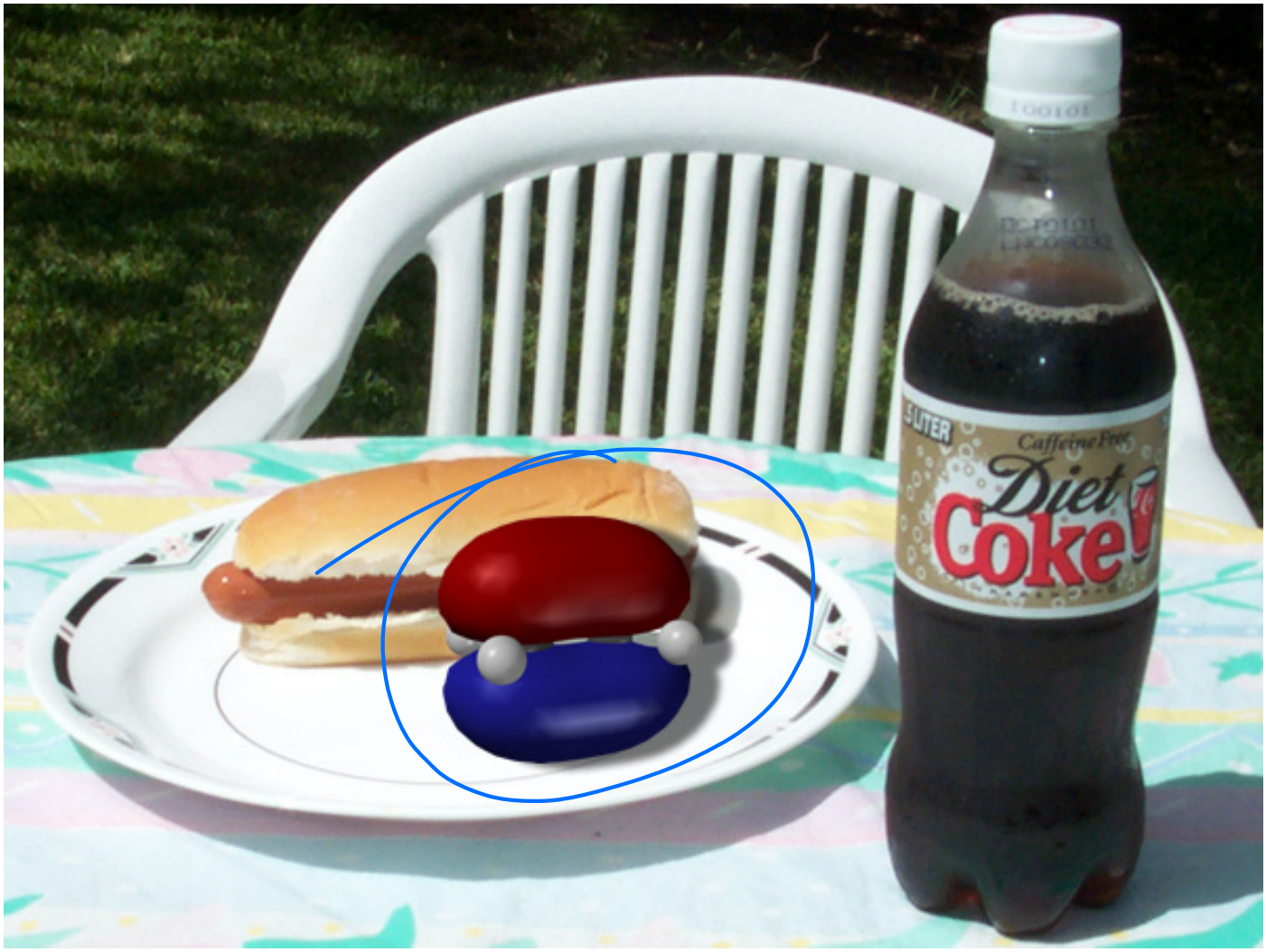
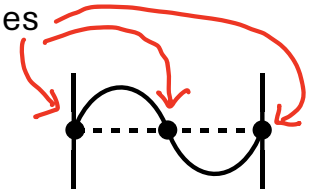

1 LITER
Caffeine Free
Diet
Coke

Properties of Waves → "Energy at a location

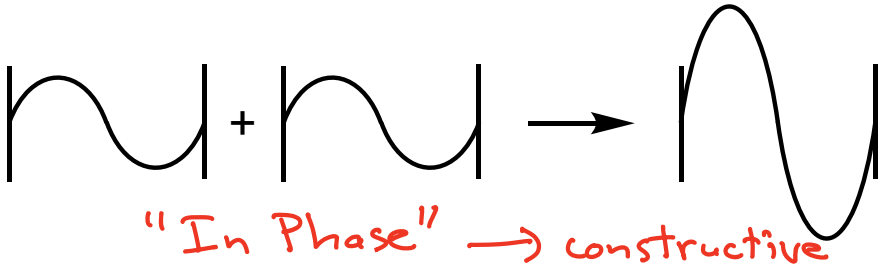
1) Quantized energy → Think of guitar strings
2) Nodes



No energy at certain points in space

3) Waves add constructively and destructively

Peaks and troughs add

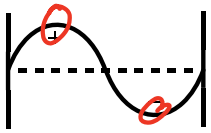


"In Phase" → constructive wave addition

Peaks and troughs cancel

"Out of Phase" → destructive wave addition

4) There is just as much energy at the top (+) amplitude of a wave as there is as the bottom (-) amplitude of a wave.



5) If you add X wave equations you get X new equations

The basis of molecular orbital theory

6) Around atoms, the location of electron density is described by the Schrödinger equation

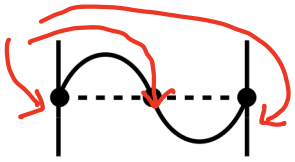
A wave equation that describes energy and location

Properties of Waves

→ "Energy at a location

1) Quantized energy
2) Nodes

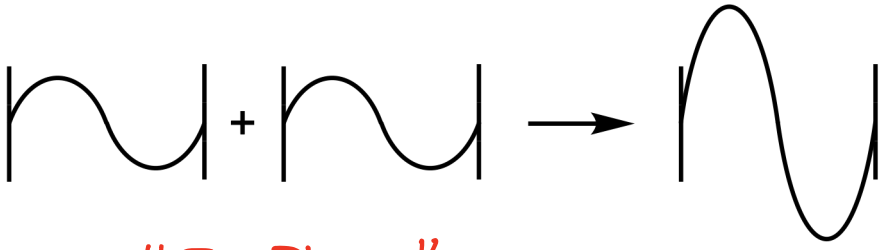
→ Think of guitar strings



No energy at certain points in space

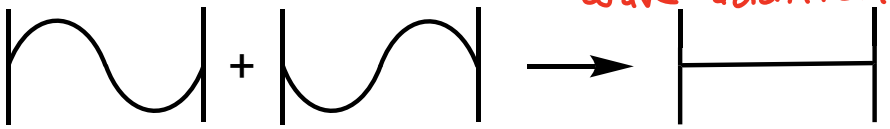
3) Waves add constructively and destructively

Peaks and troughs add



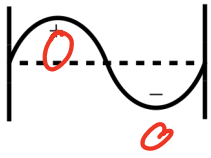
"In Phase" → constructive wave addition

Peaks and troughs cancel



"Out of Phase" → destructive wave addition

4) There is just as much energy at the top (+) amplitude of a wave as there is as the bottom (-) amplitude of a wave.



5) If you add X wave equations you get

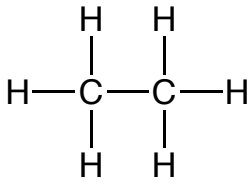
X new equations

The basis of molecular orbital theory

6) Around atoms, the location of electron density is described by

the Schrödinger equation

A wave equation that describes energy and location



Ethane

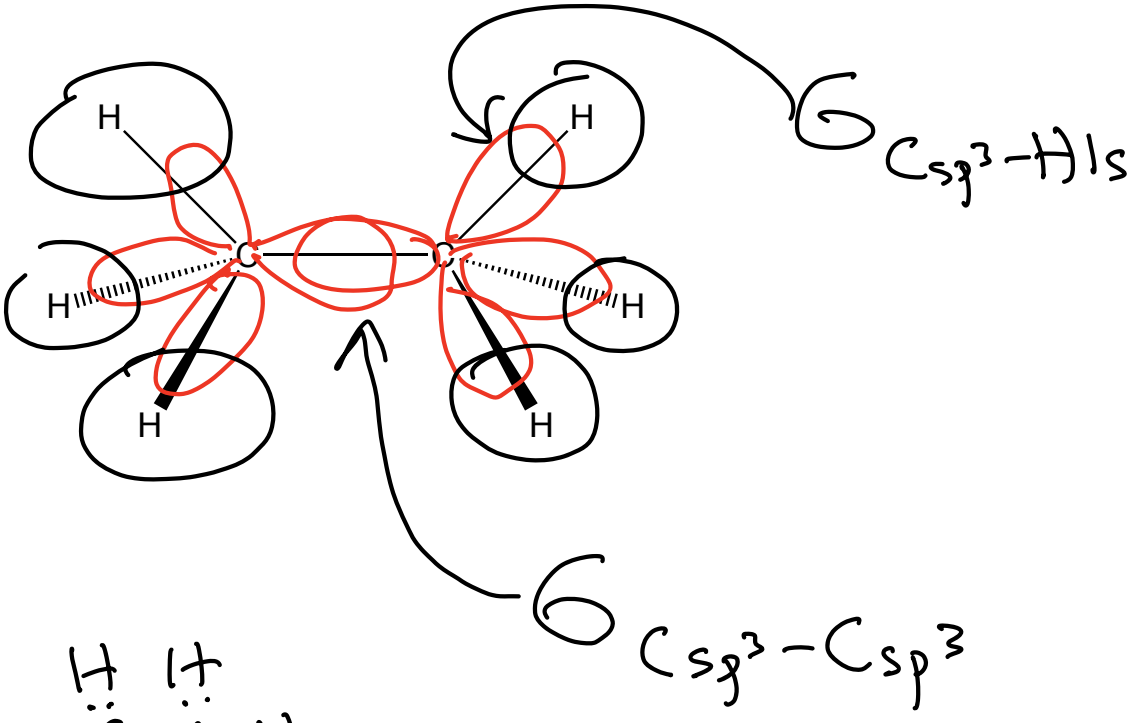
Molecular Orbital Theory approach to bonding: Just add the individual orbital wave functions:

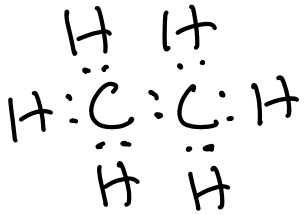
$$\Psi_{H1s} + \Psi_{H1s} + \Psi_{H1s} + \Psi_{H1s} + \Psi_{H1s} + \Psi_{H1s} + \Psi_{C1s} + \Psi_{C2s} + \Psi_{C2px} + \Psi_{C2py} + \Psi_{C2pz} + \Psi_{C1s} + \Psi_{C2s} + \Psi_{C2px} + \Psi_{C2py} + \Psi_{C2pz}$$

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

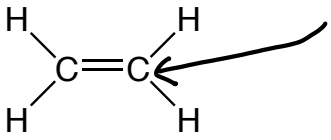
$$\Psi_{H1s} + \Psi_{H1s} + \Psi_{H1s} + \Psi_{H1s} + \Psi_{H1s} + \Psi_{H1s} + \Psi_{C1s} + (\Psi_{C2s} + \Psi_{C2px} + \Psi_{C2py} + \Psi_{C2pz}) + \Psi_{C1s} + (\Psi_{C2s} + \Psi_{C2px} + \Psi_{C2py} + \Psi_{C2pz})$$

sp^3 sp^3





Review from up above!



Three bonds to atoms and I π bond

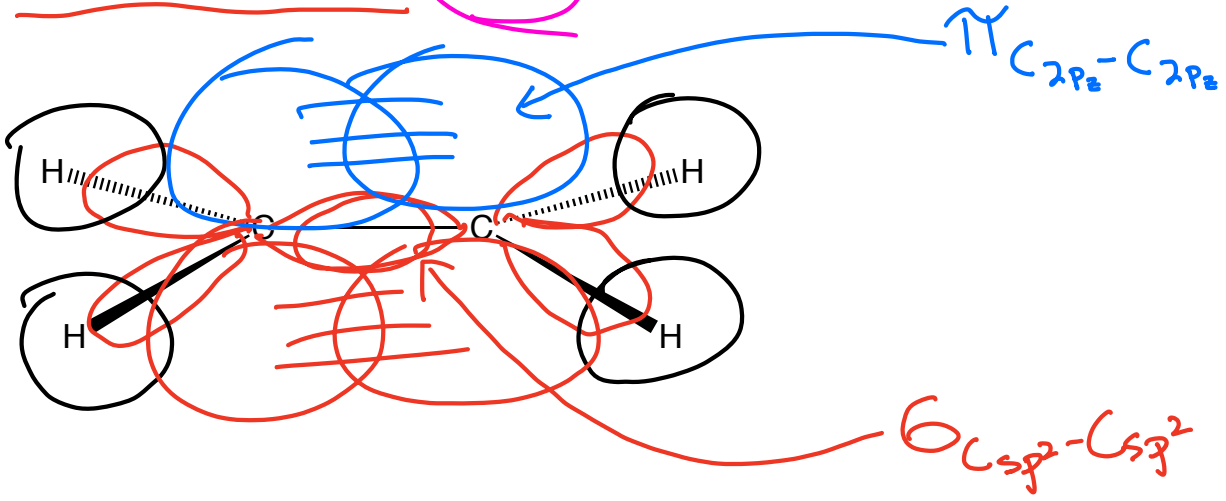
Ethene
(Ethylene)

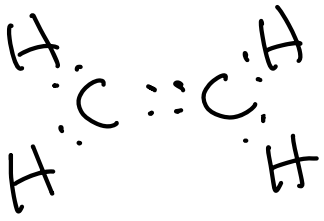
Molecular Orbital Theory approach to bonding: Just add the individual orbital wave functions:

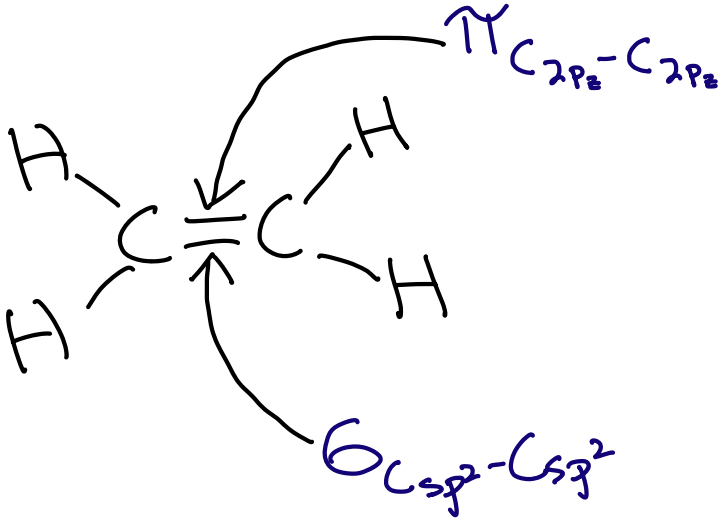
$$\Psi_{H1s} + \Psi_{H1s} + \Psi_{H1s} + \Psi_{H1s} + \Psi_{C1s} + \Psi_{C2s} + \Psi_{C2px} + \Psi_{C2py} + \Psi_{C2pz}$$
$$+ \Psi_{C1s} + \Psi_{C2s} + \Psi_{C2px} + \Psi_{C2py} + \Psi_{C2pz}$$

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

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







HC≡CH

Ethyne
(Acetylene)

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

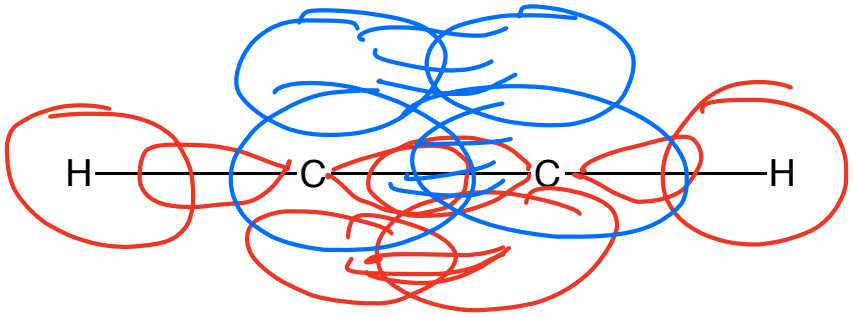
$$\Psi_{H1s} + \Psi_{H1s} + \Psi_{C1s} + \Psi_{C2s} + \Psi_{C2px} + \Psi_{C2py} + \Psi_{C2pz} + \Psi_{C1s} + \Psi_{C2s} + \Psi_{C2px} + \Psi_{C2py} + \Psi_{C2pz}$$

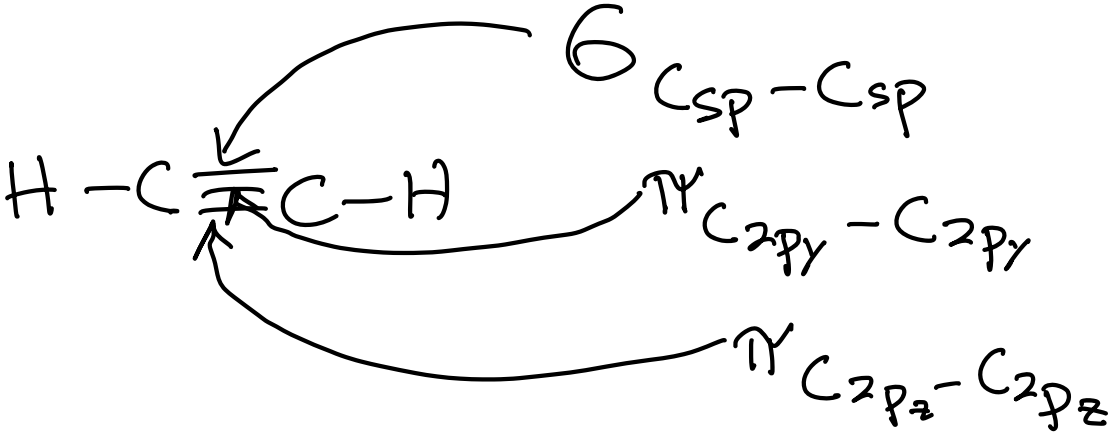
Valence Bond Theory approach to bonding: Hybridize the atomic orbitals on atoms first, then look for overlap with remaining orbital wave functions:

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

sp

sp





Line angle drawings → Ignore all H atoms bonded to C atoms → They are assumed to fill the C atom valence shells.

→ Draw all bonds and lone pairs

Don't draw C-H bonds

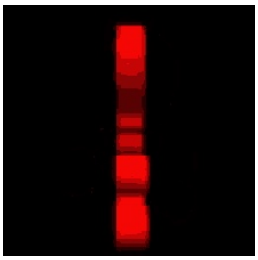
"zig-zag"

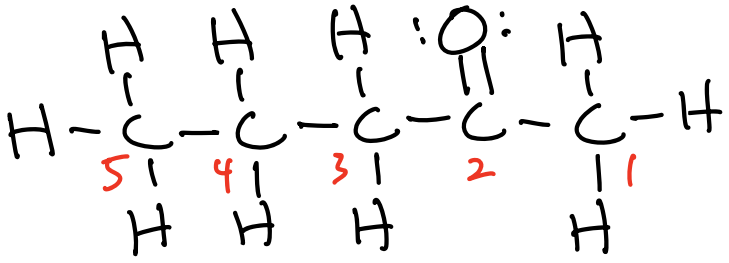
→ C atoms are assumed to be where each bond ends if there is no label

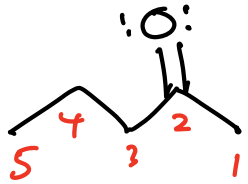
→ All non-C atoms (N, O, F, Cl, Br, I, P, S etc.) are shown

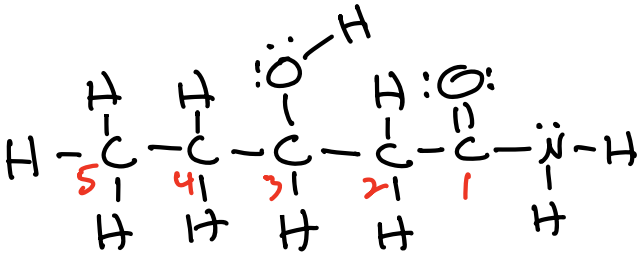
→ All H atoms on non-C atoms are shown

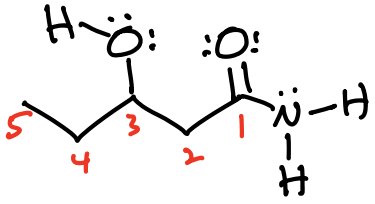
Pro tip → Number the C atoms!



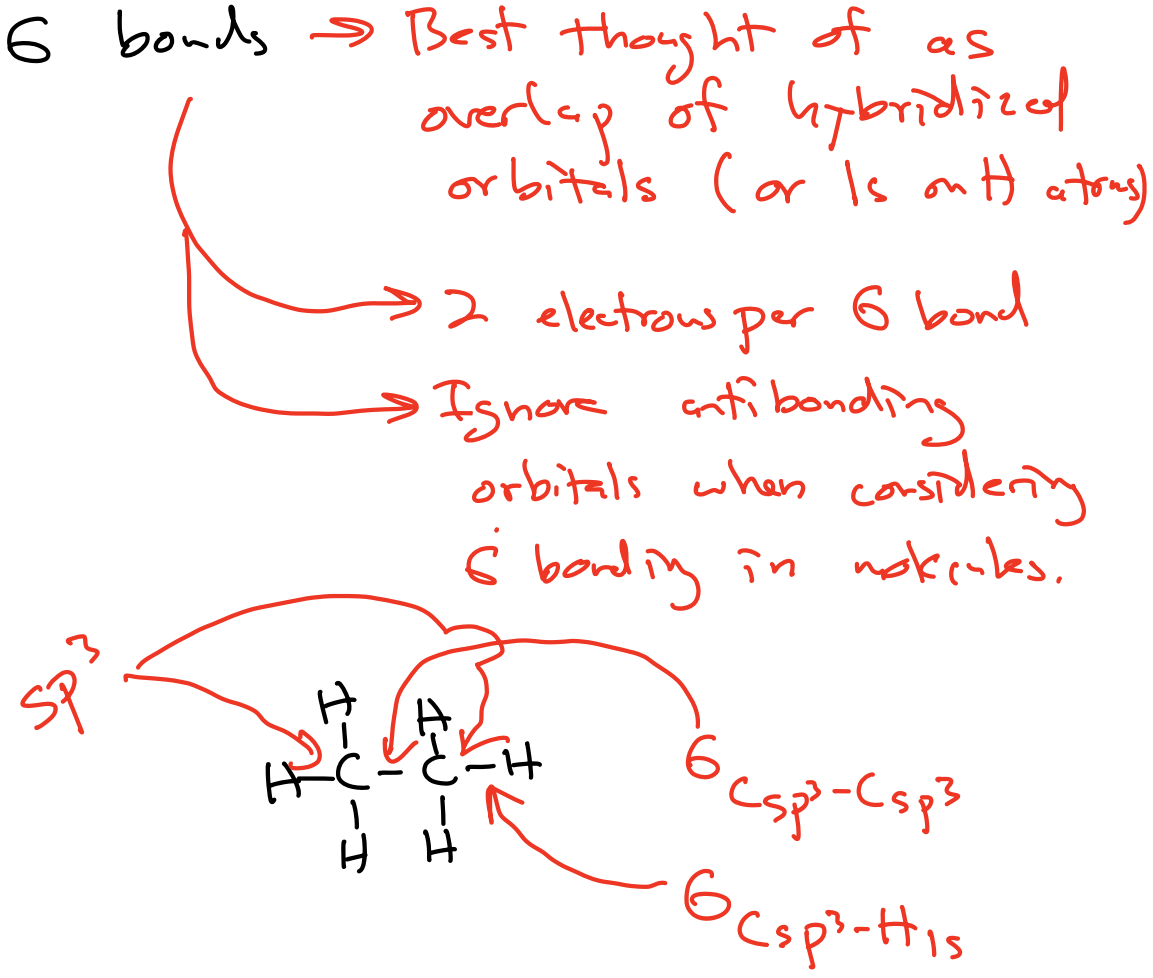


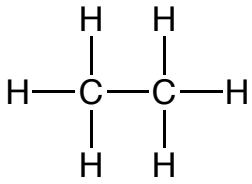






Where we are!


6 bonds → Best thought of as overlap of hybridized orbitals (or 1s on H atoms)
2 electrons per 6 bond
Ignore antibonding orbitals when considering 6 bonding in molecules.
sp^3
$6_{C_{sp^3}-C_{sp^3}}$
$6_{C_{sp^3}-H_{1s}}$



Ethane

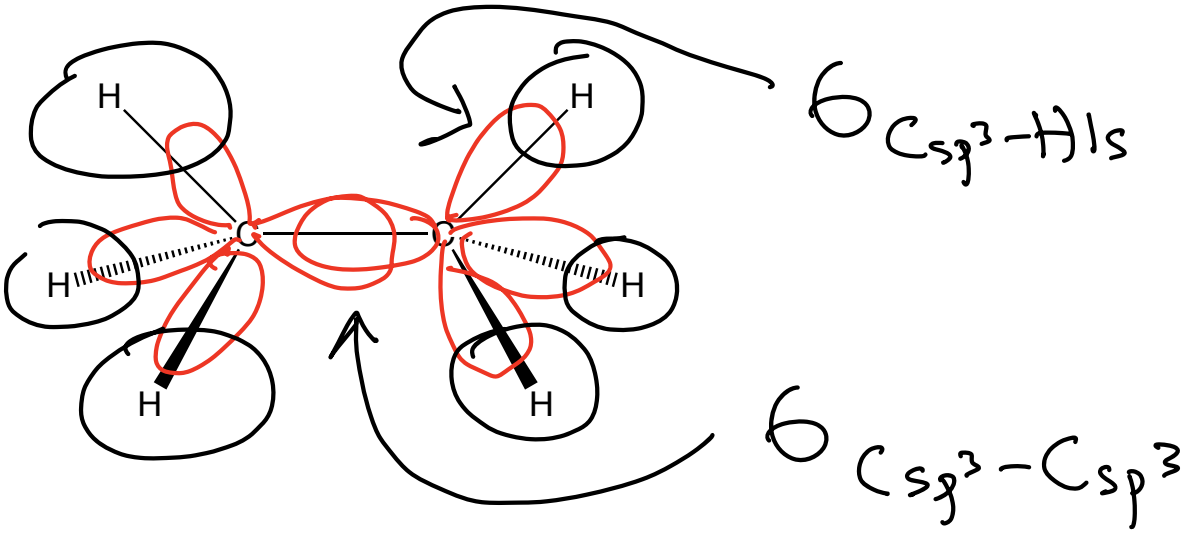
Molecular Orbital Theory approach to bonding: Just add the individual orbital wave functions:

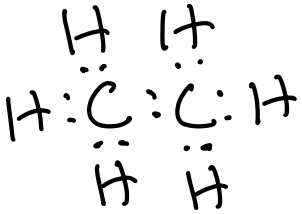
$$\Psi_{H1s} + \Psi_{H1s} + \Psi_{H1s} + \Psi_{H1s} + \Psi_{H1s} + \Psi_{H1s} + \Psi_{C1s} + \Psi_{C2s} + \Psi_{C2px} + \Psi_{C2py} + \Psi_{C2pz} + \Psi_{C1s} + \Psi_{C2s} + \Psi_{C2px} + \Psi_{C2py} + \Psi_{C2pz}$$

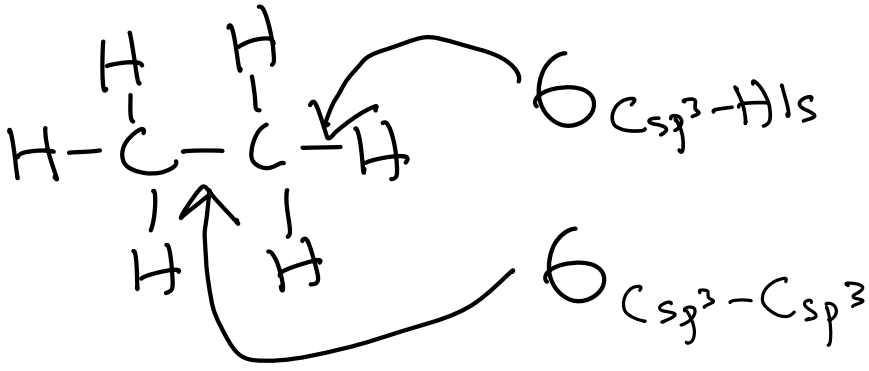
Valence Bond Theory approach to bonding: Hybridize the atomic orbitals on atoms first, then look for overlap with remaining orbital wave functions:

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

sp^3 sp^3







π bonds → For cases in which π bonds are between 2 atoms

1) overlap of unhybridized 2p orbitals

2) 2 electrons per π bond

3) We ignore antibonding orbitals when considering bonding in molecules

However: π bonds can extend over more than 2 atoms → described by molecular orbital theory → These extended π bonding orbitals still only contain 2 electrons

Not consistent with Lewis structure model → this is why we have contributing structures

Molecular Orbital Theory

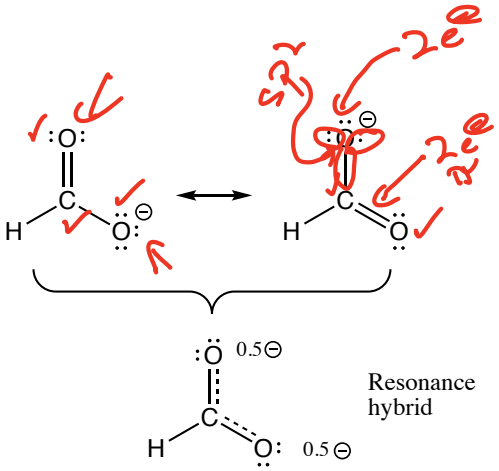
To quantify bonding in molecules we simply add all of the atomic orbital wave functions in the molecule

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 desity equal to 2 electrons

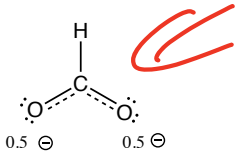
$\Rightarrow$ NEVER MORE



Carboxylate anion

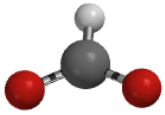
A common situation, and the one many resonance contributing structures describe, occurs when three 2p orbitals combine on adjacent atoms. A good example is the carboxylate anion. When three adjacent 2p orbitals interact (we add the three 2p orbital wave functions $\Psi_{C2pz} + \Psi_{O2pz} + \Psi_{O2pz}$),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

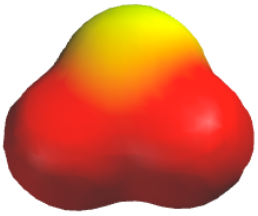
$$\Psi_{C2pz} + \Psi_{O2pz} + \Psi_{O2pz}$$

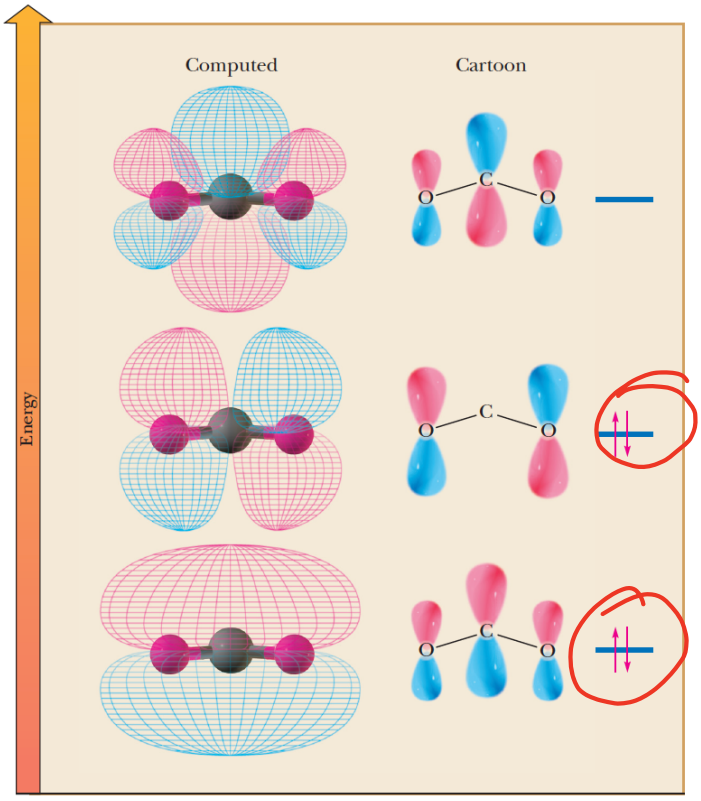


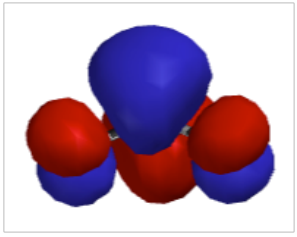
Carboxylate anion

Resonance hybrid

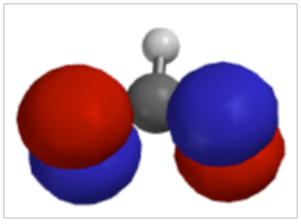




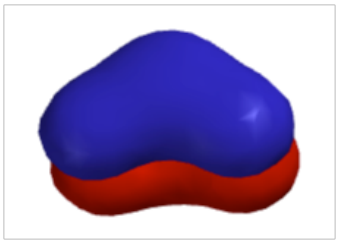




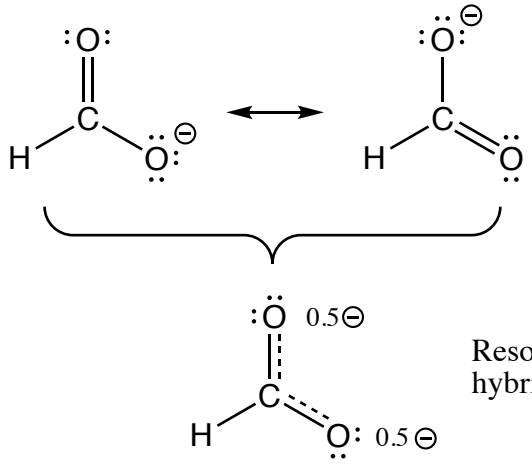
Antibonding orbital



Non-bonding orbital



"π-way" orbital



Carboxylate anion

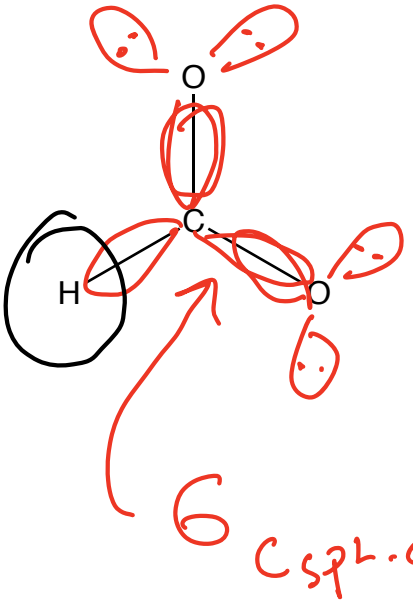
Molecular Orbital Theory approach to bonding: Just add the individual orbital wave functions:

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

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

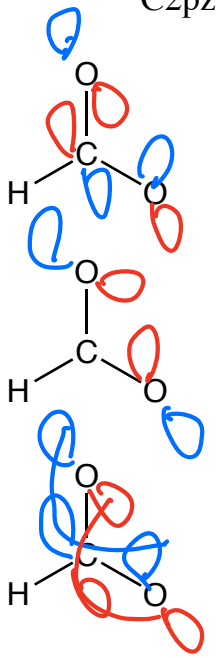
$$\Psi_{H1s} + \Psi_{C1s} + (\Psi_{C2s} + \Psi_{C2px} + \Psi_{C2py}) + \Psi_{C2pz} + \Psi_{O1s} + (\Psi_{O2s} + \Psi_{O2px} + \Psi_{O2py}) + \Psi_{O2pz} + \Psi_{O1s} + (\Psi_{O2s} + \Psi_{O2px} + \Psi_{O2py}) + \Psi_{O2pz}$$

Sigma (σ) bonding - overlap of hybridized orbitals



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

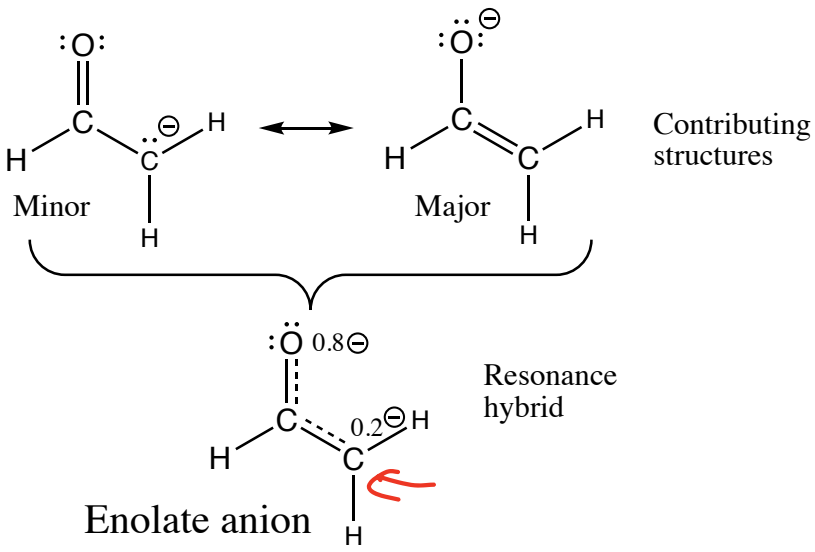
$$\Psi_{C2pz} + \Psi_{O2pz} + \Psi_{O2pz}$$



Antibonding

Non-bonding

Bonding



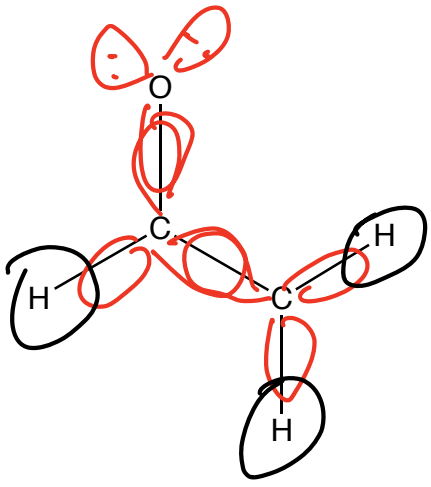
Molecular Orbital Theory approach to bonding: Just add the individual orbital wave functions:

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

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

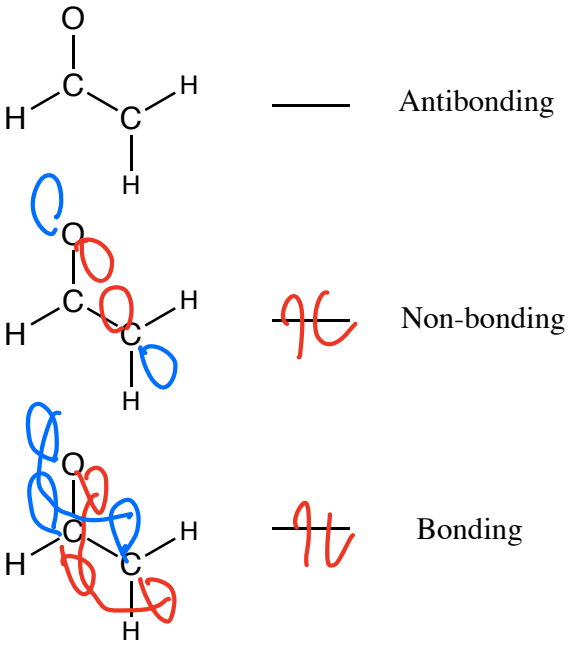
$$\Psi_{H1s} + \Psi_{H1s} + \Psi_{H1s} + \Psi_{C1s} + (\Psi_{C2s} + \Psi_{C2px} + \Psi_{C2py}) + \Psi_{C2pz} + \Psi_{C1s} + (\Psi_{C2s} + \Psi_{C2px} + \Psi_{C2py}) + \Psi_{C2pz} + \Psi_{O1s} + (\Psi_{O2s} + \Psi_{O2px} + \Psi_{O2py}) + \Psi_{O2pz}$$

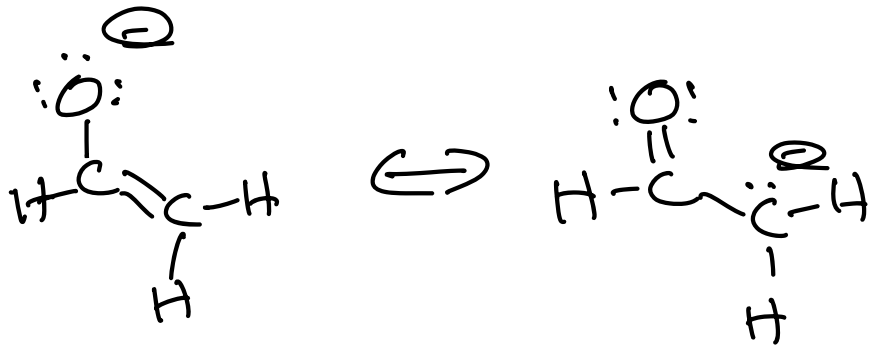
Sigma (σ) bonding - overlap of hybridized orbitals



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

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





This anion is more stable than you might think.

1) Delocalization of a charge is stabilizing
Golden Rule #5
⊖ on both C and O

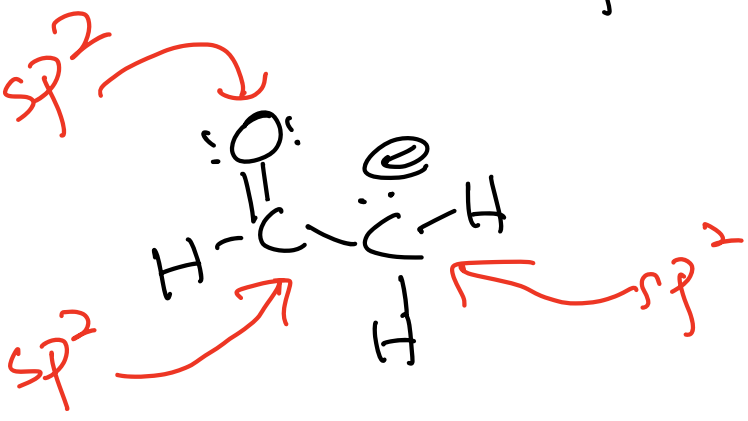
2) Delocalization of a π bond over more atoms is stabilizing
Golden Rule #7

Epi2 structure considerations

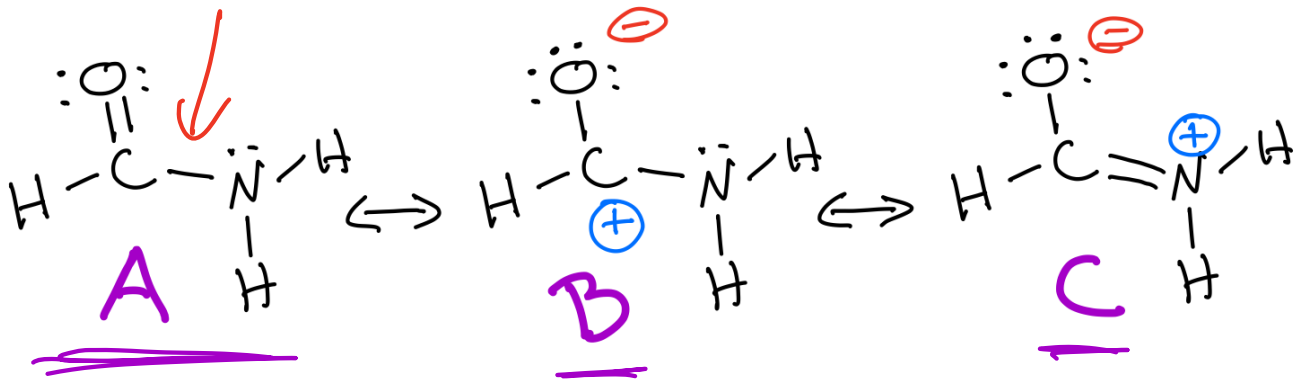
1) There is partial double bond across all 3 atoms

3) All atoms of the π-way must be sp^2 → so there are 3 2p orbitals to

overlap



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

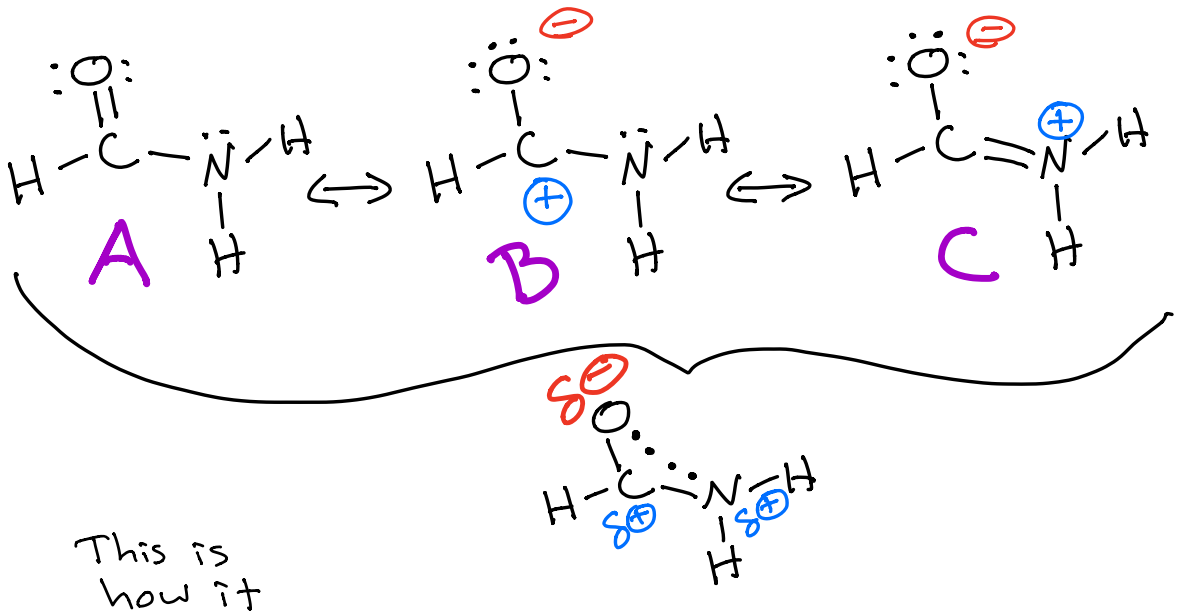


Why are B and C worth considering?

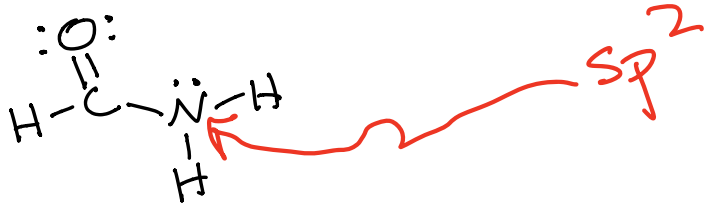
1) Golden Rules of Chemistry #5 and #7

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



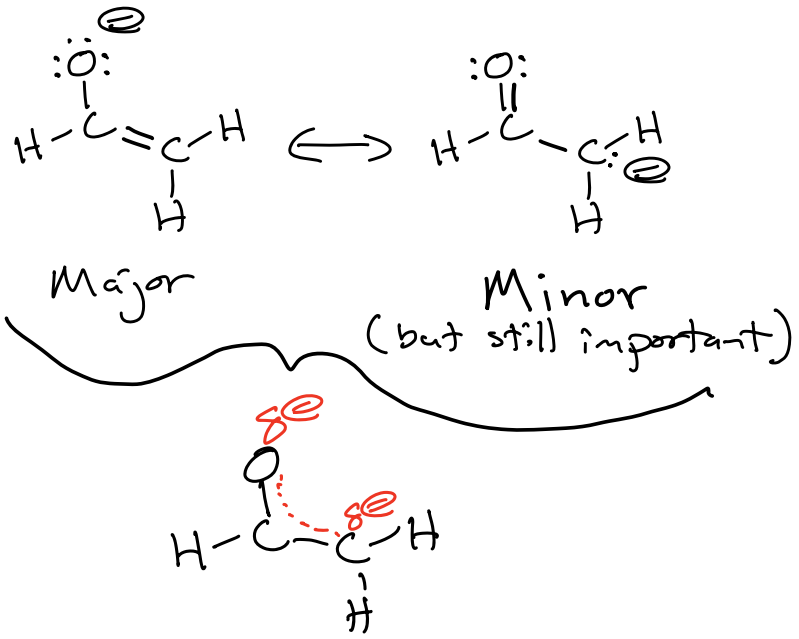
5. Delocalization of charge over a larger area is stabilizing. The majority of molecules you will encounter will be neutral, but some carry negative or positive charges because they contain an imbalance in their total number of electrons and protons. In general, charges are destabilizing (higher Gibbs 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).

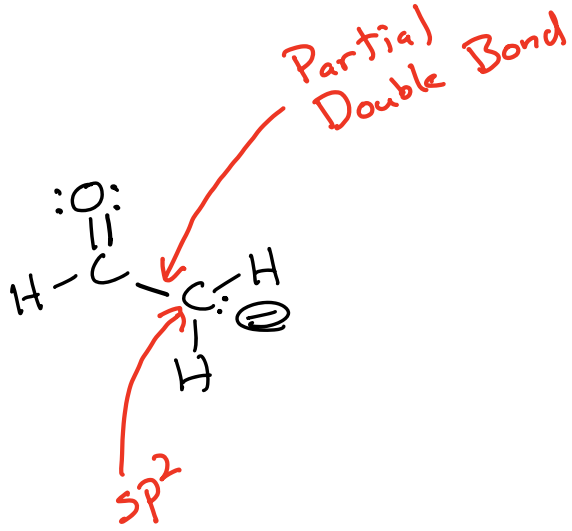
The reason "B" is important

7. Delocalization of pi electron density over a larger area is stabilizing. Pi electron density delocalization occurs through overlapping 2*p* orbitals, so to take part in pi electron density delocalization atoms must be *sp2* 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 *sp3* hybridized atoms because an *sp3* atom has no 2*p* 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.

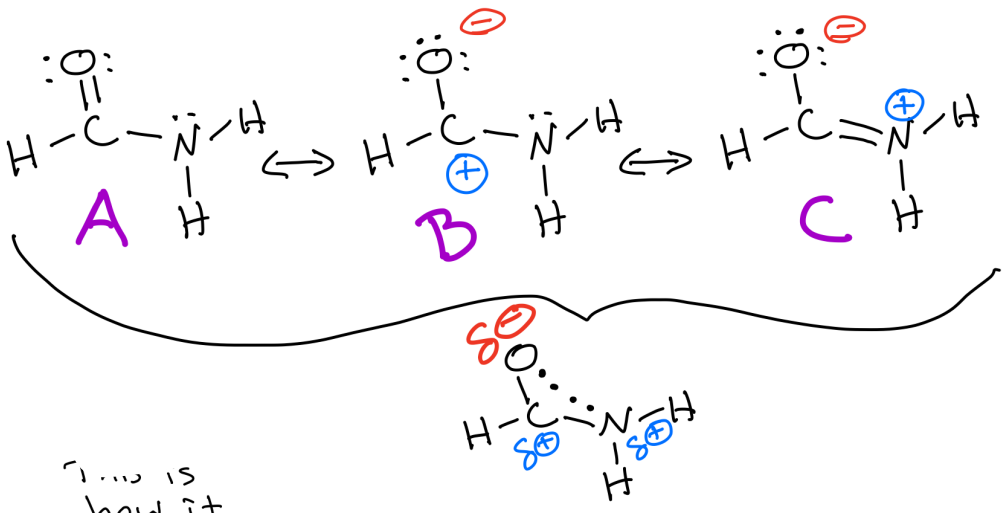
The reason "C" is important

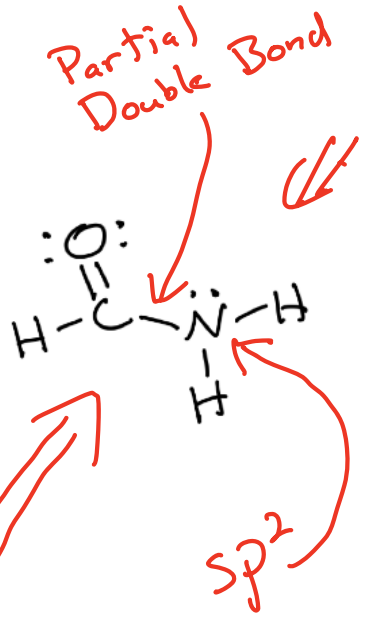
Enolate ion contributing structures





Amide contributing structures





The partial double bond of the C–N bond does not rotate at room temperature so this adds considerable rigidity to protein chains → enables precise 3-dimensional folding and LIFE AS WE KNOW IT!!!

Look at the POTD for today!