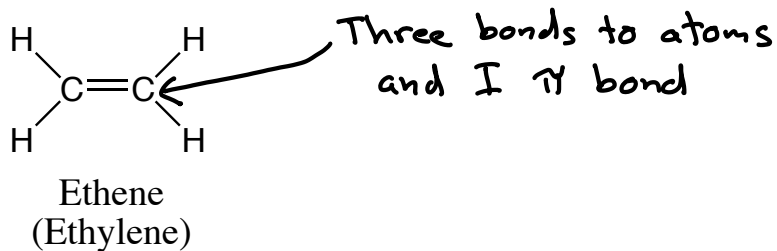




Review from up above!

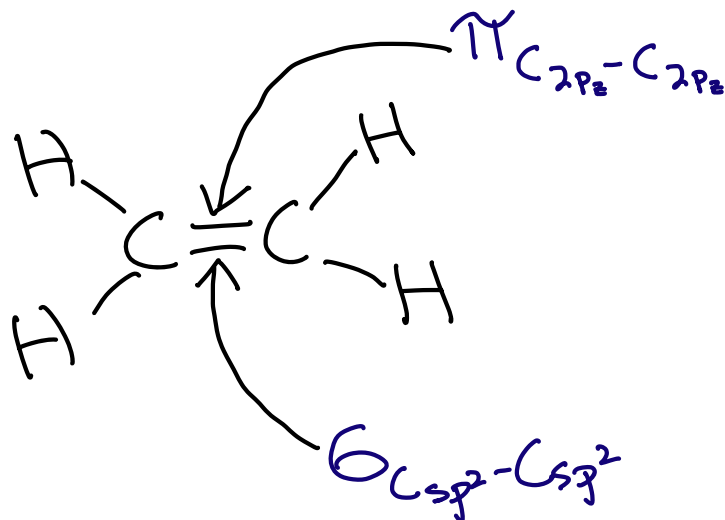
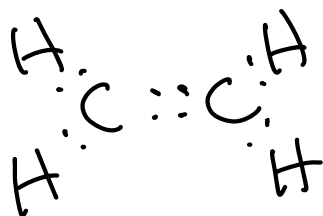
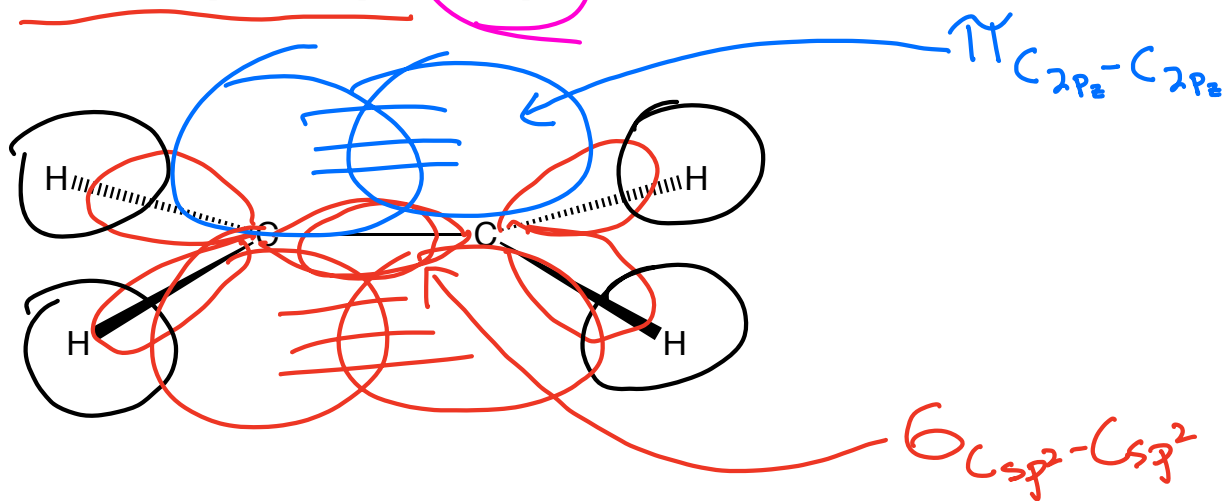


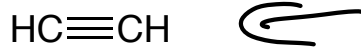
Molecular Orbital Theory approach to bonding: Just add the individual orbital wave functions:

$$\Psi_{H1s} + \Psi_{H1s} + \Psi_{H1s} + \Psi_{H1s} + \Psi_{C1s} + \Psi_{C2s} + \Psi_{C2px} + \Psi_{C2py} + \Psi_{C2pz} + \Psi_{C1s} + \Psi_{C2s} + \Psi_{C2px} + \Psi_{C2py} + \Psi_{C2pz}$$

Valence Bond Theory approach to bonding: Hybridize the atomic orbitals on atoms first, then look for overlap with remaining orbital wave functions:

$$\Psi_{H1s} + \Psi_{H1s} + \Psi_{H1s} + \Psi_{H1s} + \Psi_{C1s} + (\Psi_{C2s} + \Psi_{C2px} + \Psi_{C2py}) + \Psi_{C2pz} + \Psi_{C1s} + (\Psi_{C2s} + \Psi_{C2px} + \Psi_{C2py}) + \Psi_{C2pz}$$





Ethyne
(Acetylene)

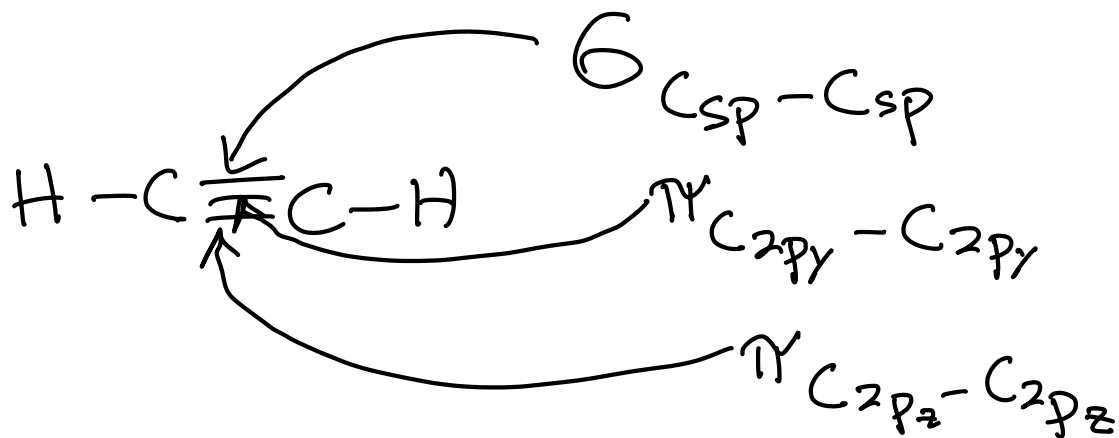
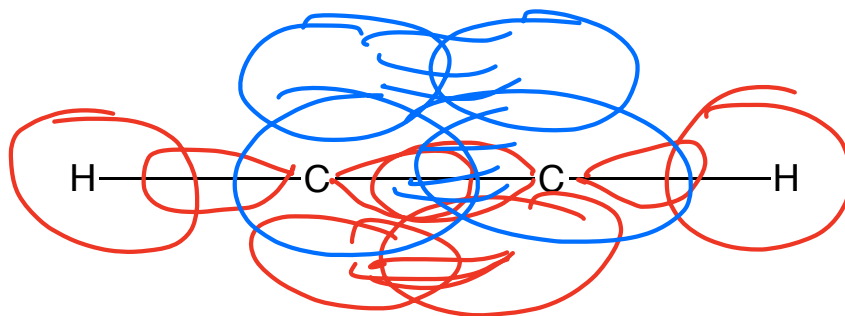
Molecular Orbital Theory approach to bonding: Just add the individual orbital wave functions:

$$\begin{aligned} &\Psi_{\text{H}1s} + \Psi_{\text{H}1s} + \Psi_{\text{C}1s} + \Psi_{\text{C}2s} + \Psi_{\text{C}2p_x} + \Psi_{\text{C}2p_y} + \Psi_{\text{C}2p_z} + \Psi_{\text{C}1s} \\ &+ \Psi_{\text{C}2s} + \Psi_{\text{C}2p_x} + \Psi_{\text{C}2p_y} + \Psi_{\text{C}2p_z} \end{aligned}$$

Valence Bond Theory approach to bonding: Hybridize the atomic orbitals on atoms first, then look for overlap with remaining orbital wave functions:

$$\begin{aligned} &\Psi_{\text{H}1s} + \Psi_{\text{H}1s} + \Psi_{\text{C}1s} + (\Psi_{\text{C}2s} + \Psi_{\text{C}2p_x}) + \Psi_{\text{C}2p_y} + \Psi_{\text{C}2p_z} + \Psi_{\text{C}1s} \\ &+ (\Psi_{\text{C}2s} + \Psi_{\text{C}2p_x}) + \Psi_{\text{C}2p_y} + \Psi_{\text{C}2p_z} \end{aligned}$$

(Handwritten annotations: a bracket labeled 's' under the first two H 1s orbitals; a bracket labeled 'sp' over the first C 2s and 2p_x orbitals; blue circles around the second C 2p_y and 2p_z orbitals; a blue circle around the second C 2p_y orbital; a blue circle around the second C 2p_z orbital.)



Line angle drawings → Ignore all H atoms bonded to C atoms → They are assumed to fill C valence shell

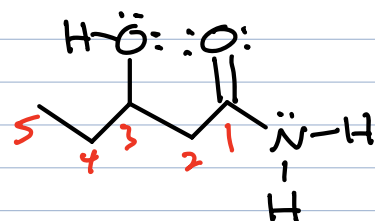
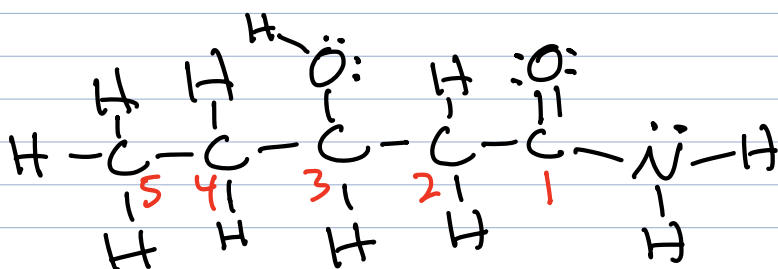
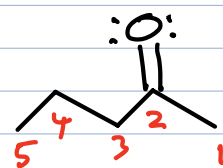
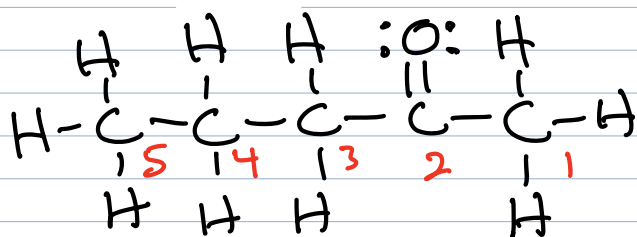
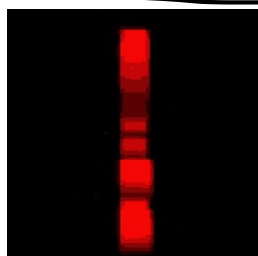
→ Draw all bonds and lone pairs → "zig-zag" → not C-H bonds

→ C atoms are assumed to be where each bond ends if not labeled

→ All non-C (N, O, F, Cl, Br, I, P, S etc.) atoms are labeled

→ All H atoms directly bonded to non-C atoms are shown

Pro tip → Number the C atoms



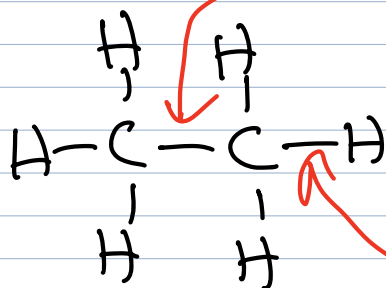
(The numbers are for reference only)

When we are:

σ bonds \rightarrow Best thought of as overlap of hybridized orbitals (or 1s on H atoms)

\rightarrow 2 electrons per σ bond

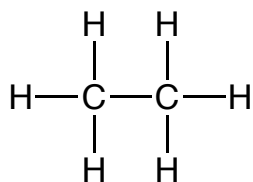
\rightarrow IGNORE antibonding orbitals when considering σ bonding in stable molecules.



$\sigma_{\text{Csp}^3-\text{Csp}^3}$

$\sigma_{\text{Csp}^3-\text{H}1s}$

Recall



Ethane

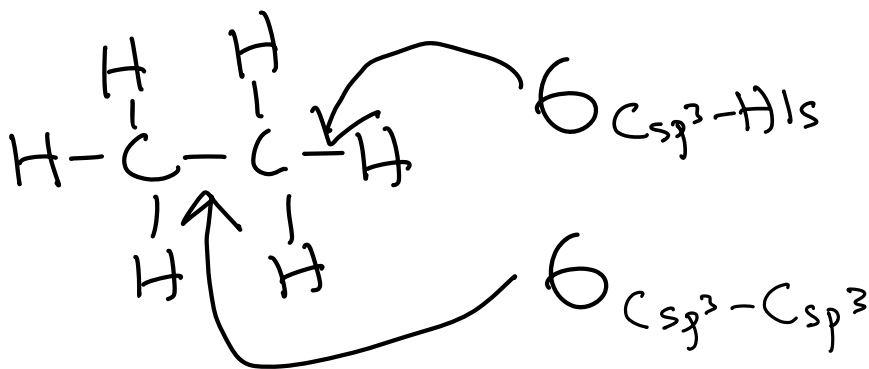
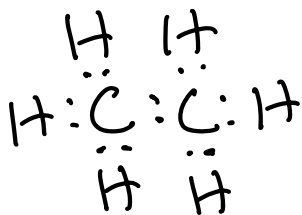
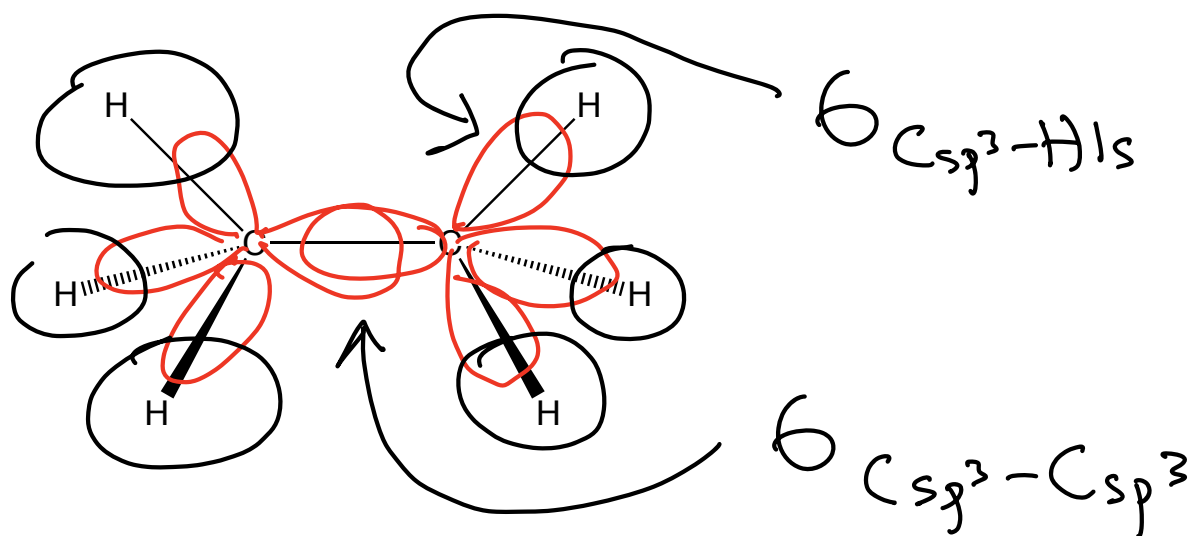
Molecular Orbital Theory approach to bonding: Just add the individual orbital wave functions:

$$\Psi_{\text{H}1s} + \Psi_{\text{H}1s} + \Psi_{\text{H}1s} + \Psi_{\text{H}1s} + \Psi_{\text{H}1s} + \Psi_{\text{H}1s} + \Psi_{\text{C}1s} + \Psi_{\text{C}2s} + \Psi_{\text{C}2p_x} \\
 + \Psi_{\text{C}2p_y} + \Psi_{\text{C}2p_z} + \Psi_{\text{C}1s} + \Psi_{\text{C}2s} + \Psi_{\text{C}2p_x} + \Psi_{\text{C}2p_y} + \Psi_{\text{C}2p_z}$$

Valence Bond Theory approach to bonding: Hybridize the atomic orbitals on atoms first, then look for overlap with remaining orbital wave functions:

$$\Psi_{\text{H}1s} + \Psi_{\text{H}1s} + \Psi_{\text{H}1s} + \Psi_{\text{H}1s} + \Psi_{\text{H}1s} + \Psi_{\text{H}1s} + \Psi_{\text{C}1s} + (\Psi_{\text{C}2s} + \Psi_{\text{C}2p_x} \\
 + \Psi_{\text{C}2p_y} + \Psi_{\text{C}2p_z}) + \Psi_{\text{C}1s} + (\Psi_{\text{C}2s} + \Psi_{\text{C}2p_x} + \Psi_{\text{C}2p_y} + \Psi_{\text{C}2p_z})$$

$\begin{matrix} s p^3 & & s p^3 \end{matrix}$



π bonds \rightarrow For cases in π bonds between only 2 atoms

1) Overlap of unhybridized $2p$ orbitals
 \rightarrow atoms must be sp^2 or sp

2) 2 electrons per π bond

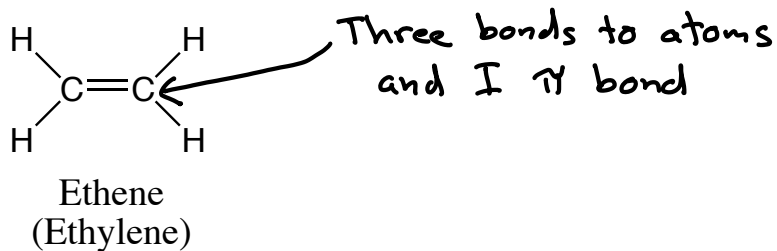
3) We ignore antibonding orbitals when considering bonding and structure

HOWEVER \rightarrow π bonds can extend over more than

2 atoms \rightarrow described by molecular orbital theory \rightarrow these extended π bonding orbitals still only contain 2 electrons

NOT consistent with Lewis structures \rightarrow this is why we have contributing structures!!

Review from up above!

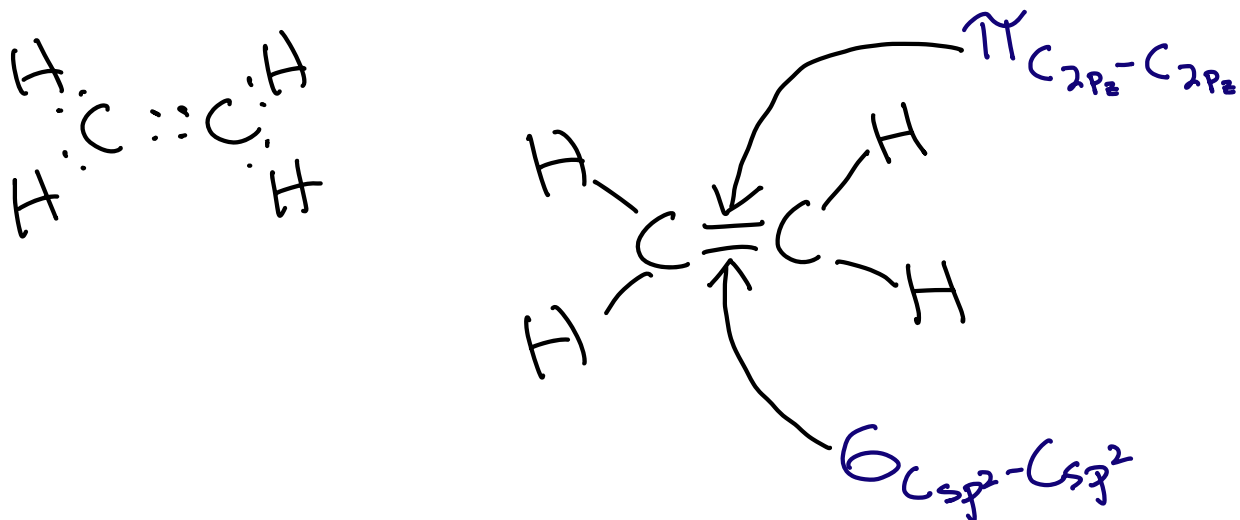
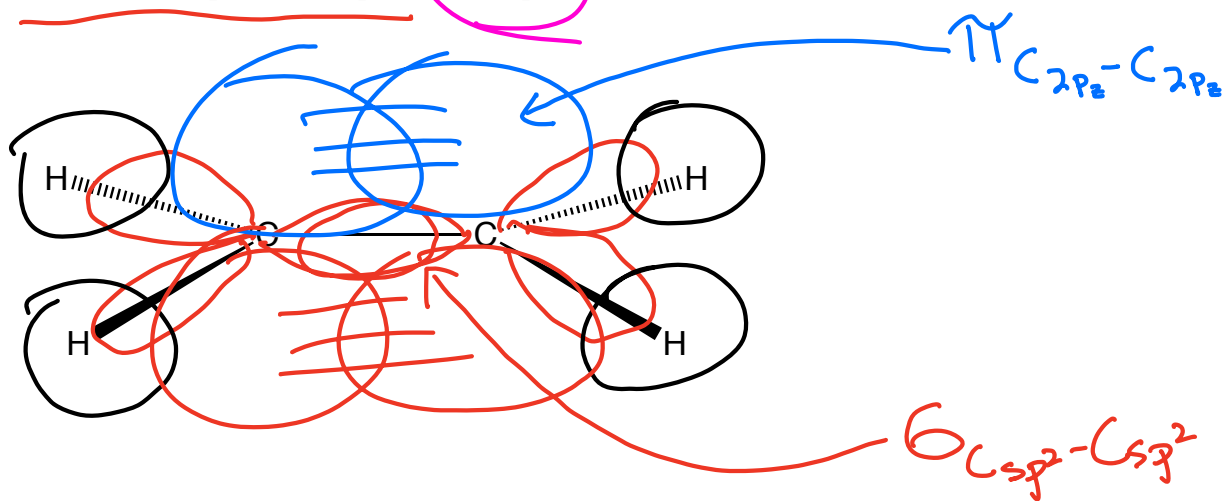


Molecular Orbital Theory approach to bonding: Just add the individual orbital wave functions:

$$\Psi_{H1s} + \Psi_{H1s} + \Psi_{H1s} + \Psi_{H1s} + \Psi_{C1s} + \Psi_{C2s} + \Psi_{C2px} + \Psi_{C2py} + \Psi_{C2pz} + \Psi_{C1s} + \Psi_{C2s} + \Psi_{C2px} + \Psi_{C2py} + \Psi_{C2pz}$$

Valence Bond Theory approach to bonding: Hybridize the atomic orbitals on atoms first, then look for overlap with remaining orbital wave functions:

$$\Psi_{H1s} + \Psi_{H1s} + \Psi_{H1s} + \Psi_{H1s} + \Psi_{C1s} + (\Psi_{C2s} + \Psi_{C2px} + \Psi_{C2py}) + \Psi_{C2pz} + \Psi_{C1s} + (\Psi_{C2s} + \Psi_{C2px} + \Psi_{C2py}) + \Psi_{C2pz}$$





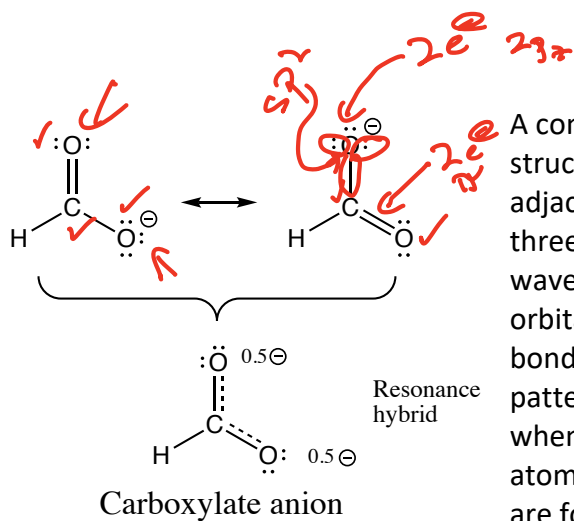
Molecular Orbital Theory

→ To quantify bonding in molecules we simply add all of the atomic orbital wave functions in the molecule

1) This creates as many new molecular orbitals as there are component orbitals being added.

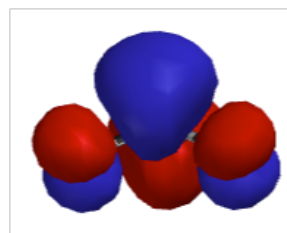
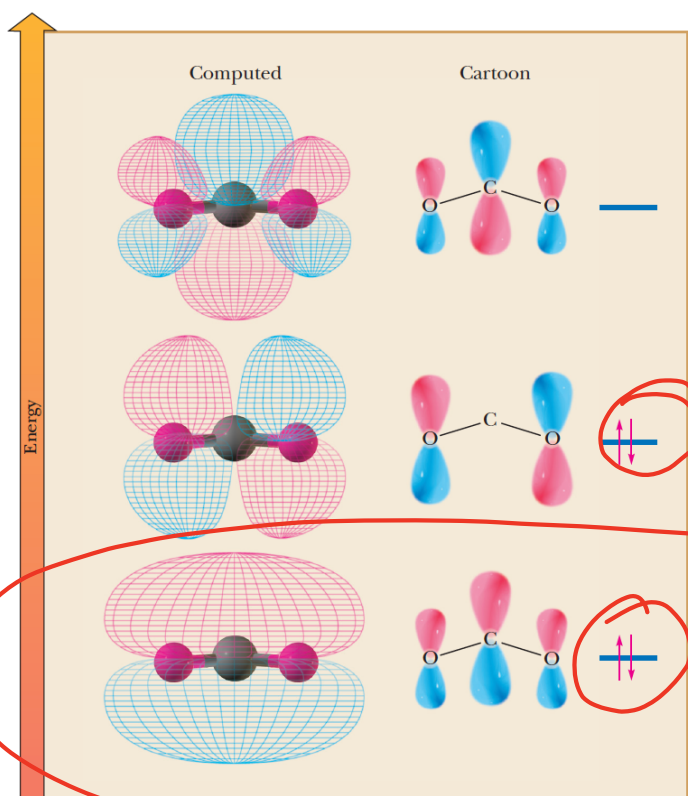
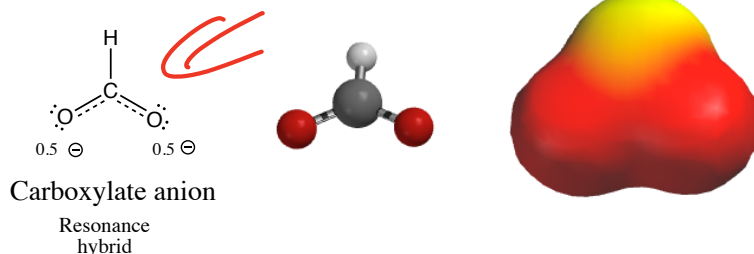
2) Each molecular orbital extends over the ENTIRE molecule

★ 3) Each new molecular orbital contains up to the electron density equal to 2 electrons
⇒ NEVER MORE

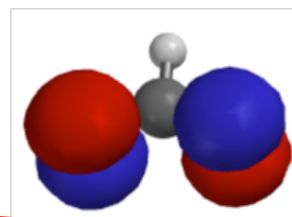


A common situation, and the one many resonance contributing structures describe, occurs when three 2p orbitals combine on adjacent atoms. A good example is the carboxylate anion. When three adjacent 2p orbitals interact (we add the three 2p orbital wave functions $\Psi_{C2pz} + \Psi_{O2pz} + \Psi_{O2pz}$), three new molecular orbitals are produced; a low energy bonding "pi-way", a non-bonding orbital and an antibonding orbital as shown below. This pattern of three molecular orbitals is generally the same whenever three 2p orbitals interact even if there are different atoms involved, for example the enolate ion or allyl cation. There are four electrons in the pi system of the carboxylate anion, (you can see this by looking at either of the contributing structures; two electrons from the pi bond and two from the third lone pair on the negatively charge O atom). Note the non-bonding orbital contains the electron density of two electrons that are paired, do NOT think of it as having one unpaired electron on each O atom. I know, weird, but remember it is best to think of bonding electrons as waves, not particles. Note the electron density on only the O atoms of the non-bonding orbital explains why the negative charge is localized on the O atoms in the carboxylate anion.

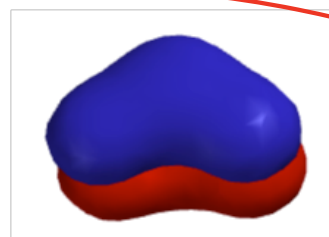
$$\Psi_{C2pz} + \Psi_{O2pz} + \Psi_{O2pz}$$



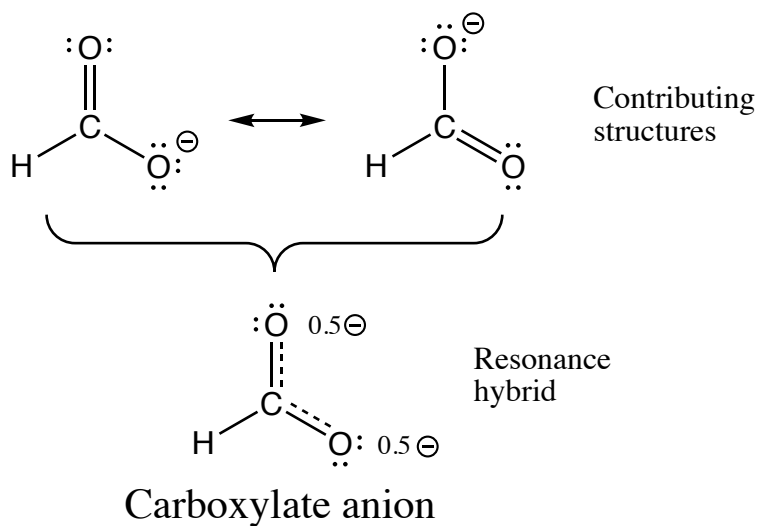
Antibonding orbital



Non-bonding orbital



"pi-way" orbital



Molecular Orbital Theory approach to bonding: Just add the individual orbital wave functions:

$$\Psi_{H1s} + \Psi_{C1s} + \Psi_{C2s} + \Psi_{C2px} + \Psi_{C2py} + \Psi_{C2pz} + \Psi_{O1s} + \Psi_{O2s} + \Psi_{O2px} + \Psi_{O2py} + \Psi_{O2pz} + \Psi_{O1s} + \Psi_{O2s} + \Psi_{O2px} + \Psi_{O2py} + \Psi_{O2pz}$$

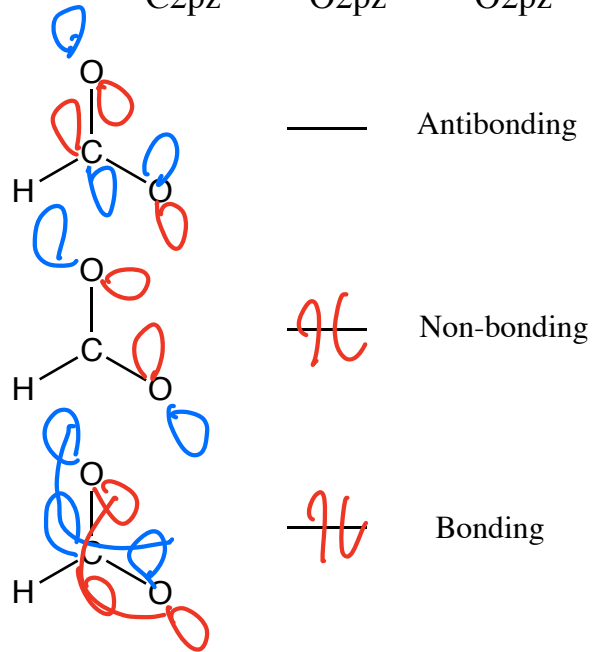
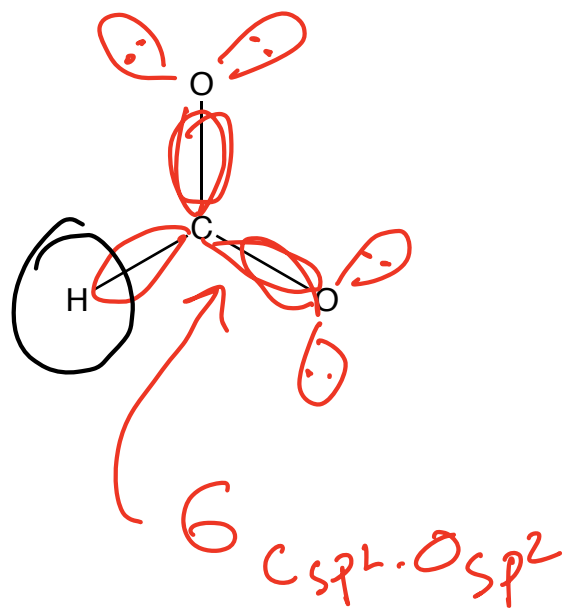
Valence Bond Theory approach to bonding: Hybridize the atomic orbitals on atoms first, then look for overlap with remaining orbital wave functions:

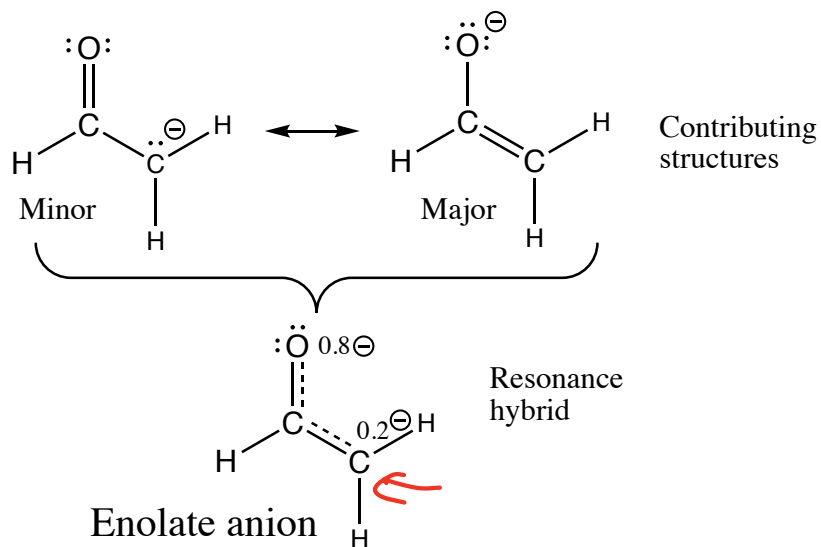
$$\Psi_{H1s} + \Psi_{C1s} + (\Psi_{C2s} + \Psi_{C2px} + \Psi_{C2py}) + \Psi_{C2pz} + \Psi_{O1s} + (\Psi_{O2s} + \Psi_{O2px} + \Psi_{O2py}) + \Psi_{O2pz} + \Psi_{O1s} + (\Psi_{O2s} + \Psi_{O2px} + \Psi_{O2py}) + \Psi_{O2pz}$$

Sigma (σ) bonding - overlap of hybridized orbitals

π -way bonding - overlap of 3 adjacent unhybridized 2p orbitals

$$\Psi_{C2pz} + \Psi_{O2pz} + \Psi_{O2pz}$$





Molecular Orbital Theory approach to bonding: Just add the individual orbital wave functions:

$$\Psi_{H1s} + \Psi_{H1s} + \Psi_{H1s} + \Psi_{C1s} + \Psi_{C2s} + \Psi_{C2px} + \Psi_{C2py} + \Psi_{C2pz} + \Psi_{C1s} + \Psi_{C2s} + \Psi_{C2px} + \Psi_{C2py} + \Psi_{C2pz} + \Psi_{O1s} + \Psi_{O2s} + \Psi_{O2px} + \Psi_{O2py} + \Psi_{O2pz}$$

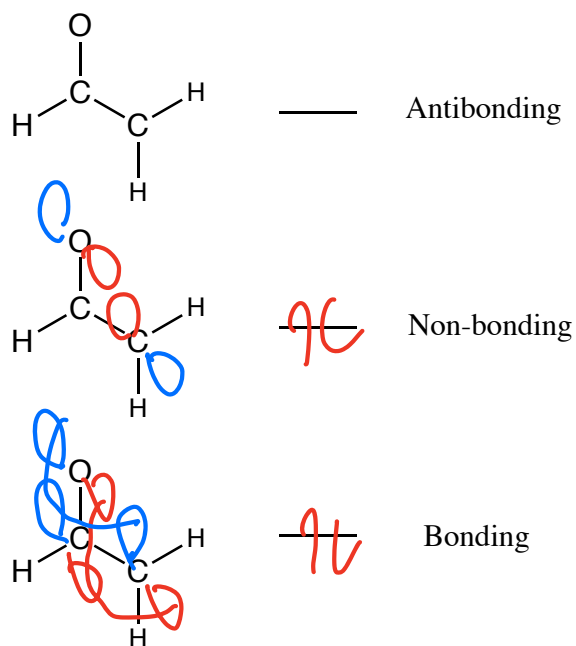
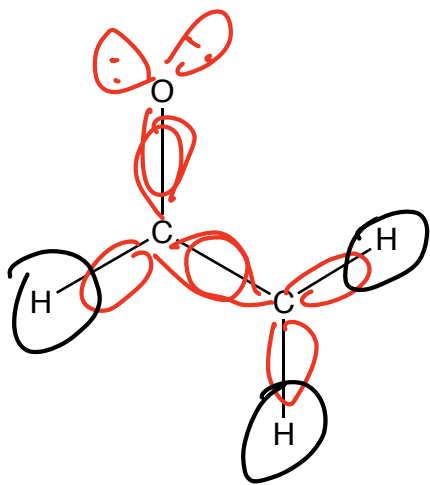
Valence Bond Theory approach to bonding: Hybridize the atomic orbitals on atoms first, then look for overlap with remaining orbital wave functions:

$$\Psi_{H1s} + \Psi_{H1s} + \Psi_{H1s} + \Psi_{C1s} + (\Psi_{C2s} + \Psi_{C2px} + \Psi_{C2py}) + \Psi_{C2pz} + \Psi_{C1s} + (\Psi_{C2s} + \Psi_{C2px} + \Psi_{C2py}) + \Psi_{C2pz} + \Psi_{O1s} + (\Psi_{O2s} + \Psi_{O2px} + \Psi_{O2py}) + \Psi_{O2pz}$$

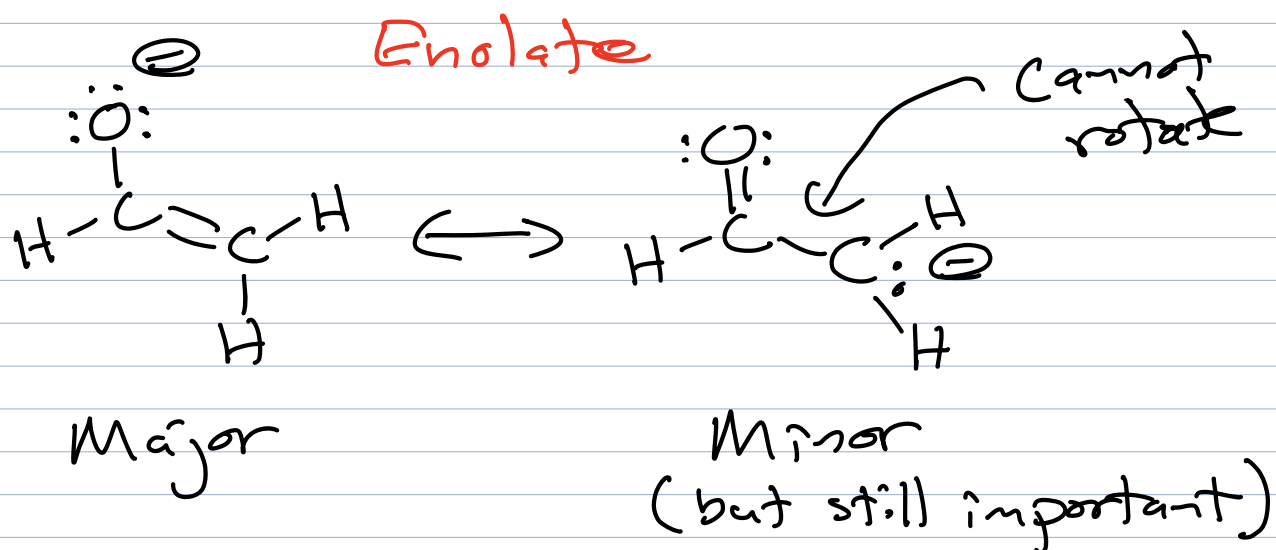
Sigma (σ) bonding - overlap of hybridized orbitals

π -way bonding - overlap of 3 adjacent unhybridized 2p orbitals

$$\Psi_{C2pz} + \Psi_{C2pz} + \Psi_{O2pz}$$



What have we learned?



→ This anion is more stable than you might think

1) Delocalization of a charge is stabilizing
(Golden Rule #5)

The \ominus is delocalized on
both O and C atoms

2) Delocalization of π electron density
over a larger area is stabilizing
(Golden Rule #7)

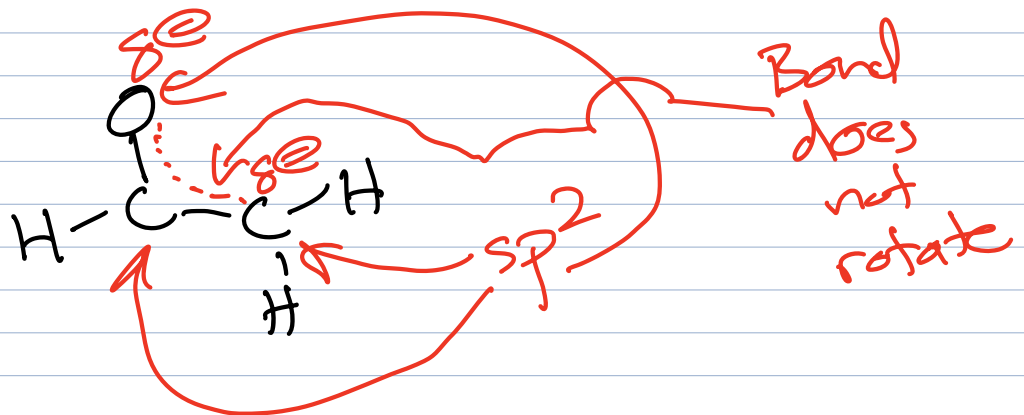
Epic structural considerations:

1) There is partial double bond
character between all
three atoms of the π way

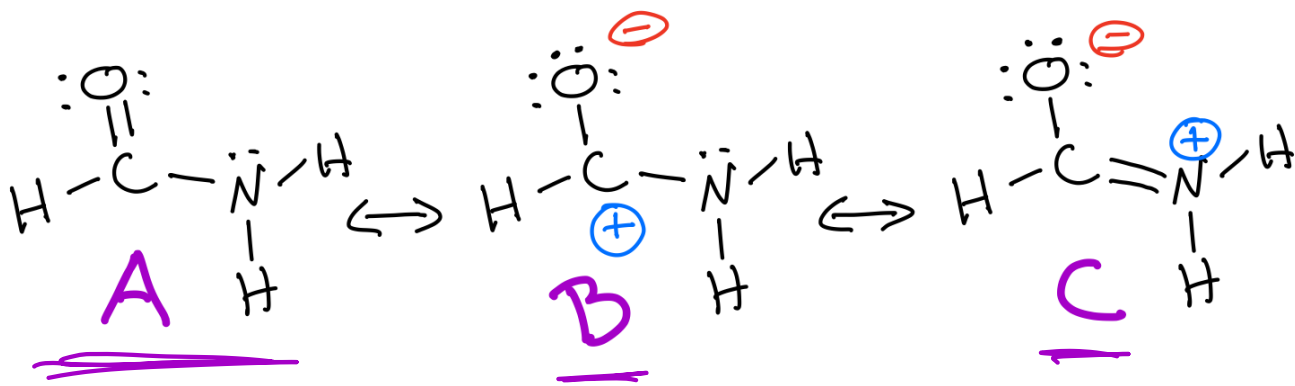
The C-C bond

cannot rotate

2) All atoms of the π bond
MUST contribute a $2p$
orbital \rightarrow means they are all
 sp^2 hybridized



The curious case of amide contributing structures: All three are important



Why are B and C worth considering?

1) Golden Rules of Chemistry #5 and #7

2) Quantum Mechanics (that explain Golden Rules of Chemistry #5 and #7)