





Ethyne
(Acetylene)

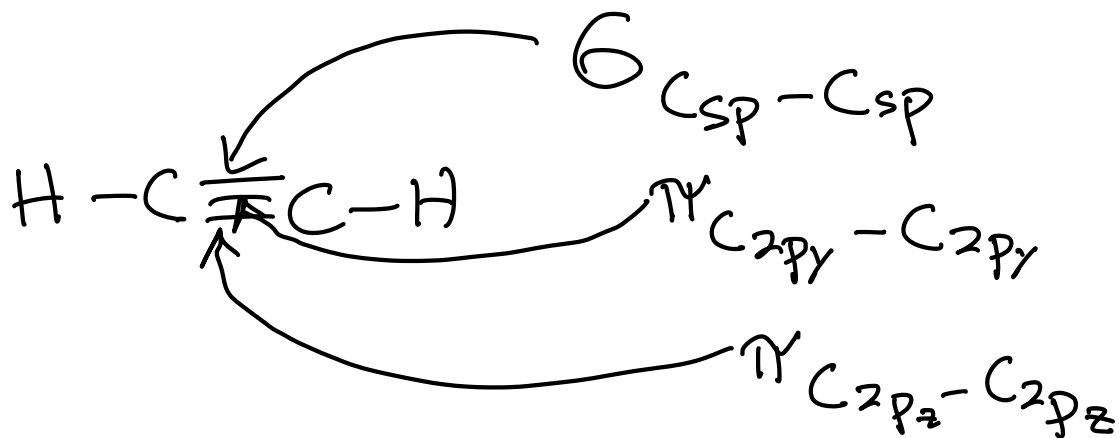
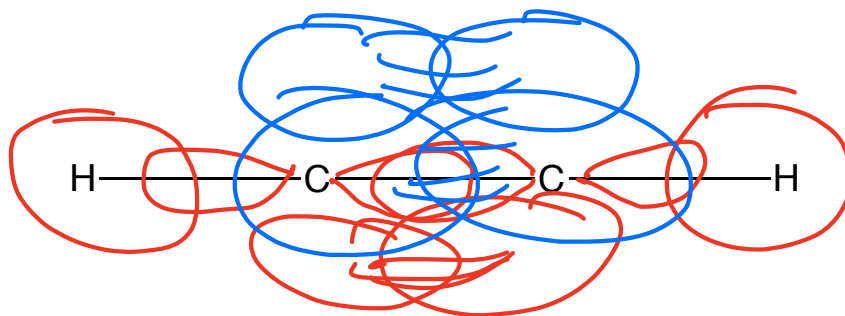
Molecular Orbital Theory approach to bonding: Just add the individual orbital wave functions:

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

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

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

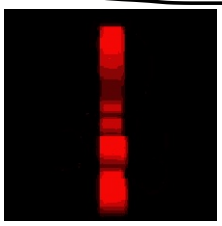
(Handwritten annotations: a bracket labeled 's' under the first two H 1s orbitals; a bracket labeled 'sp' over the first C 2s and 2p_x orbitals; blue circles around the second C 2p_y and 2p_z orbitals; a blue circle around the second C 2p_y orbital; a blue circle around the second C 2p_z orbital.)



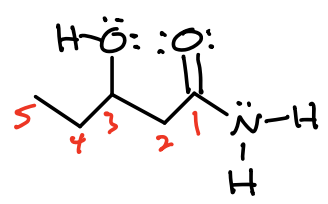
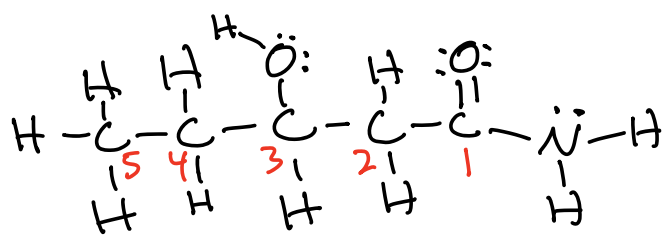
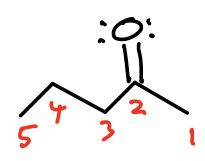
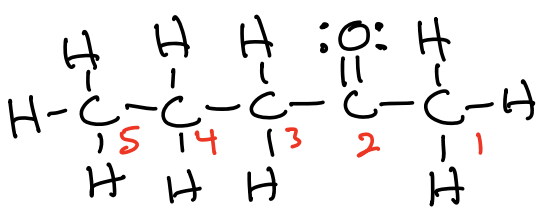
Line angle drawings → Ignore all H atoms bonded to C atoms → They are assumed to fill C valence shell

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

Pro tip → Number the C atoms



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

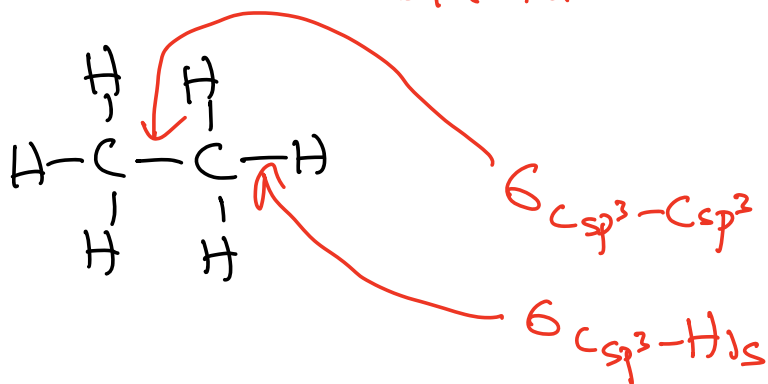


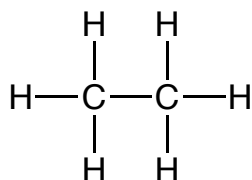
When we are:

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.





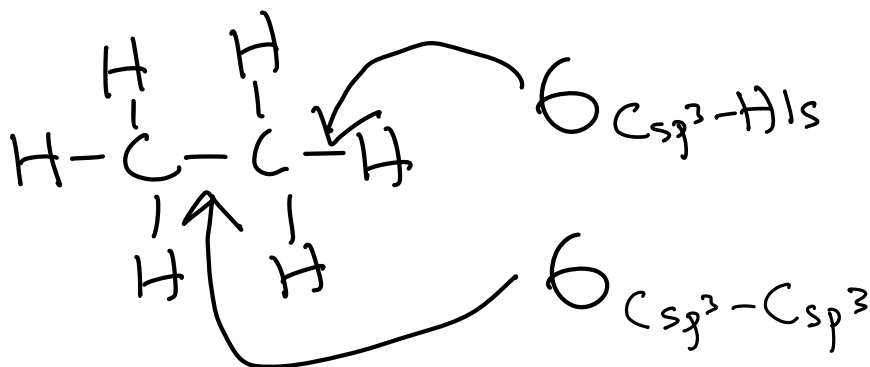
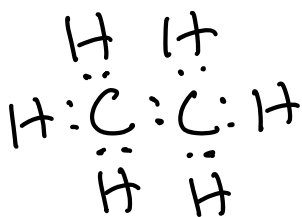
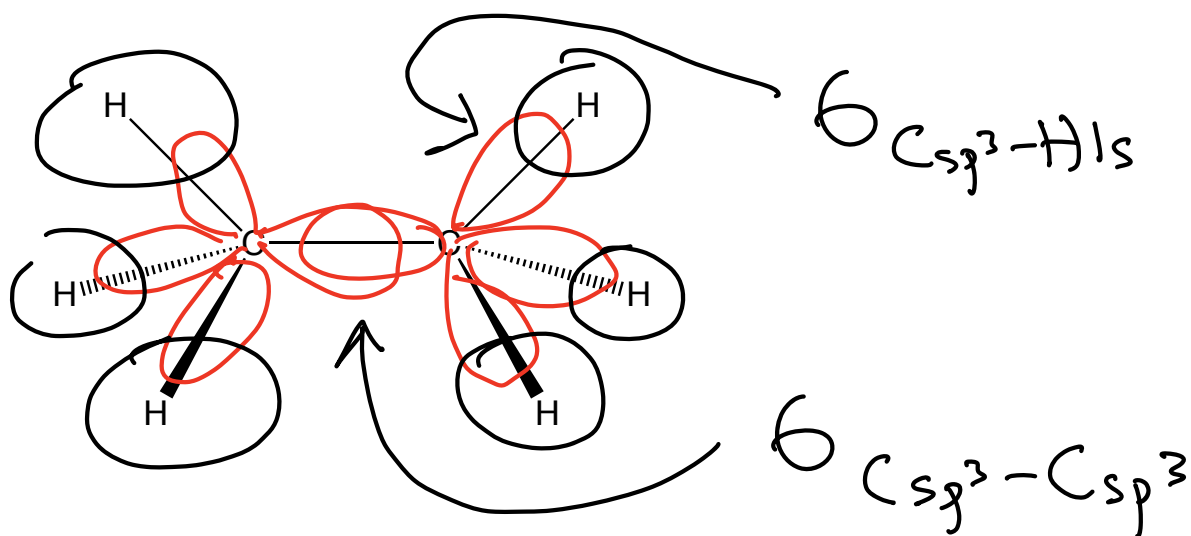
Ethane

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

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

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

$$\begin{aligned}
 &\Psi_{\text{H}1s} + \Psi_{\text{H}1s} + \Psi_{\text{H}1s} + \Psi_{\text{H}1s} + \Psi_{\text{H}1s} + \Psi_{\text{H}1s} + \Psi_{\text{C}1s} + (\Psi_{\text{C}2s} + \Psi_{\text{C}2p_x} \\
 &+ \Psi_{\text{C}2p_y} + \Psi_{\text{C}2p_z}) + \Psi_{\text{C}1s} + (\Psi_{\text{C}2s} + \Psi_{\text{C}2p_x} + \Psi_{\text{C}2p_y} + \Psi_{\text{C}2p_z}) \quad \begin{matrix} s^3 \\ s^3 \end{matrix}
 \end{aligned}$$



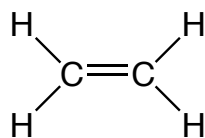
π bonds \rightarrow For cases in π bonds between only 2 atoms

- 1) Overlap of unhybridized 2p orbitals
 \hookrightarrow 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!!



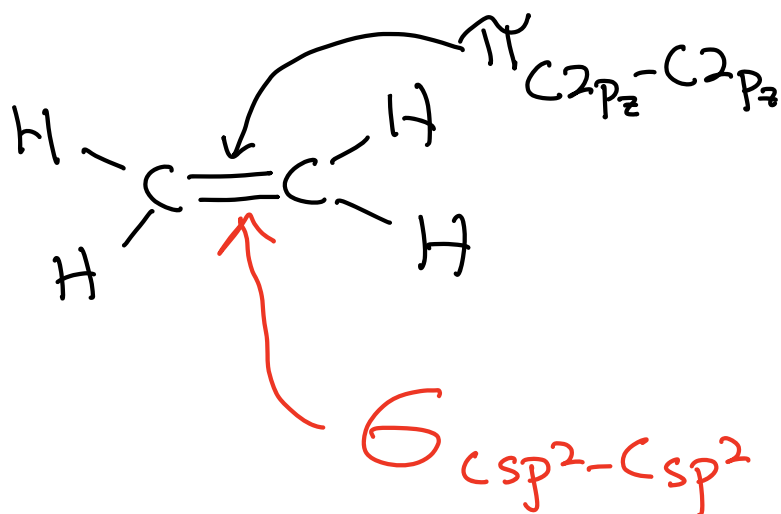
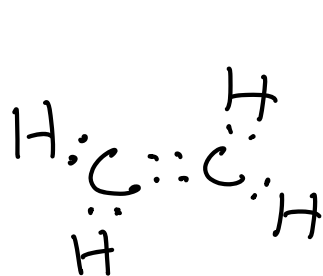
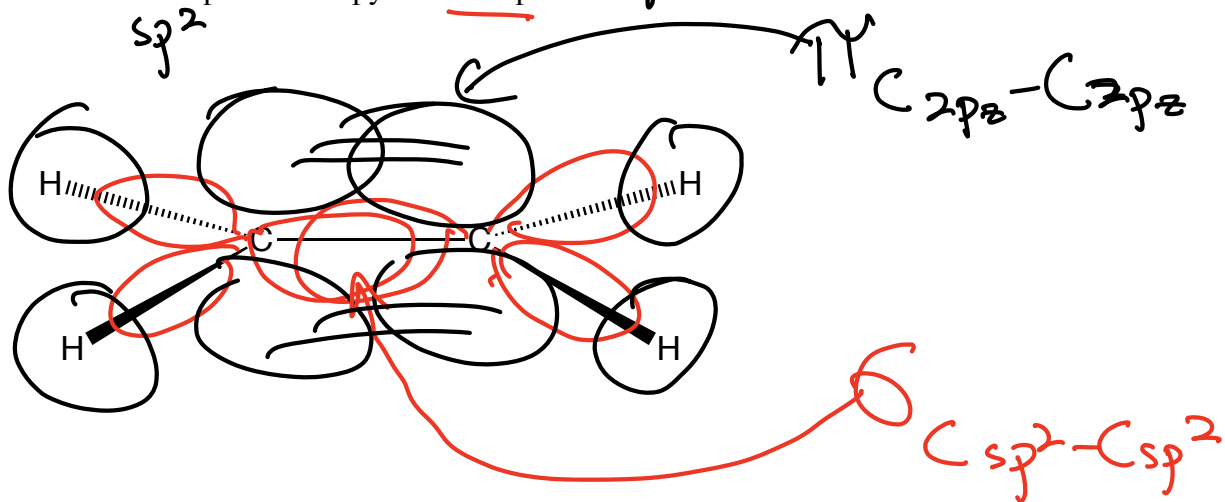
Ethene
(Ethylene)

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

$$\begin{aligned}
 &\Psi_{\text{H}1s} + \Psi_{\text{H}1s} + \Psi_{\text{H}1s} + \Psi_{\text{H}1s} + \Psi_{\text{C}1s} + \Psi_{\text{C}2s} + \Psi_{\text{C}2px} + \Psi_{\text{C}2py} + \Psi_{\text{C}2pz} \\
 &+ \Psi_{\text{C}1s} + \Psi_{\text{C}2s} + \Psi_{\text{C}2px} + \Psi_{\text{C}2py} + \Psi_{\text{C}2pz}
 \end{aligned}$$

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

$$\begin{aligned}
 &\Psi_{\text{H}1s} + \Psi_{\text{H}1s} + \Psi_{\text{H}1s} + \Psi_{\text{H}1s} + \Psi_{\text{C}1s} + (\underbrace{\Psi_{\text{C}2s} + \Psi_{\text{C}2px} + \Psi_{\text{C}2py}}_{sp^2}) + \underbrace{\Psi_{\text{C}2pz}} \\
 &+ \Psi_{\text{C}1s} + (\underbrace{\Psi_{\text{C}2s} + \Psi_{\text{C}2px} + \Psi_{\text{C}2py}}_{sp^2}) + \underbrace{\Psi_{\text{C}2pz}}
 \end{aligned}$$



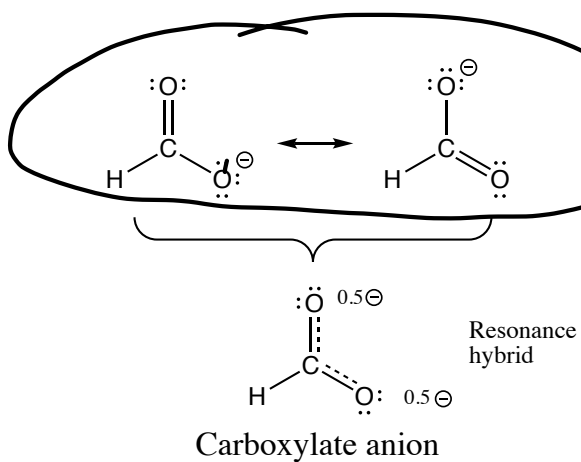


Molecular Orbital Theory

↳ 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

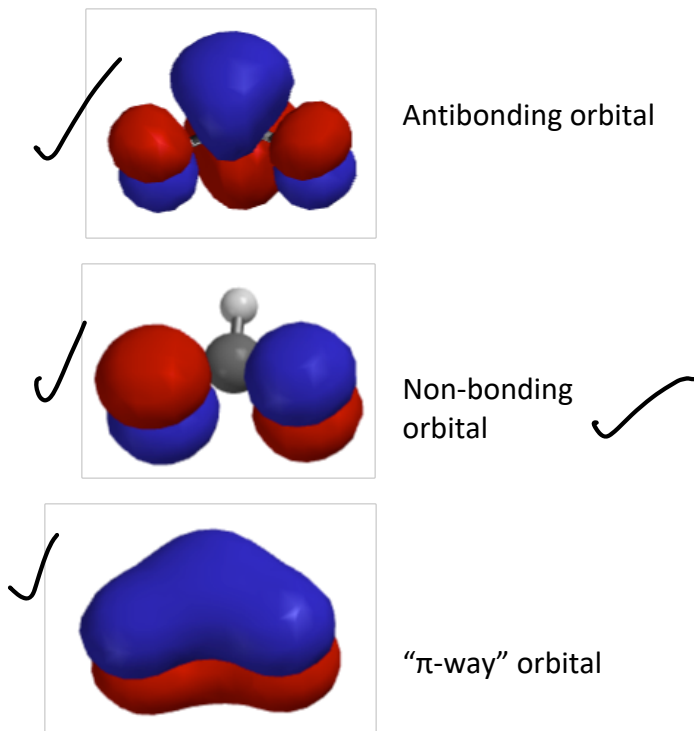
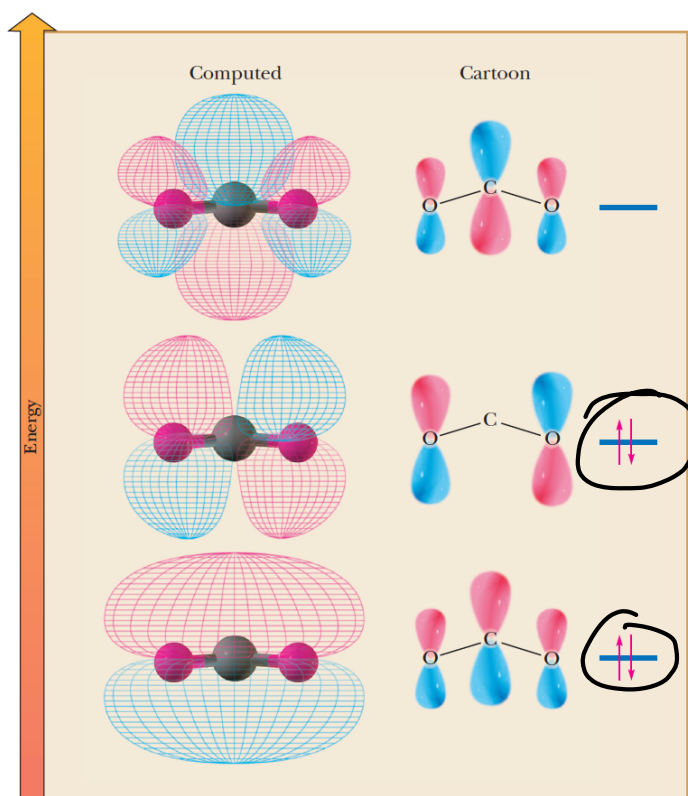
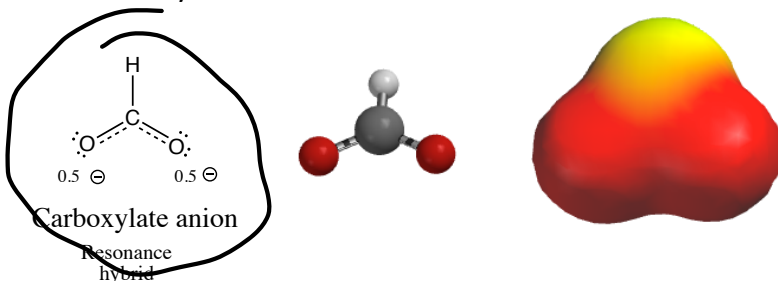
what this looks like \rightarrow 3 atoms
 3 overlapping 2p orbitals
 4 electrons

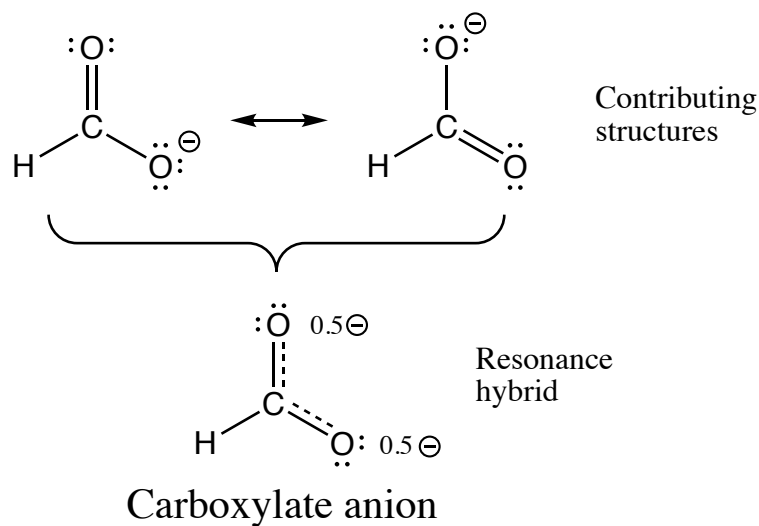


A common situation, and the one many resonance contributing structures describe, occurs when three 2p orbitals combine on adjacent atoms. A good example is the carboxylate anion. When three adjacent 2p orbitals interact (we add the three 2p orbital wave functions $\Psi_{C2pz} + \Psi_{O2pz} + \Psi_{O2pz}$), 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.

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





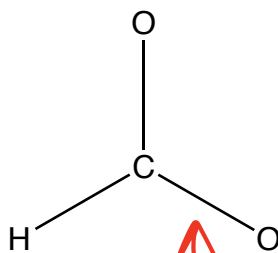
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$$\Psi_{H1s} + \Psi_{C1s} + \Psi_{C2s} + \Psi_{C2p_x} + \Psi_{C2p_y} + \Psi_{C2p_z} + \Psi_{O1s} + \Psi_{O2s} + \Psi_{O2p_x} + \Psi_{O2p_y} + \Psi_{O2p_z} + \Psi_{O1s} + \Psi_{O2s} + \Psi_{O2p_x} + \Psi_{O2p_y} + \Psi_{O2p_z}$$

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

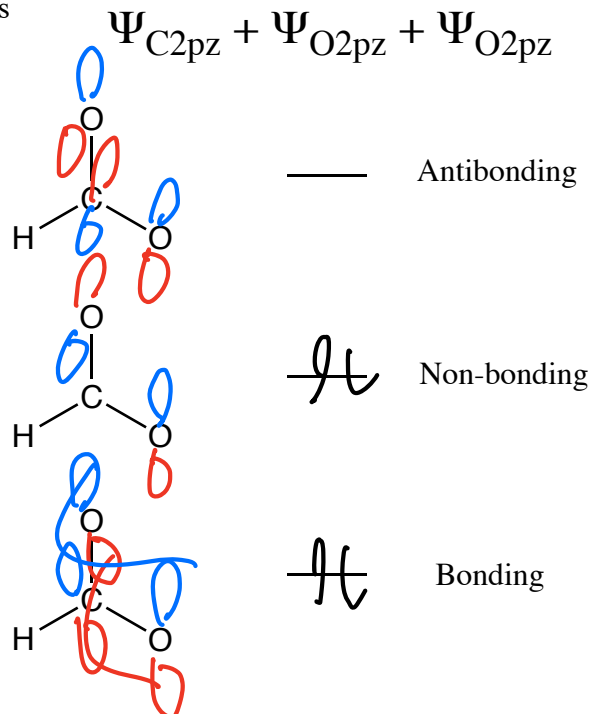
$$\Psi_{H1s} + \Psi_{C1s} + (\Psi_{C2s} + \Psi_{C2p_x} + \Psi_{C2p_y}) + \Psi_{C2p_z} + \Psi_{O1s} + (\Psi_{O2s} + \Psi_{O2p_x} + \Psi_{O2p_y}) + \Psi_{O2p_z} + \Psi_{O1s} + (\Psi_{O2s} + \Psi_{O2p_x} + \Psi_{O2p_y}) + \Psi_{O2p_z}$$

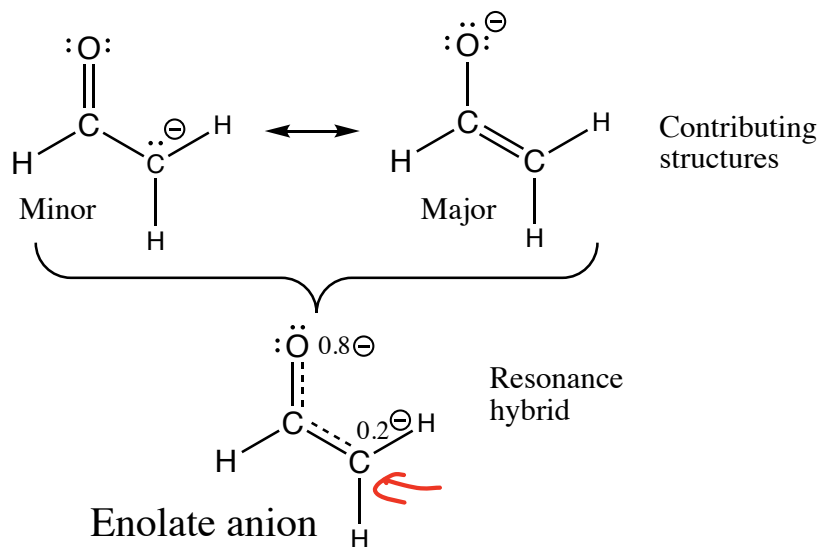
Sigma (σ) bonding - overlap of hybridized orbitals



$6 Csp^2 - O sp^2$

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





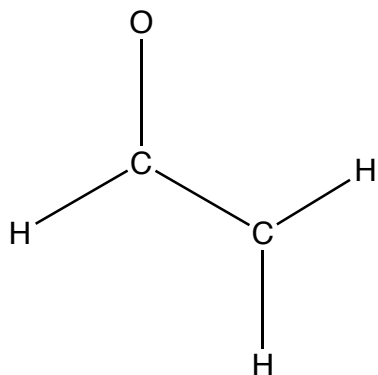
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$$\Psi_{H1s} + \Psi_{H1s} + \Psi_{H1s} + \Psi_{C1s} + \Psi_{C2s} + \Psi_{C2px} + \Psi_{C2py} + \Psi_{C2pz} + \Psi_{C1s} + \Psi_{C2s} + \Psi_{C2px} + \Psi_{C2py} + \Psi_{C2pz} + \Psi_{O1s} + \Psi_{O2s} + \Psi_{O2px} + \Psi_{O2py} + \Psi_{O2pz}$$

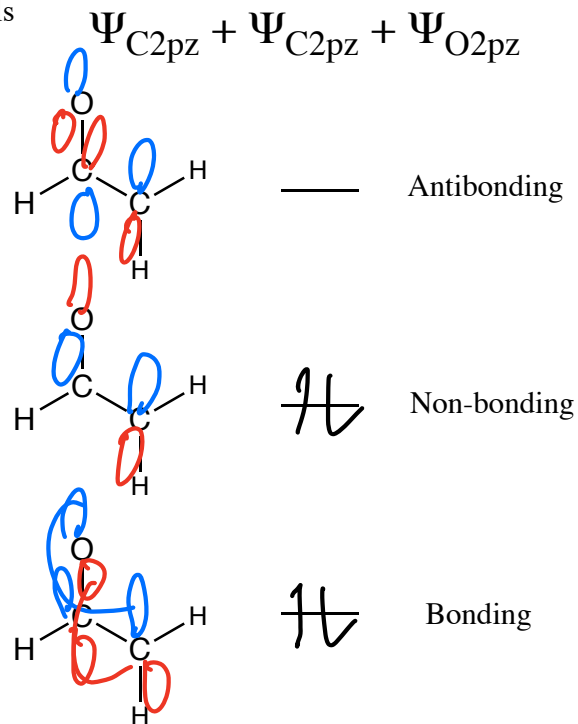
Valence Bond Theory approach to bonding: Hybridize the atomic orbitals on atoms first, then look for overlap with remaining orbital wave functions:

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Sigma (σ) bonding - overlap of hybridized orbitals

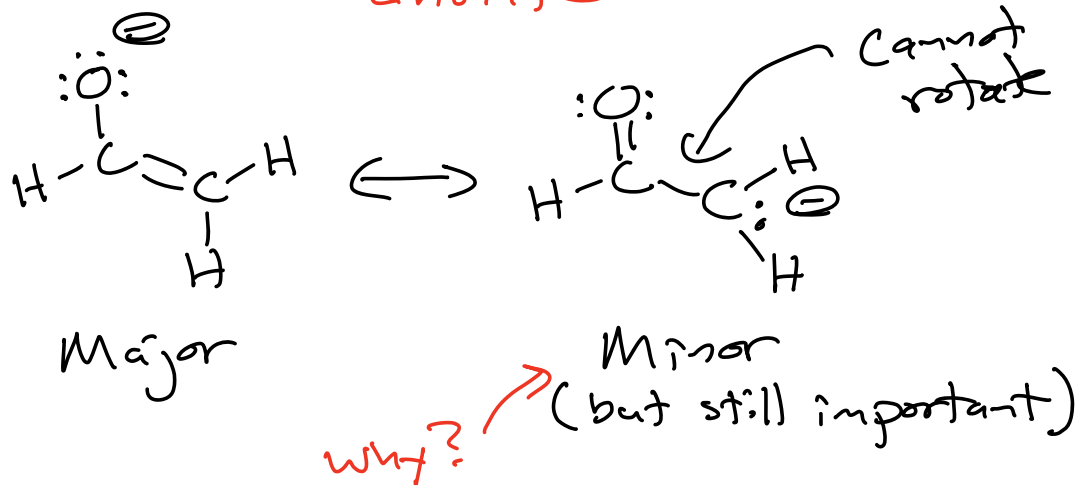


π -way bonding - overlap of 3 adjacent unhybridized 2p orbitals



What have we learned?

Enolate



→ 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:

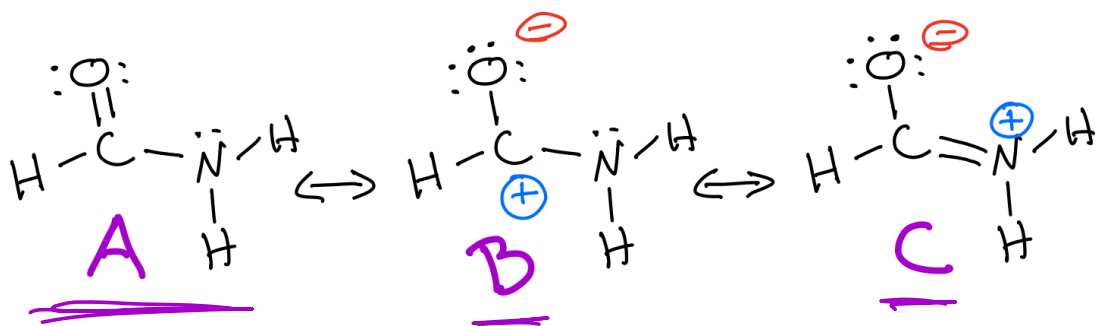
1) There is partial double bond character between all three atoms of the π way
The C-C bond

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

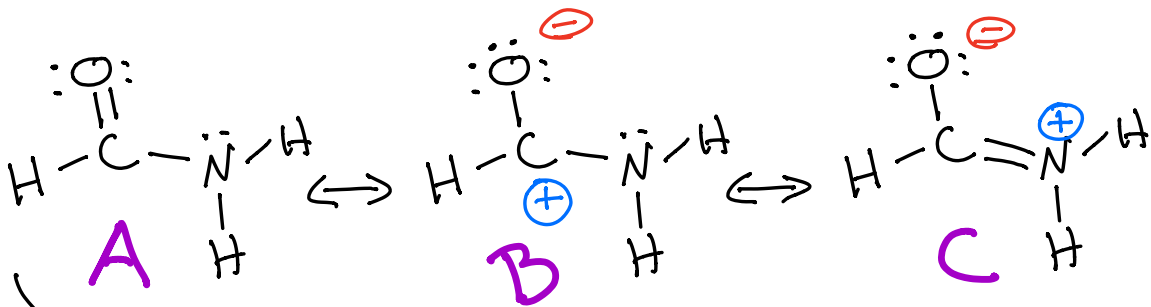


Why are B and C worth considering?

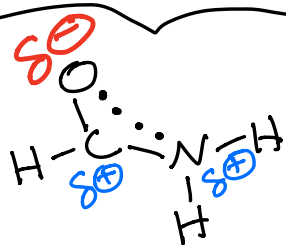
1) Golden Rules of Chemistry #5 and #7

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

Amide contributing structures revisited



This is how it is drawn, but all 3 contributing structures must be considered



This Bond Cannot Rotate

sp^2

5. Delocalization of charge over a larger area is stabilizing. The majority of molecules you will encounter will be neutral, but some carry negative or positive charges because they contain an imbalance in their total number of electrons and protons. In general, charges are destabilizing (higher Gibbs free energy), increasing the reactivity of the molecules that possess them. Localized charges are the most destabilizing (highest Gibbs free energy). Delocalizing the charge over a larger area through interactions such as resonance, inductive effects, and hyperconjugation is stabilizing (lowering the Gibbs free energy). In addition, it is more stabilizing to have more negative charge on a more electronegative atom (e.g. O), and more positive charge on a less electronegative atom (e.g. C).

The reason "B" is important

7. Delocalization of pi electron density over a larger area is stabilizing. Pi electron density delocalization occurs through overlapping $2p$ orbitals, so to take part in pi electron density delocalization atoms must be sp^2 or sp hybridized and reside in the same plane. Pi electron delocalization can involve even large numbers of such atoms. Pi electron density cannot delocalize onto or through sp^3 hybridized atoms because an sp^3 atom has no $2p$ orbital. Aromaticity is a special type of pi electron density delocalization involving rings and a specific number of pi electrons, and is the most stabilizing form of pi electron density delocalization.

The reason "C" is important

Survival skill in OChem

↳ Identify hybridization state of atoms in molecules

1) sp^3 → all sigma bonds and lone pairs

2) sp^2 → one pi bond and 3 sigma bonds/lone pairs

3) sp → two pi bonds and 2 sigma bonds/lone pairs

⇒ An atom counts as having a pi bond if ANY significant contributing structure has a pi bond to the atom → part of a "pi-way"

