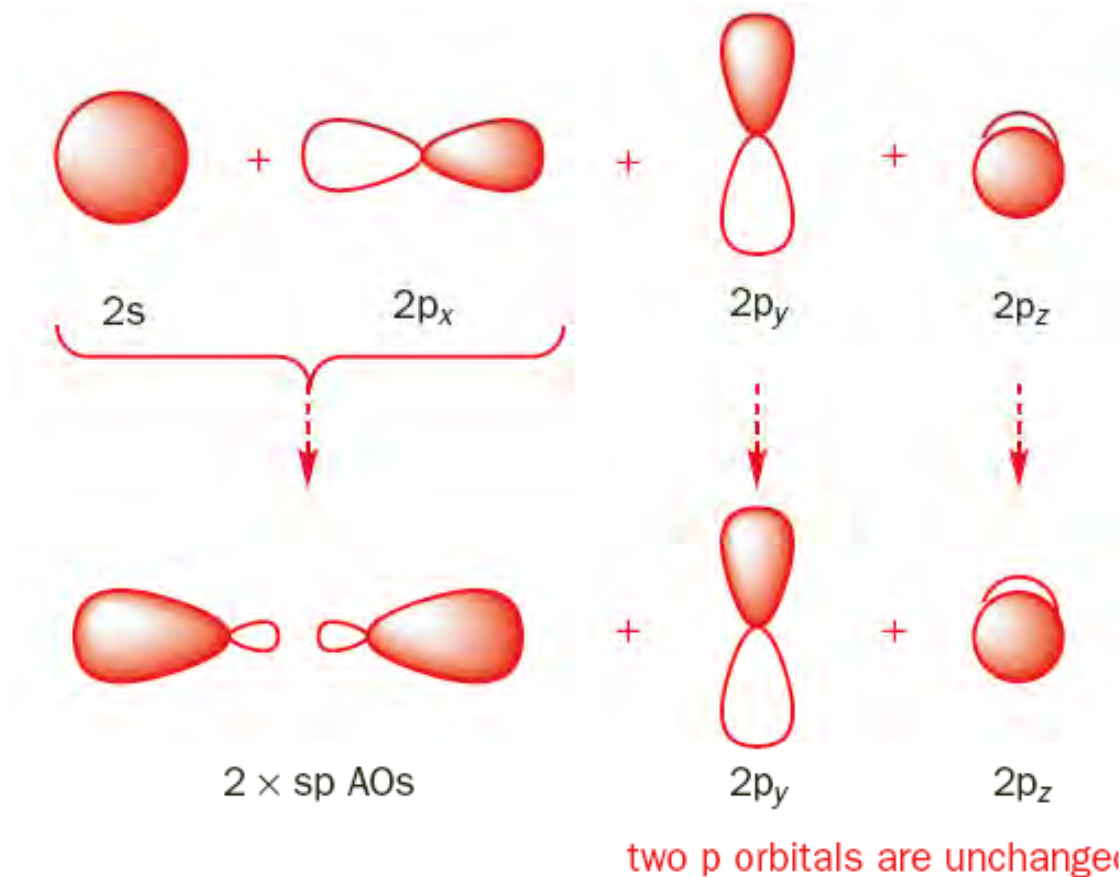


the  $90^\circ$  angles in  $\text{PH}_3$  and  $\text{H}_2\text{S}$  come from the overlap of the hydrogen 1s AO with the p AO of the phosphorus or sulfur

# An s and a p AO make two sp hybrid AOs

180° angle, for SN = 2

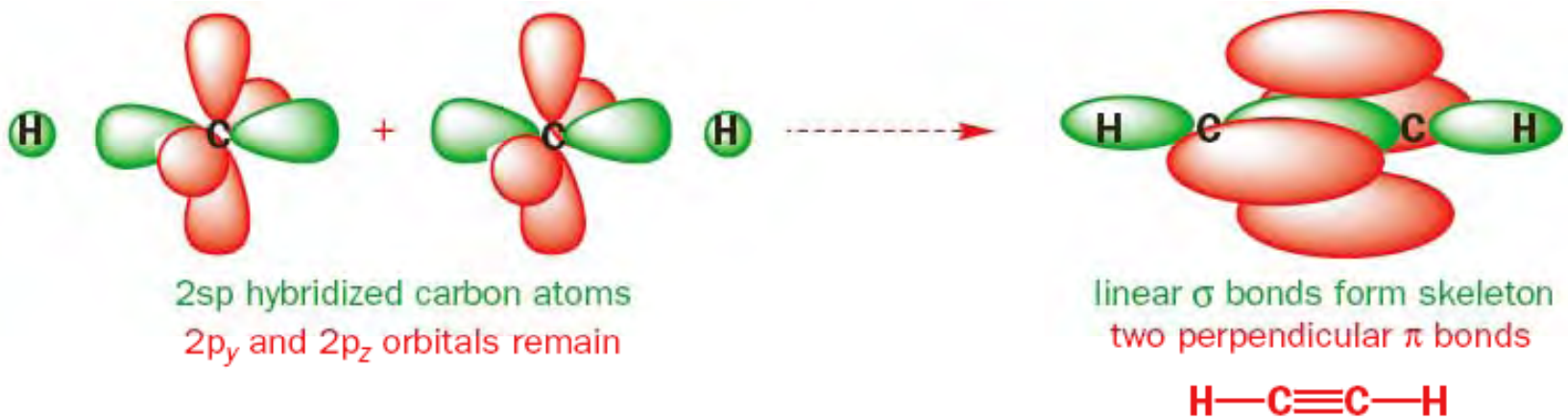
Two p's are unchanged on each atom



# sp hybrids account for *linear geometry*

180° angle, for SN = 2

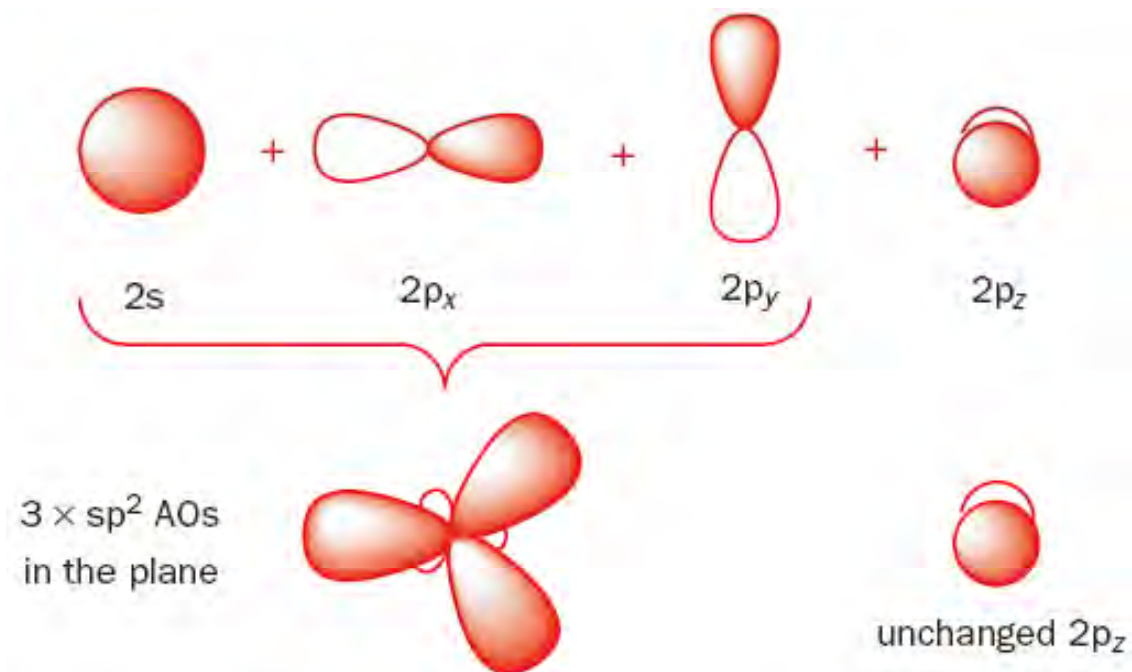
Two p's are unchanged on each atom



An s and two p AO's make  
three  $sp^2$  hybrid AO's

$120^\circ$  angle, for SN = 3

One p is unchanged on each atom



$sp^2$  hybrids account for  
***trigonal planar geometry***

$120^\circ$  angle, for SN = 3

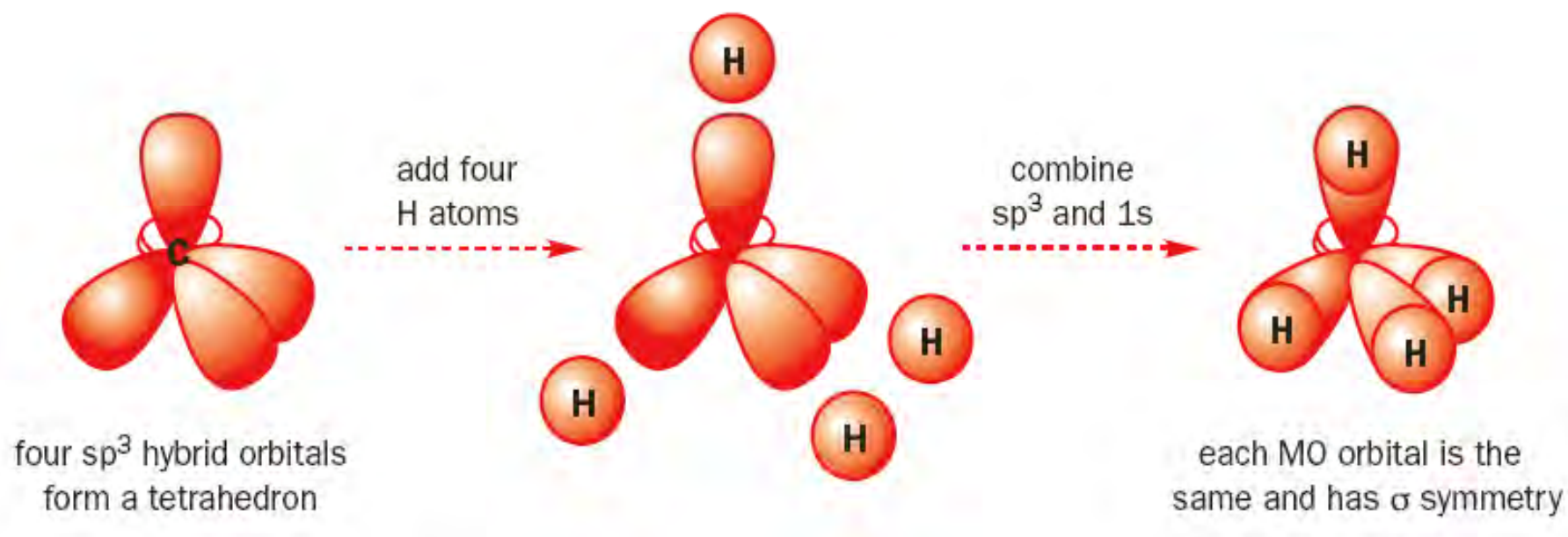
One p is unchanged on each atom



An s and three p AO's make  
four  $sp^3$  hybrid AO's

$109^\circ$  angle, for SN = 4

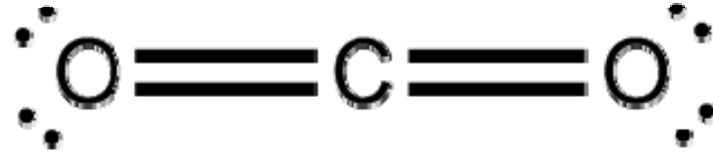
$sp^3$  hybrids account for ***tetrahedral geometry***



# $\sigma$ framework

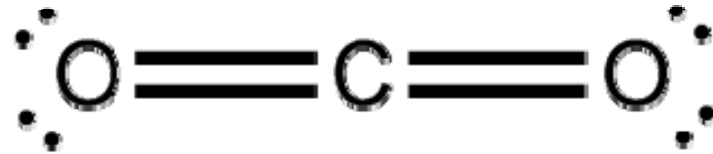
- Hybridization of terminal atoms the same as their central atom.
- Terminal H never hybridized
- One pair in each hybrid AO  ***$\sigma$  bonding MO***
- One pair in each ***non-bonded hybrid AO***

# CO<sub>2</sub> sp σ framework



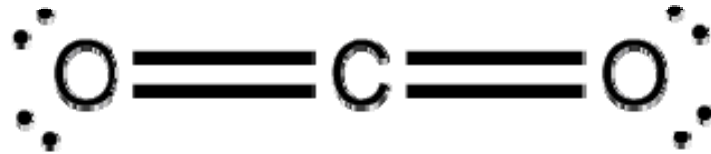
sp hybrids overlap to make...

# CO<sub>2</sub> sp σ framework



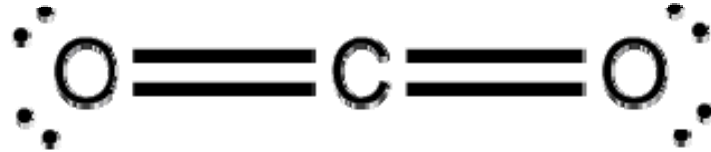
sp hybrids overlap to make  
***two sp σ bonding MO's,***  
leaving ***two sp nonbonding AO's.***  
These can hold ...

# CO<sub>2</sub> sp σ framework



sp hybrids overlap to make  
***two sp σ bonding MO's,***  
leaving ***two sp nonbonding AO's.***  
These can hold ***4 pairs of electrons.***

# CO<sub>2</sub> sp σ framework



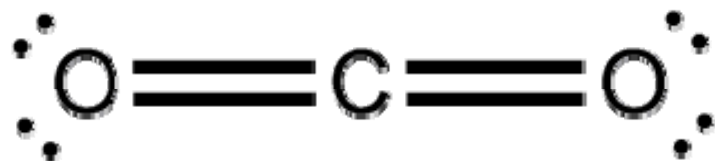
sp hybrids overlap to make  
***two sp σ bonding MO's,***  
leaving ***two sp nonbonding AO's.***  
These can hold ***4 pairs of electrons.***  
The remaining ...

# $\pi$ framework

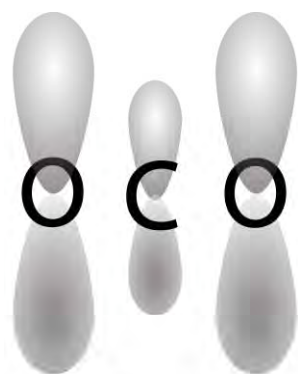
- Unused p AO's from same number of  $\pi$  MO's
- Number of loops and AO overlap determine whether  $\pi$  MO is
  - Bonding ( $\pi$ )
  - Nonbonding ( $\pi^n$ )
  - Antibonding ( $\pi^*$ )



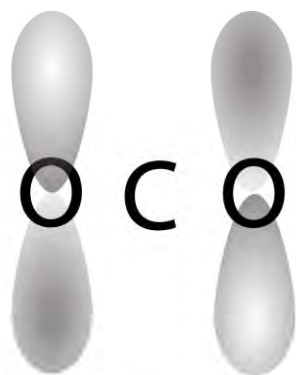
# CO<sub>2</sub> π framework



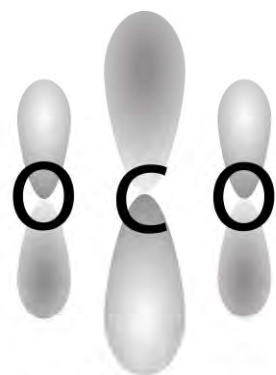
4 pairs are in the (*delocalized*) π framework



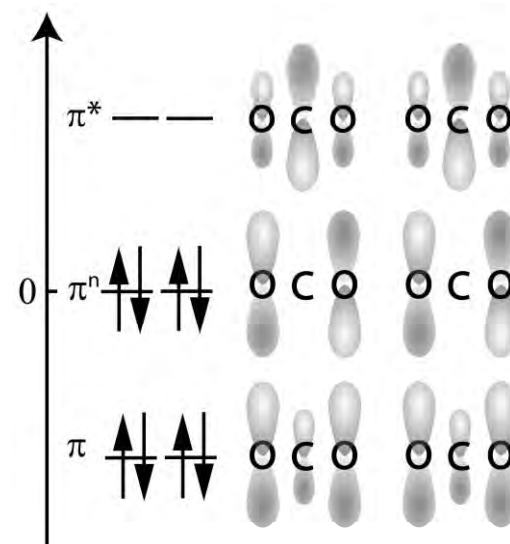
π (bonding)  
one loop  
mostly O



π<sup>n</sup> (nonbonding)  
two loops



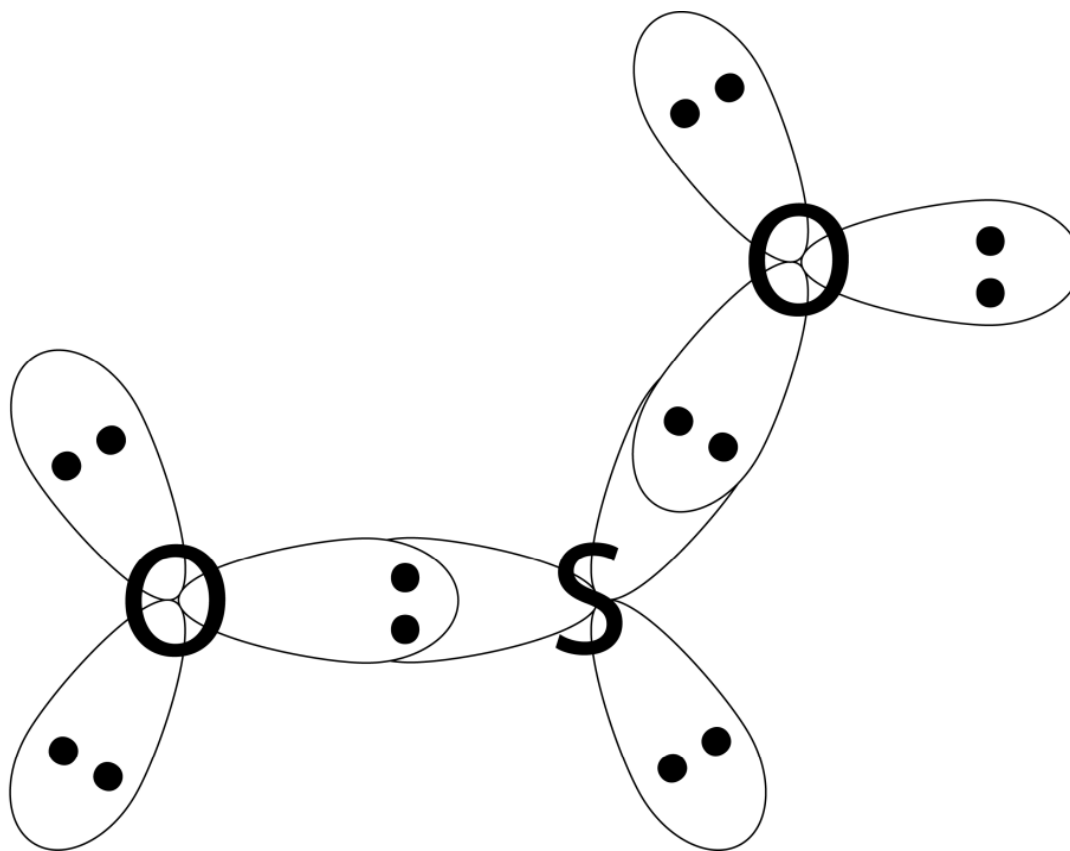
π\* (antibonding)  
three loops  
mostly C



2 pairs in π (bonding) and 2 pairs in π<sup>n</sup> (nonbonding);  
***bond order 2***

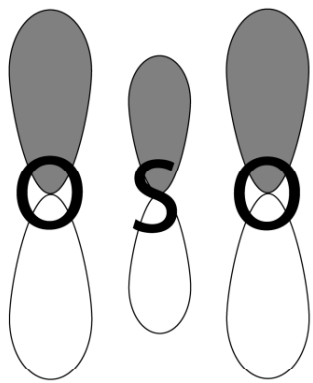
# SO<sub>2</sub> sp<sup>2</sup> σ framework

9 pairs in Lewis structure, 7 pairs in σ framework, and so 2 pairs in (*delocalized*) π framework.

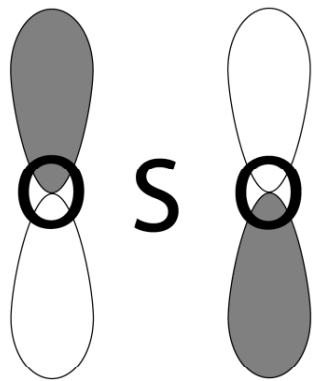


# SO<sub>2</sub> π framework

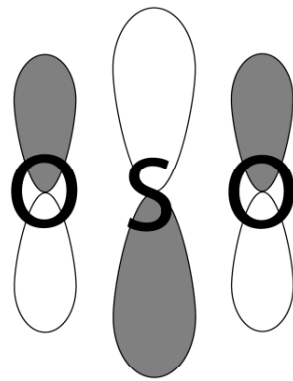
2 pairs in (*delocalized*) π framework



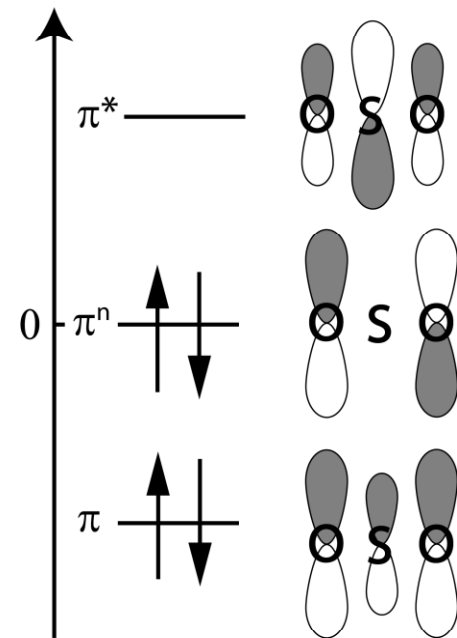
$\pi$  (bonding)  
one loop  
mostly O



$\pi^n$  (nonbonding)  
two loops

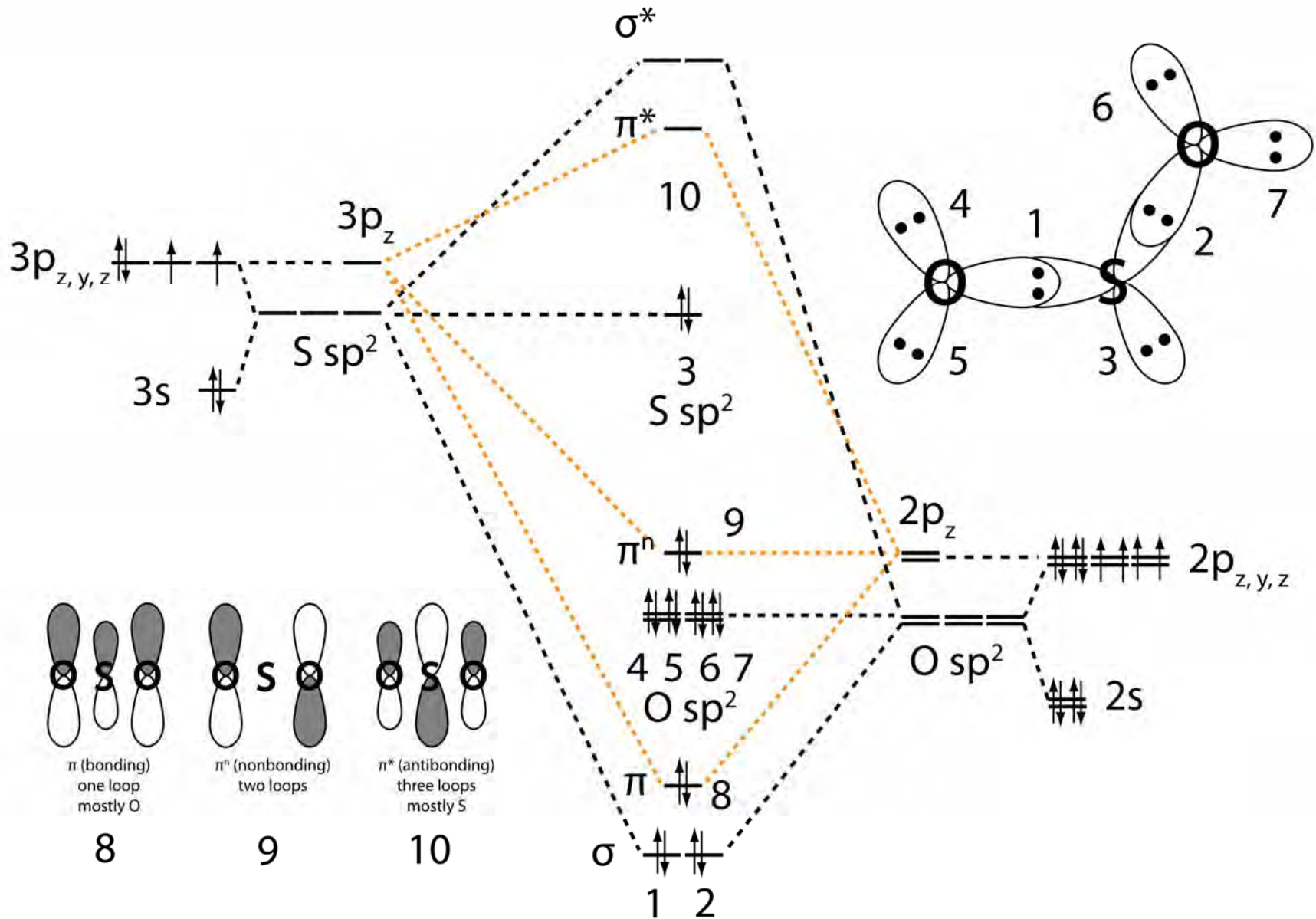


$\pi^*$  (antibonding)  
three loops  
mostly S



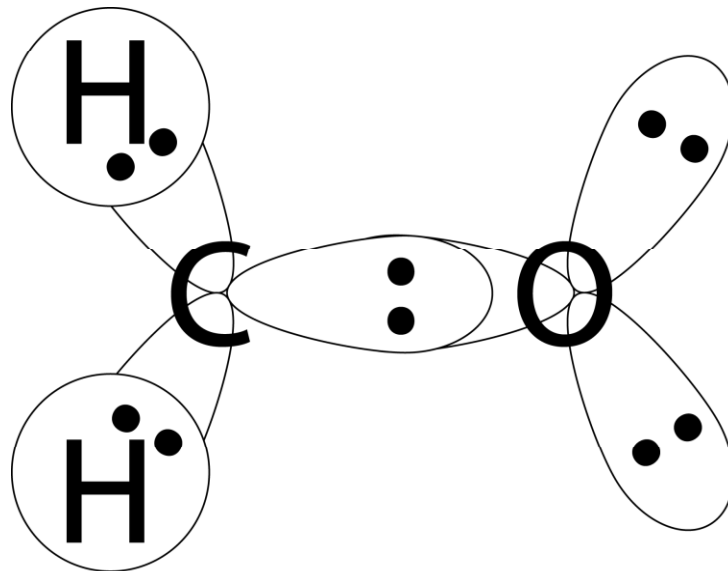
1 pair in  $\pi$  (bonding) and 1 pair in  $\pi^n$  (nonbonding);  
***bond order 1***

# SO<sub>2</sub> correlation diagram



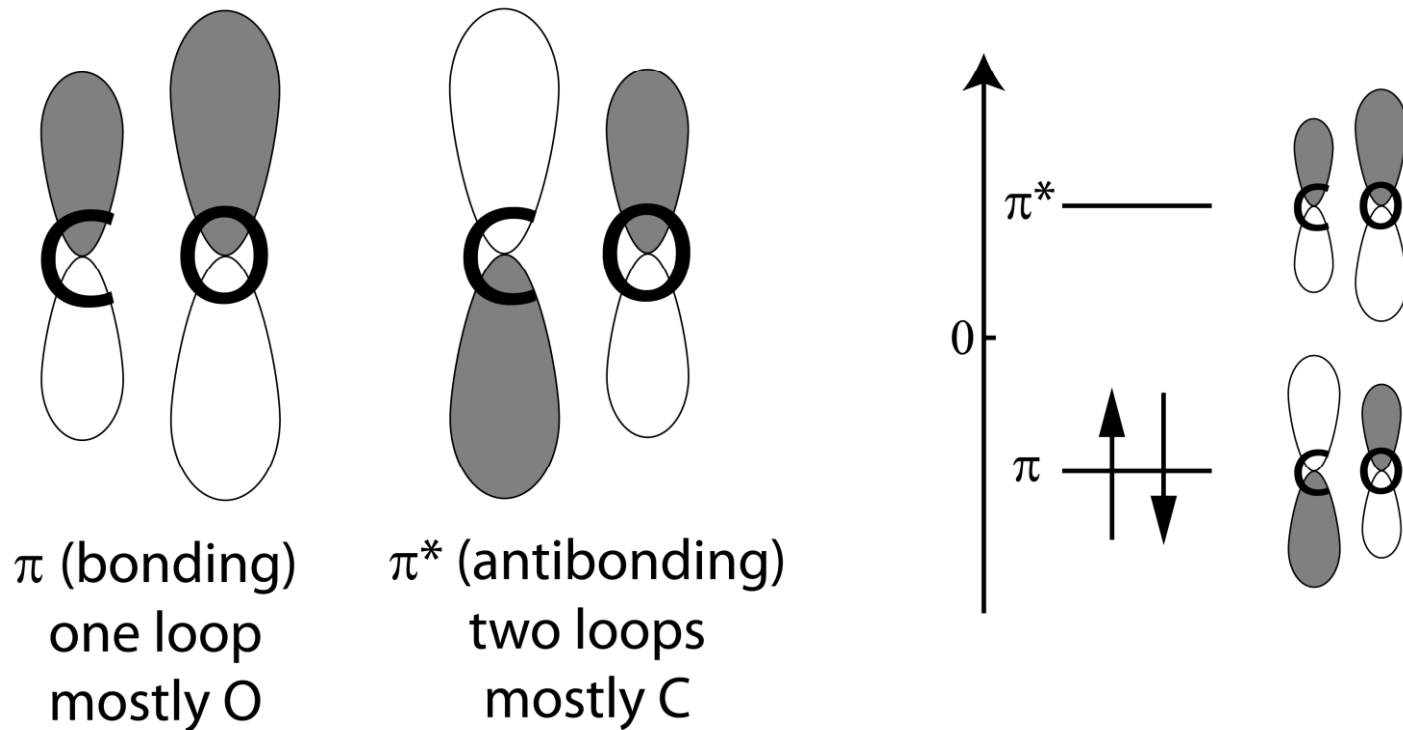
# H<sub>2</sub>CO sp<sup>2</sup> σ framework

6 pairs in Lewis structure, 5 pairs in σ framework, and so 1 pair in (*localized*) π framework.



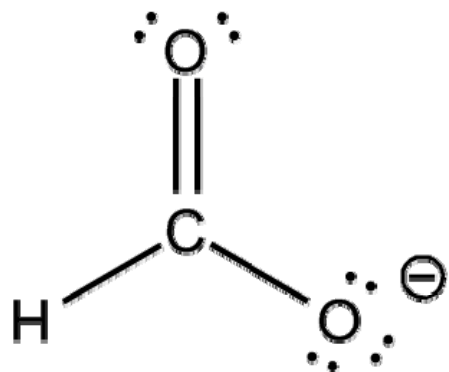
# H<sub>2</sub>CO $\pi$ framework

1 pair in (*localized*)  $\pi$  framework

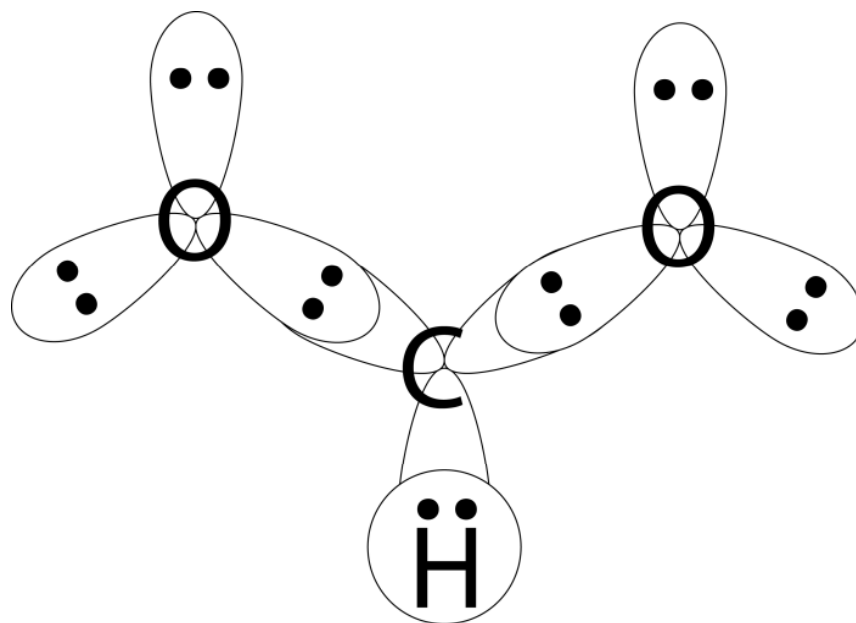


1 pair in  $\pi$  (bonding); **bond order 1**

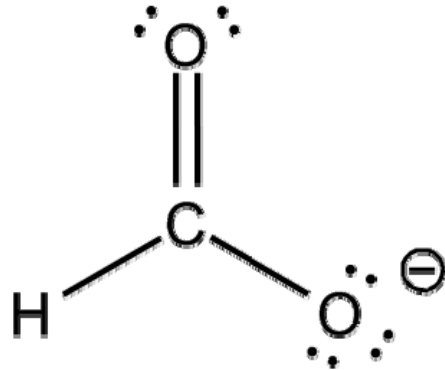
# HCOO<sup>-</sup> sp<sup>2</sup> σ framework



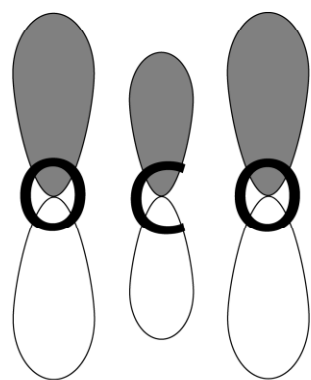
9 pairs in Lewis structure, 7 pairs in  $\sigma$  framework, and so 2 pairs in (*delocalized*)  $\pi$  framework.



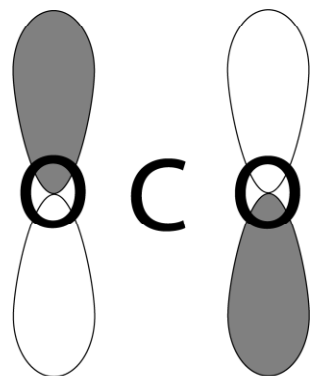
# HCOO<sup>-</sup> $\pi$ framework



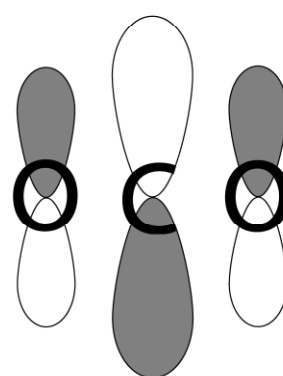
2 pairs in (*delocalized*)  $\pi$  framework



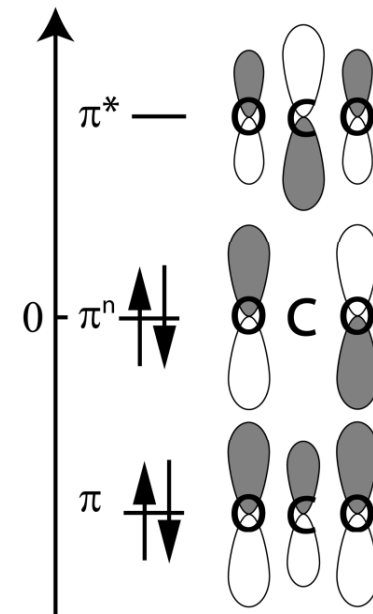
$\pi$  (bonding)  
one loop  
mostly O



$\pi^n$  (nonbonding)  
two loops

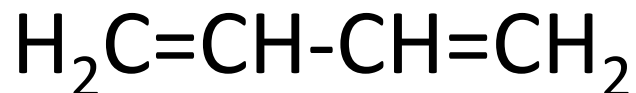


$\pi^*$  (antibonding)  
three loops  
mostly C



1 pair in  $\pi$  (bonding) and 1 pair in  $\pi^n$  (nonbonding);  
***bond order 1***

# Do these on your own



HCOOH, formic acid

$\text{NO}_3^-$ , nitrate

For each one,

- Lewis structure
- $\sigma$  framework and assign its pairs
- $\pi$  framework MO's, identify bonding, nonbonding, antibonding, assign remaining pairs, and get the  $\pi$  bond order