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

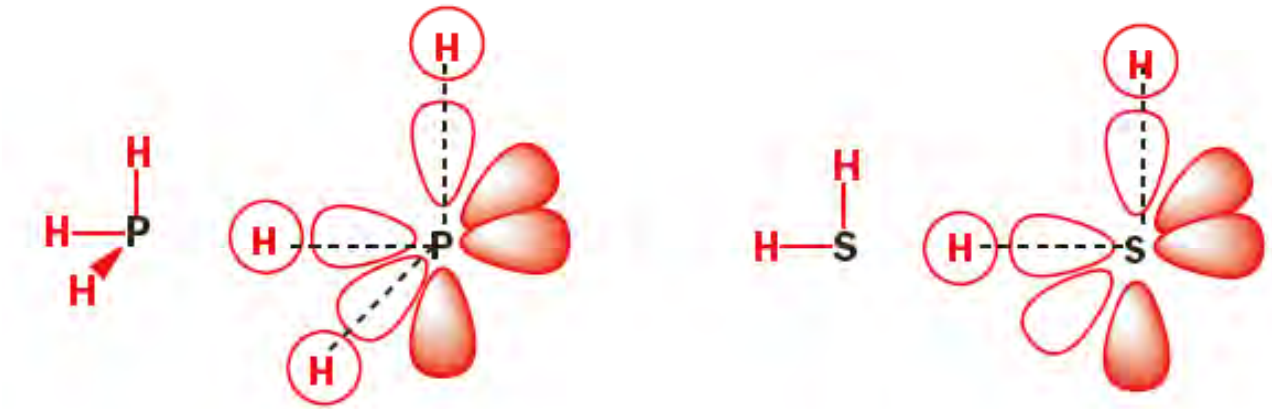
http://quantum.bu.edu/notes/GeneralChemistry/MORecipe.pdf

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 ***σ framework*** and ***place pairs***
   - in each ***bonding σ MO***
   - in each ***nonbonding hybrid AO***
3. Sketch the ***π framework MO's***,
   - mark as ***bonding***, ***nonbonding***, ***antibonding***
   - place ***remaining pairs*** (Auf Bau)
   - get the ***π bond order***

Central atom AO mixing: Hybrid AO's

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

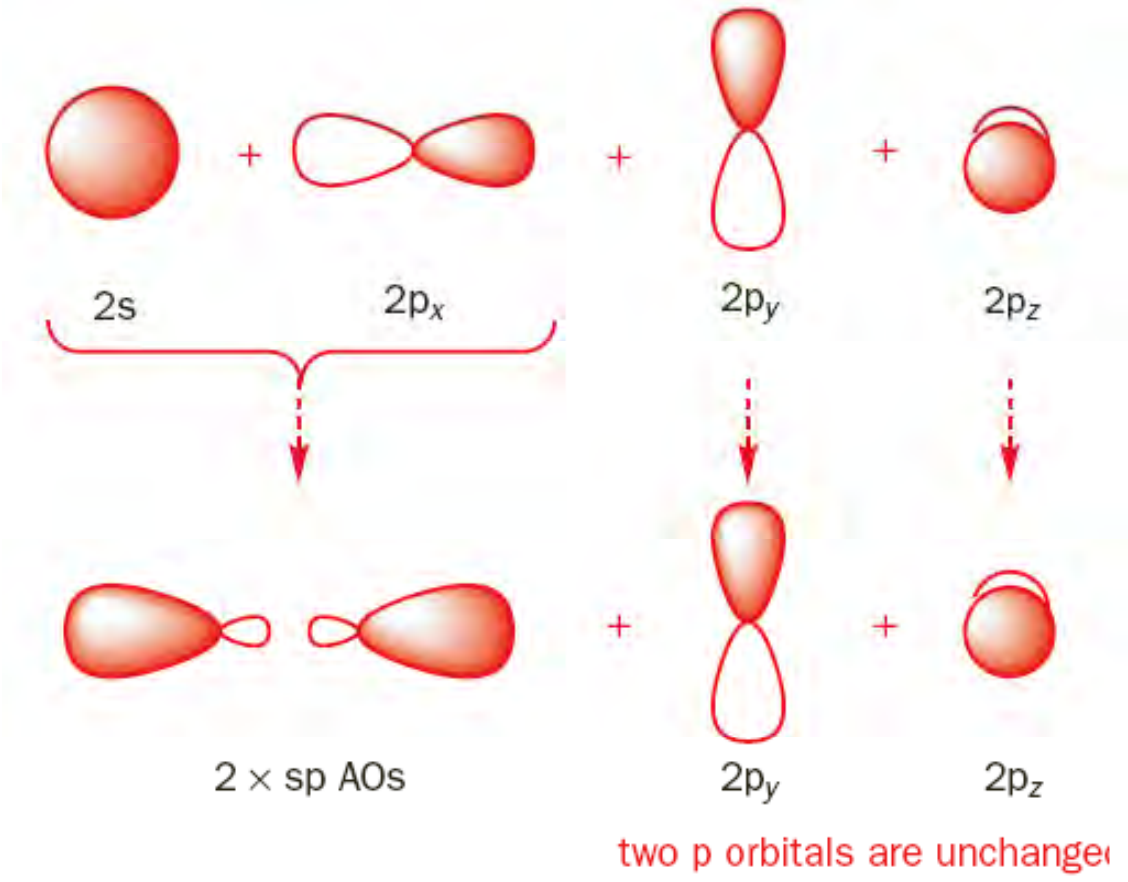


the 90° angles in PH_3 and H_2S come from the overlap of the hydrogen 1s AO with the p AO of the phosphorus or sulfur

An s and a p AO make two sp hybrid AO's

180° angle, for SN = 2

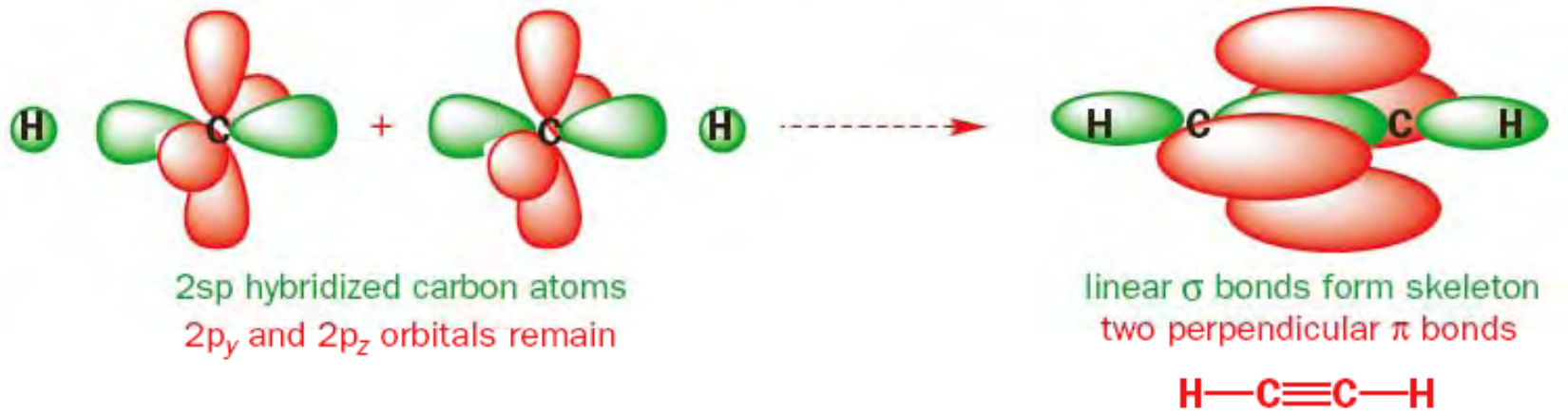
Two p's are unchanged on each atom



sp hybrids account for ***linear geometry***

180^{o} angle, for SN = 2

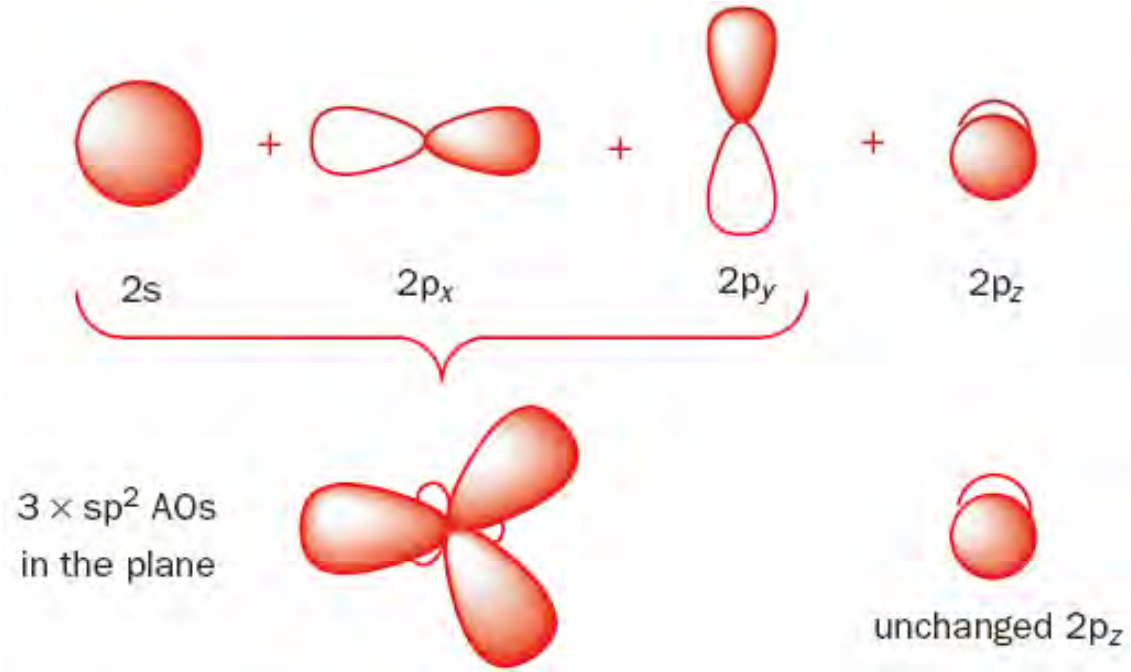
Two p's are unchanged on each atom



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

120° angle, for SN = 3

One p is unchanged on each atom



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

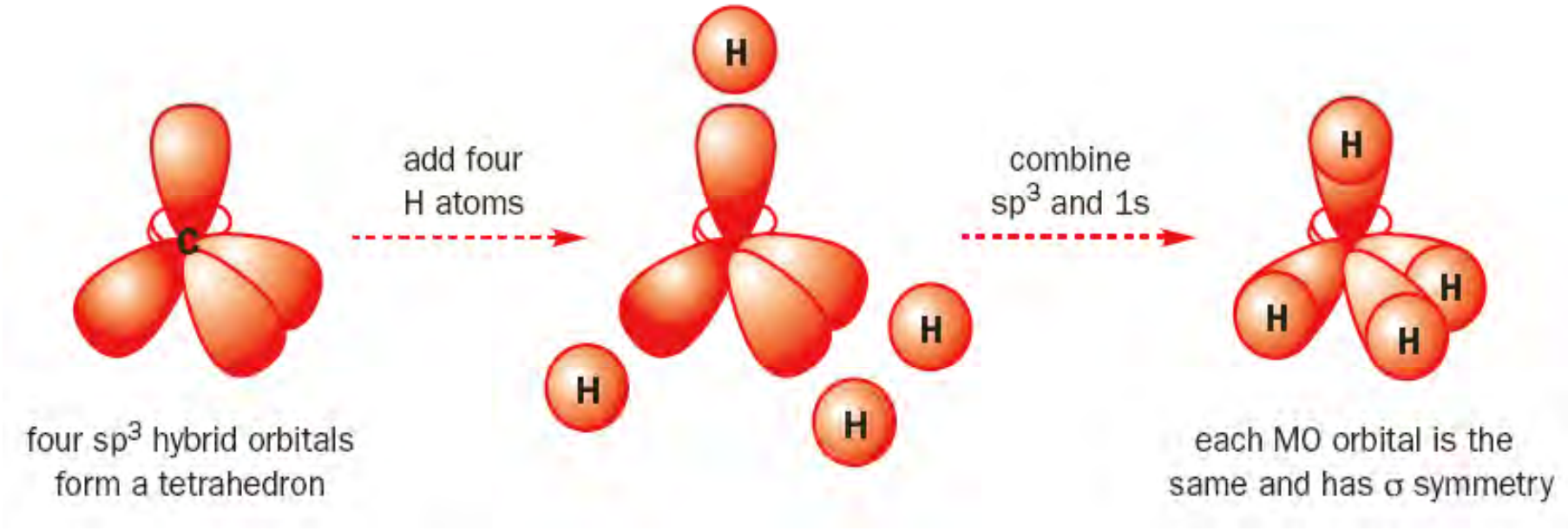
120^o angle, for SN = 3

One p is unchanged on each atom

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

109^o angle, for SN = 4

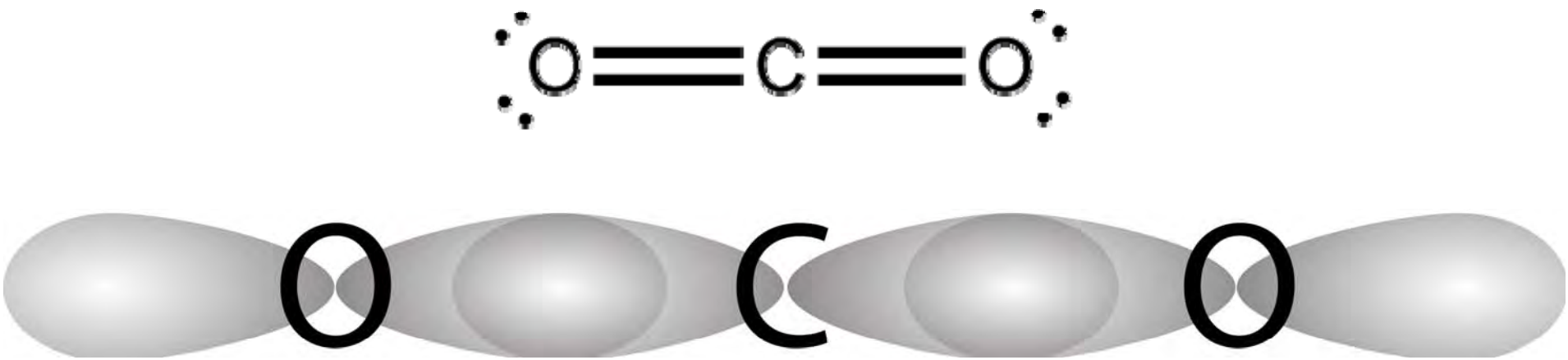
sp^3 hybrids account for ***tetrahedral geometry***



σ framework

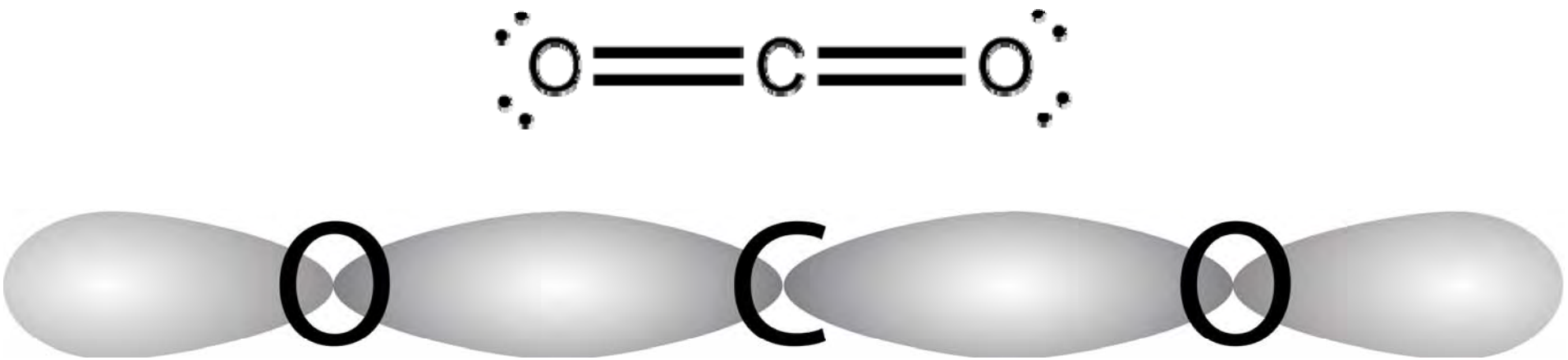
- Hybridization of terminal atoms the same as their central atom.
- Terminal H never hybridized
- One pair in each hybrid AO ***σ bonding MO***
- One pair in each ***non-bonded hybrid AO***

CO_2 sp σ framework



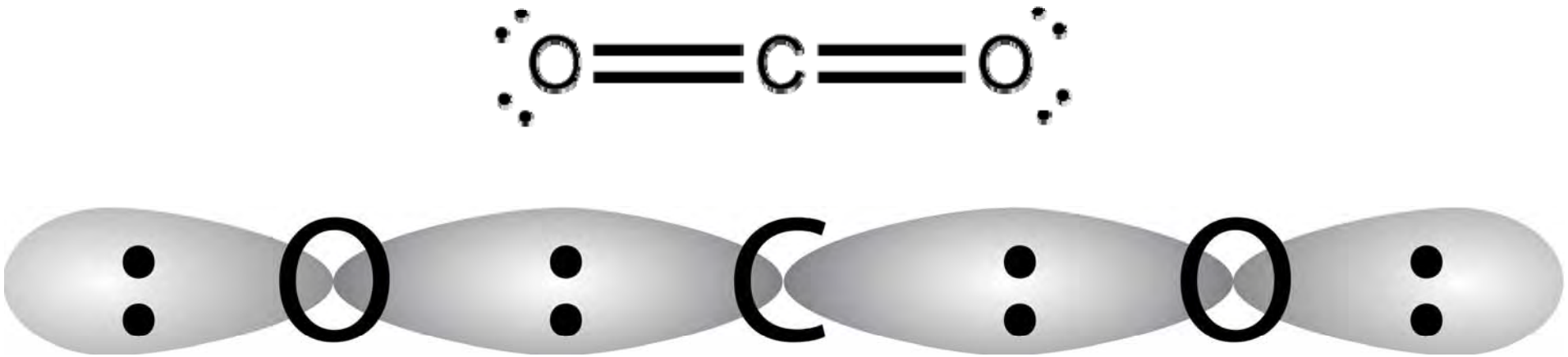
sp hybrids overlap to make…

CO_2 sp σ framework



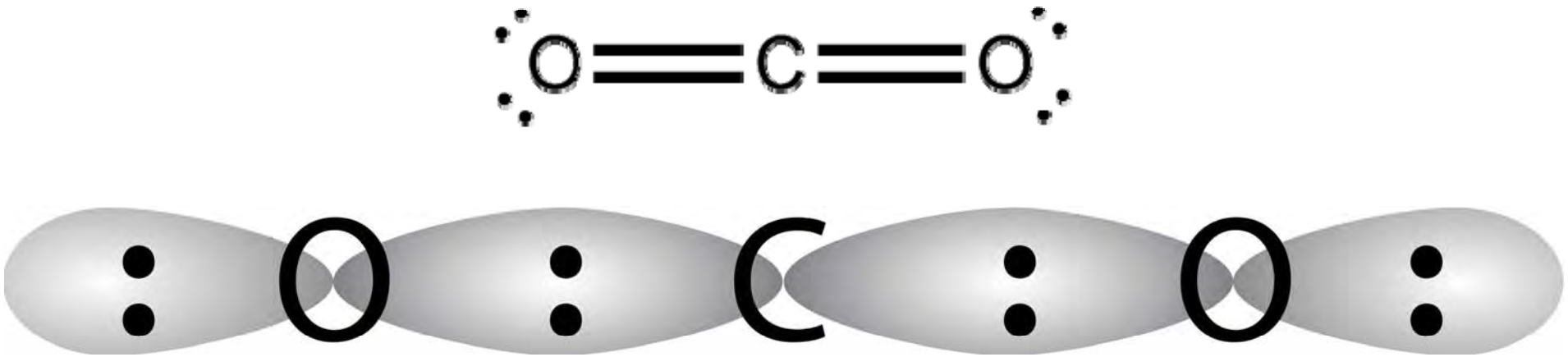
sp hybrids overlap to make
two sp σ bonding MO's,
leaving ***two sp nonbonding AO's***.
These can hold …

CO_2 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_2 sp σ framework

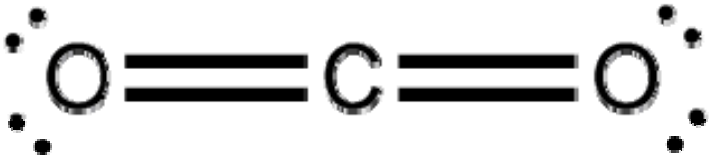


sp hybrids overlap to make
two sp σ bonding MO's,
leaving ***two sp nonbonding AO's***.
These can hold ***4 pairs of electrons***.
The remaining …

π framework

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

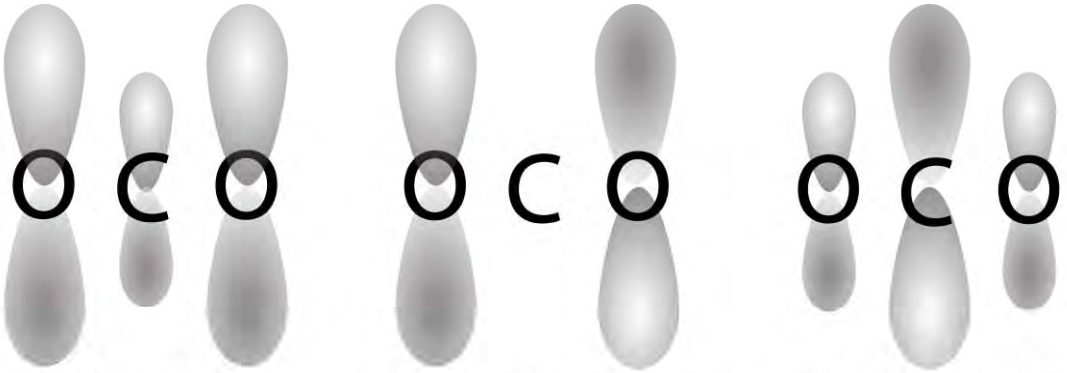
CO_2 π framework

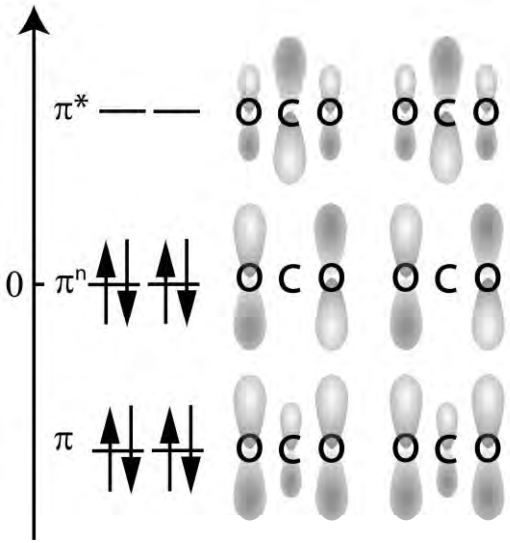


4 pairs are in the…

CO_2 π framework

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



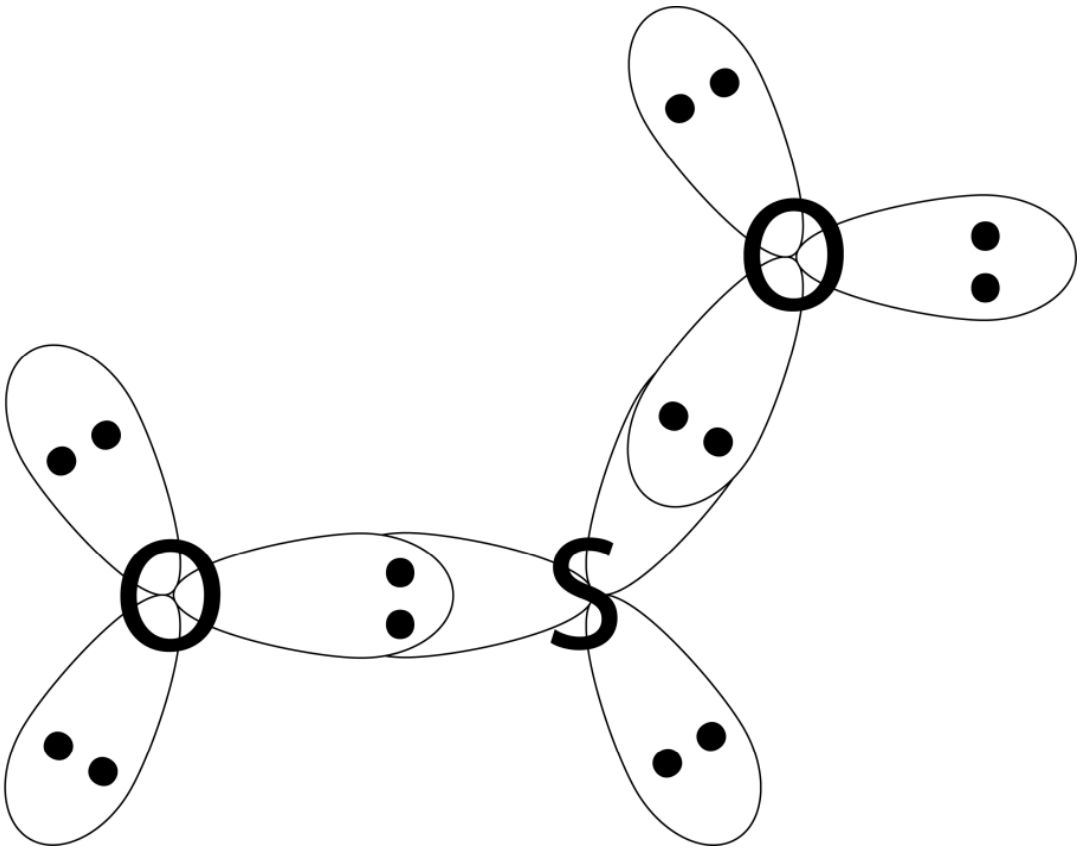


2 pairs in π (bonding) and 2 pairs in π^n (nonbonding);

bond order 2

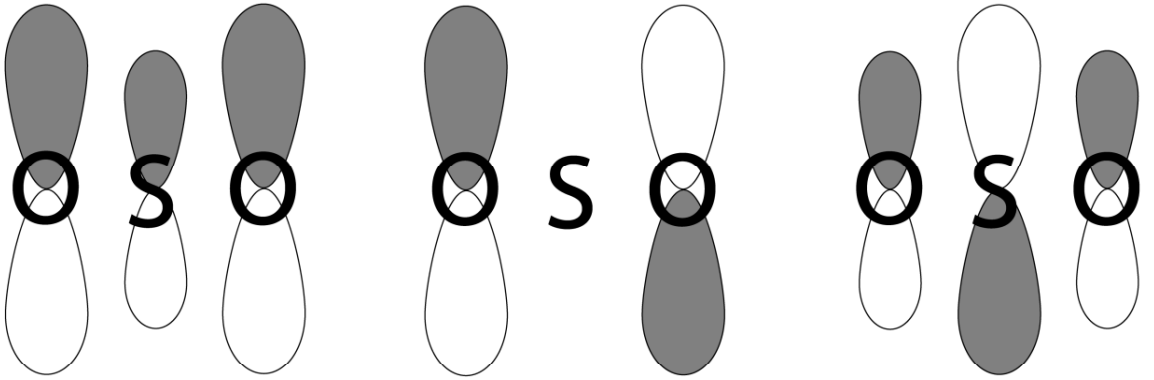
SO_2 sp^2 σ framework

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



SO_2 π framework

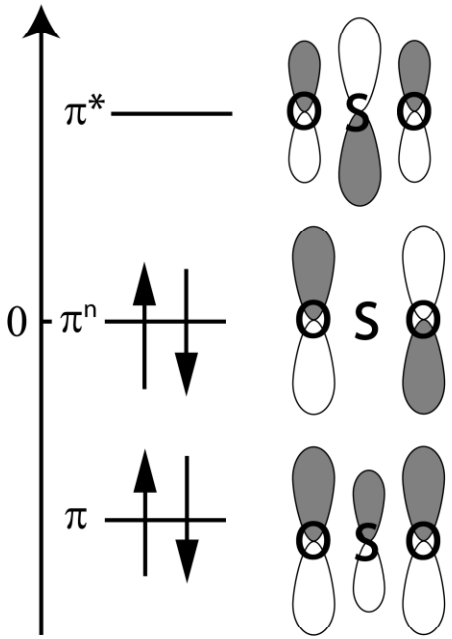
2 pairs in (***delocalized***) π framework



π (bonding)
one loop
mostly O

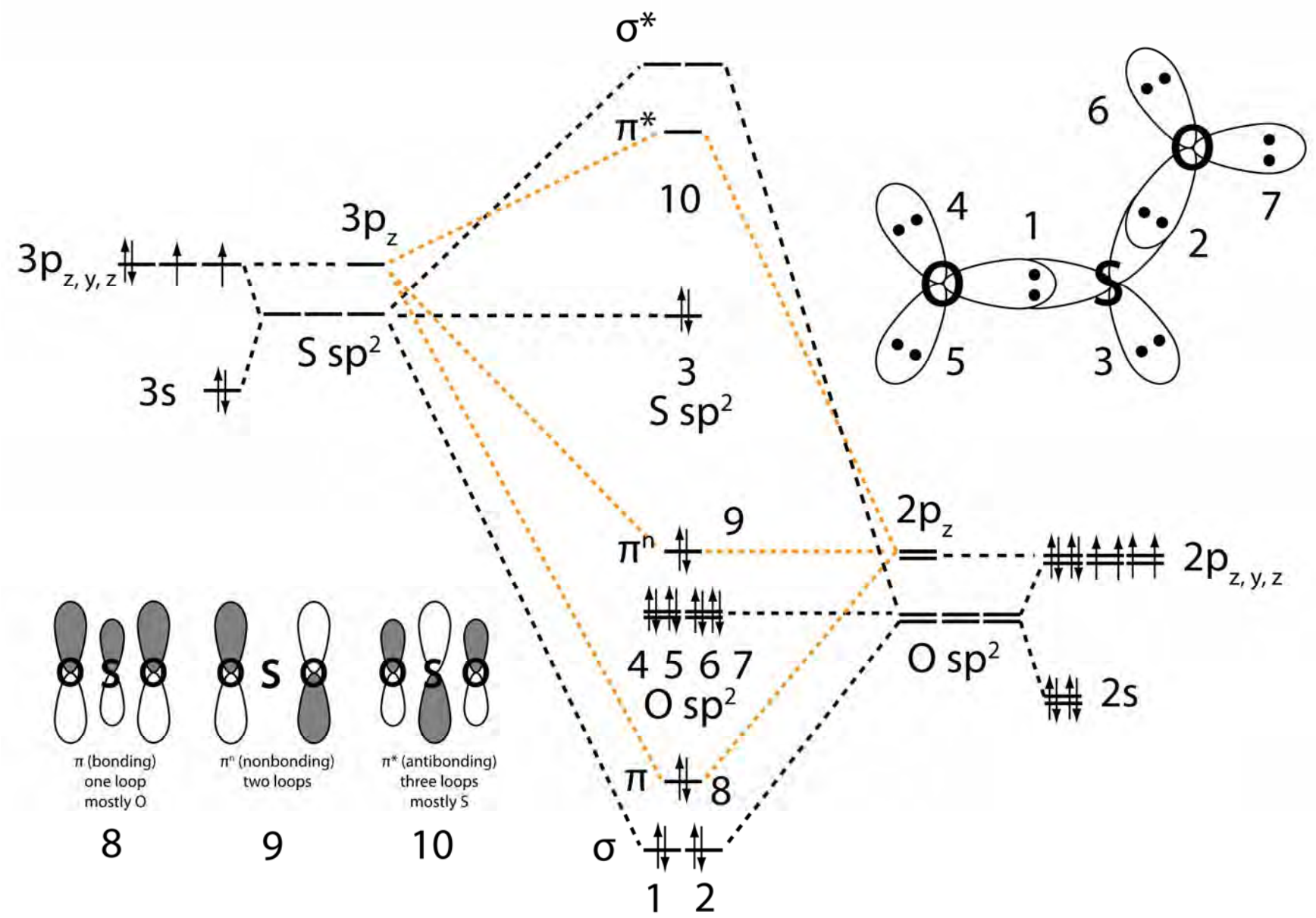
π^n (nonbonding)
two loops

π* (antibonding)
three loops
mostly S



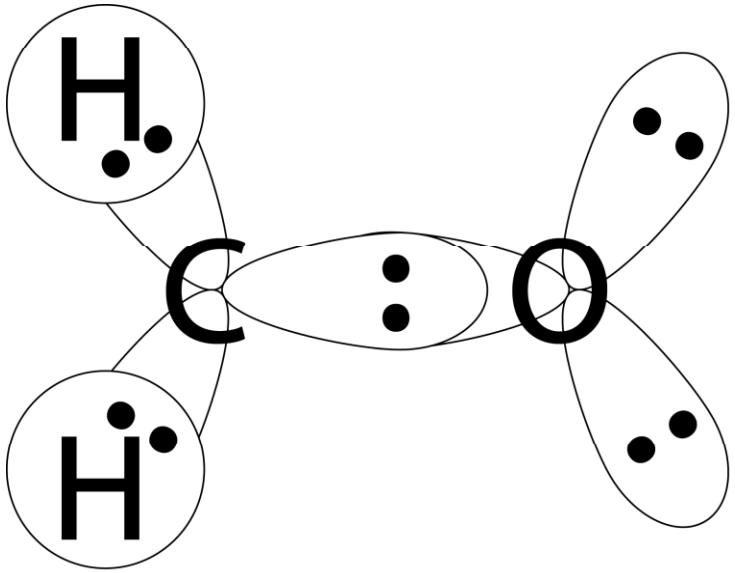
1 pair in π (bonding) and 1 pair in π^n (nonbonding);
bond order 1

SO_2 correlation diagram



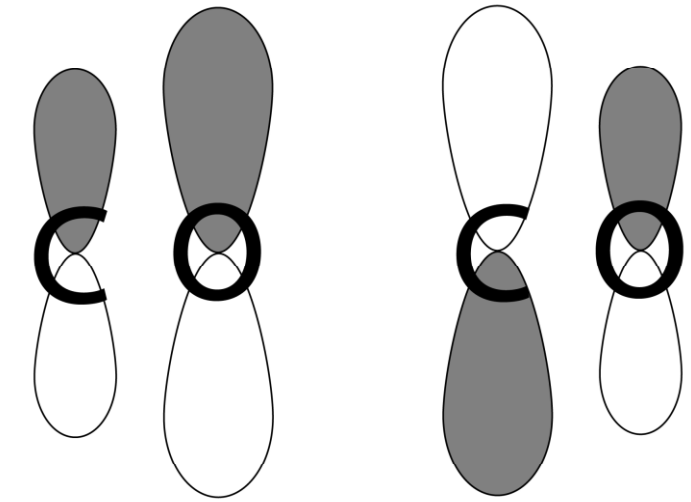
H_2CO sp^2 σ framework

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



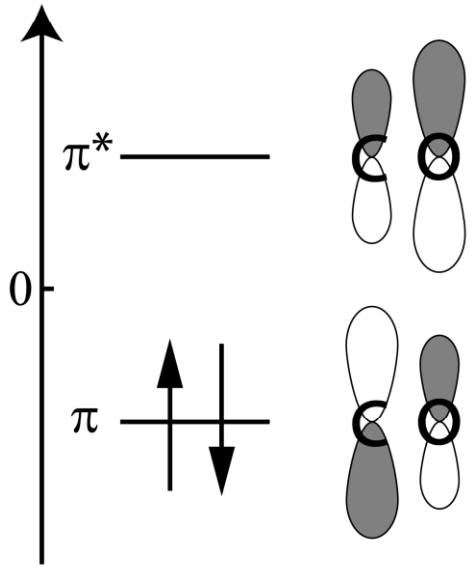
H_2CO π framework

1 pair in (***localized***) π framework



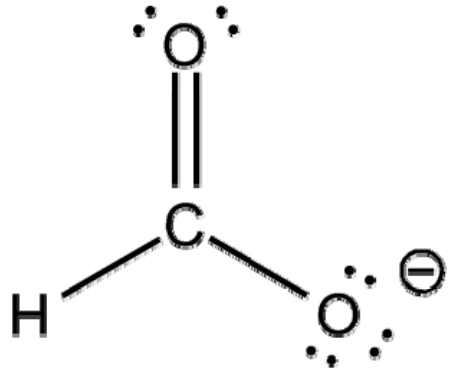
π (bonding)
one loop
mostly O

π* (antibonding)
two loops
mostly C

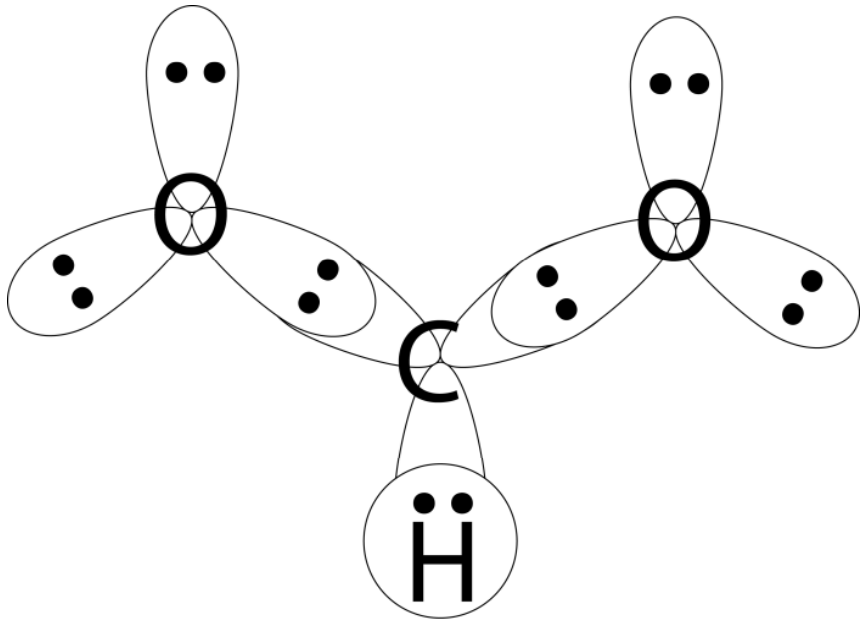


1 pair in π (bonding); ***bond order 1***

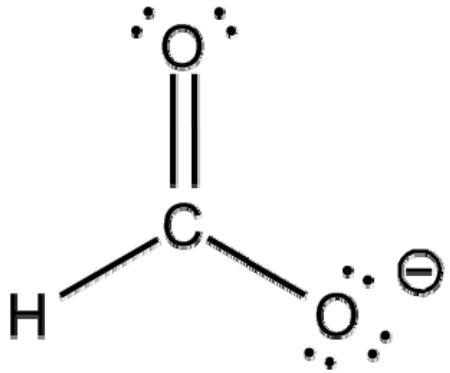
$HCOO^-$ sp^2 σ framework



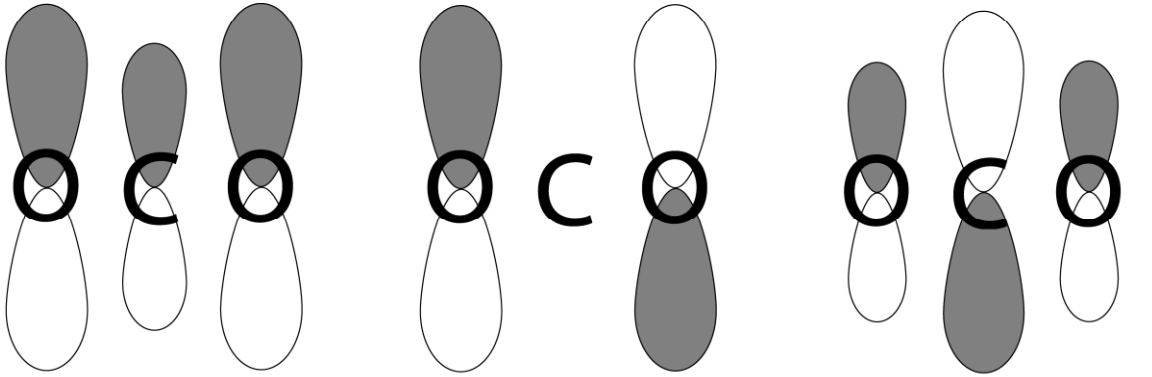
9 pairs in Lewis structure, 7 pairs in σ framework, and so 2 pairs in (***delocalized***) π framework.

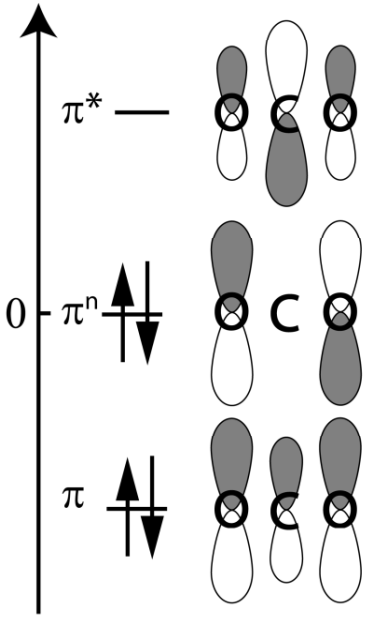


$HCOO^-$ π framework



2 pairs in (***delocalized***) π framework





1 pair in π (bonding) and 1 pair in π^n (nonbonding);

bond order 1

Do these on your own

$H_2C=CH-CH=CH_2$

HCOOH, formic acid

NO_3^-, nitrate

For each one,

- Lewis structure
- σ framework and assign its pairs
- π framework MO's, identify bonding, nonbonding, antibonding, assign remaining pairs, and get the π bond order