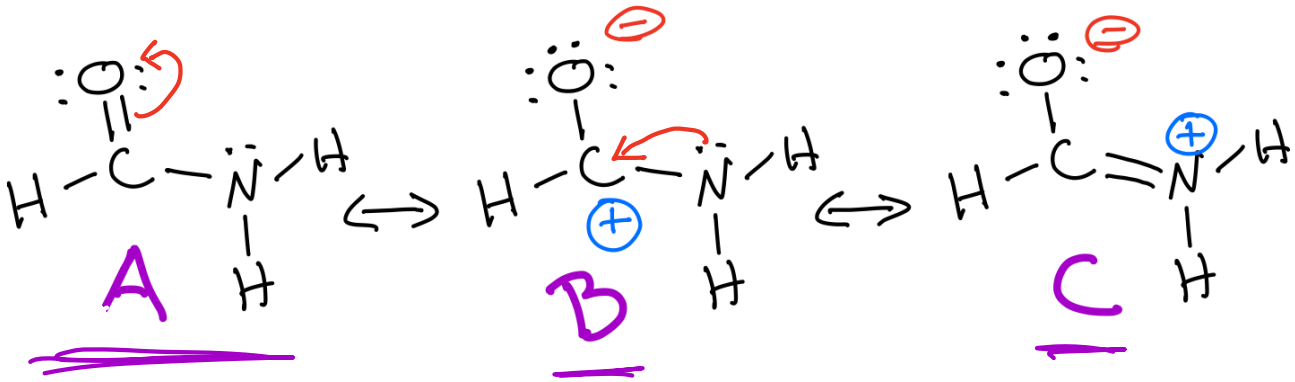
The curious case of amide contributing structures: All three are important



Why are B and C worth considering?

Time Capsule

1) Golden Rules of Chemistry #5 and #7

Quantum Mechanics Baby!!

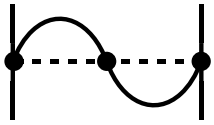
Electrons are so incredibly small that they have some properties of particles and some properties of waves

**** For organic chemistry we focus only on the wave properties of electrons!!!

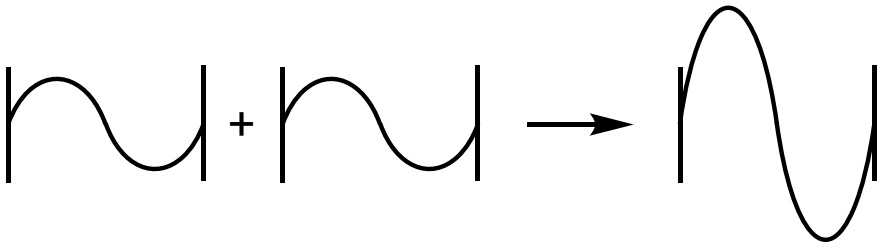
Electrons are three-dimensional waves!!

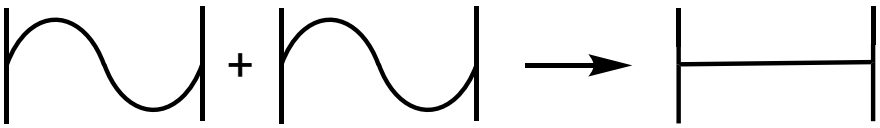
Properties of Waves

1) Quantized energy
2) Nodes

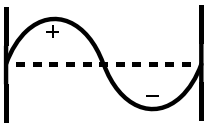


3) Waves add constructively and destructively





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

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

Solutions to the Schrodinger equation – atomic orbitals

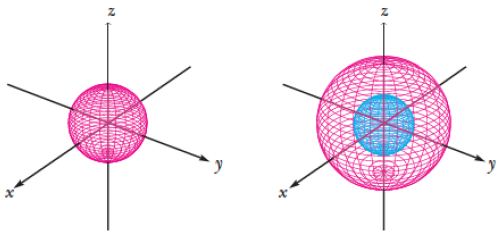
$$\psi_{n\ell m}(r,\theta,\phi) = \sqrt{\left(\frac{2}{na_0}\right)^3 \frac{(n-\ell-1)!}{2n[(n+\ell)!]}} e^{-r/na_0} \left(\frac{2r}{na_0}\right)^{\ell} L^{2\ell+1}_{n-\ell-1}\left(\frac{2r}{na_0}\right) \cdot Y^m_\ell(\theta,\phi)$$

where:

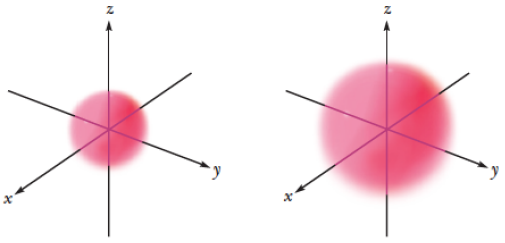
- $a_0 = \dfrac{4\pi\varepsilon_0\hbar^2}{m_e e^2}$ is the Bohr radius,
- $L^{2\ell+1}_{n-\ell-1}(\cdots)$ are the generalized Laguerre polynomials of degree $n-\ell-1$.
- n, ℓ, m are the principal, azimuthal, and magnetic quantum numbers respectively: which take the values:

$$n = 1, 2, 3, \ldots$$
$$\ell = 0, 1, 2, \ldots, n-1$$
$$m = -\ell, \ldots, \ell$$

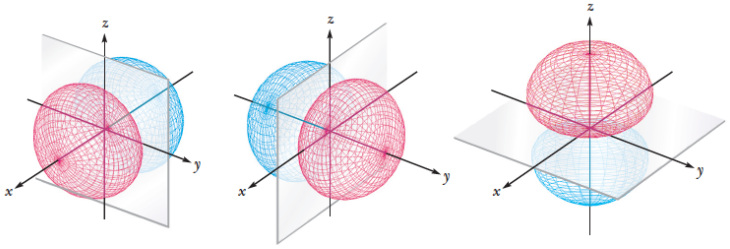
Ψ_{1s} Ψ_{2s} Ψ_{2px} Ψ_{2py} Ψ_{2pz}



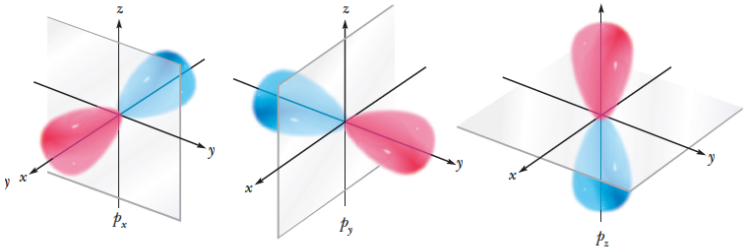
(a) 1*s* and 2*s* orbitals computed using the Schrödinger equation



(b) Cartoon representations of 1*s* and 2*s* orbitals

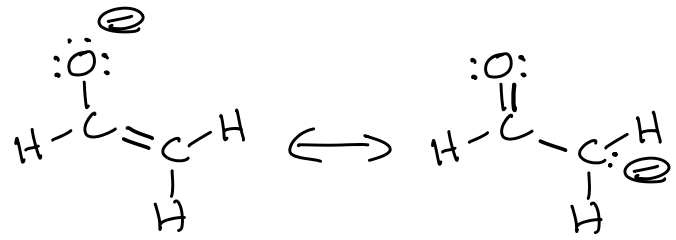


(a) 2*p* Orbitals computed using the Schrödinger equation



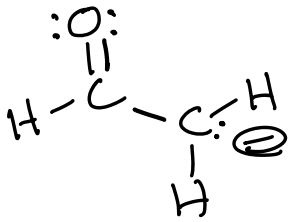
Nodal plane = *yz* Nodal plane = *xz* Nodal plane = *xy*

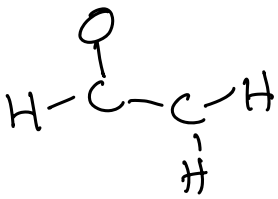
Enolate ion contributing structures



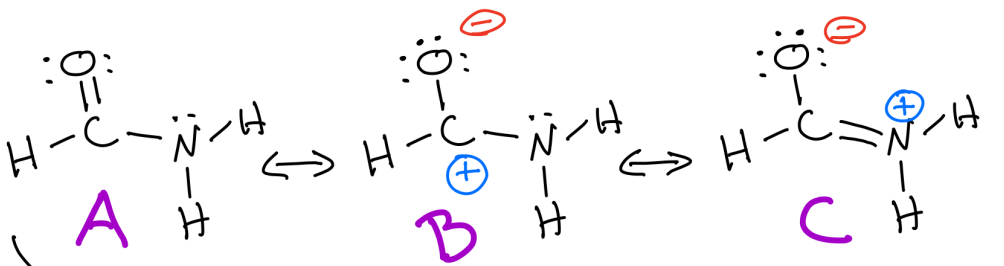
Major

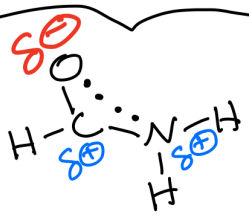
Minor
(but still important)

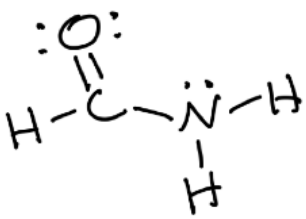




Amide contributing structures





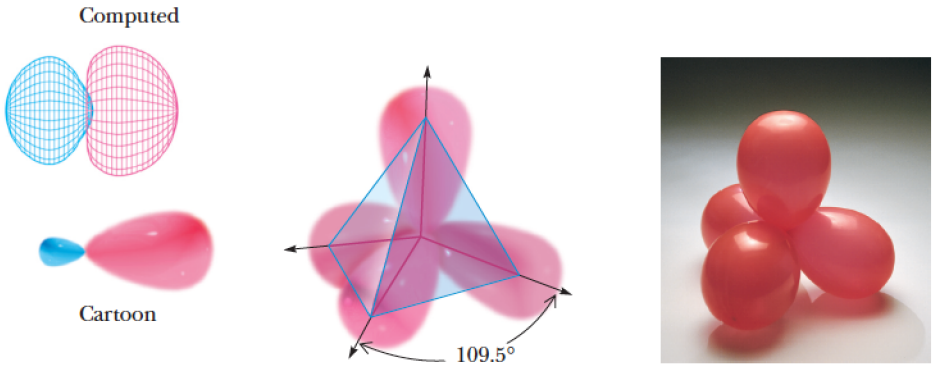


Molecular Orbital Theory

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

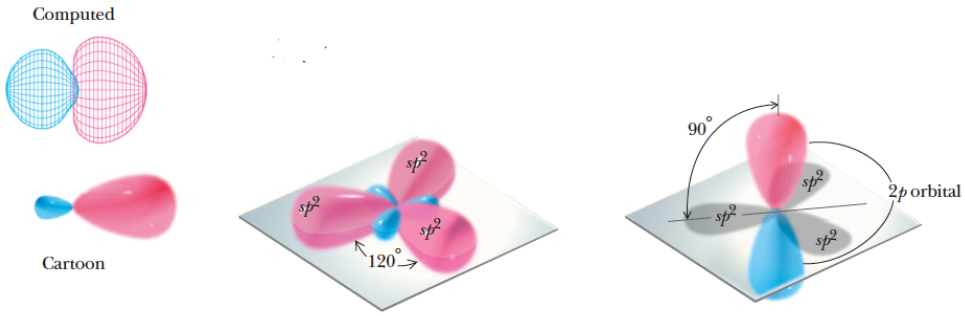
Hybridization – Valence Bond Approach to bonding

sp^3 $(\Psi_{2s} + \Psi_{2px} + \Psi_{2py} + \Psi_{2pz})$



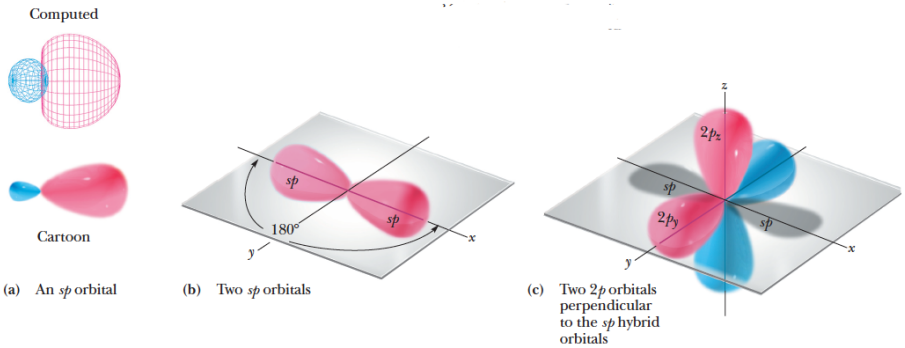
(a) An sp^3 orbital (b) Four sp^3 orbitals in a tetrahedral arrangement (c)

sp^2 $(\Psi_{2s} + \Psi_{2px} + \Psi_{2py}) + \Psi_{2pz}$



(a) An sp^2 orbital (b) Three sp^2 orbitals (c) A $2p$ orbital perpendicular to three sp^2 orbitals.

sp $(\Psi_{2s} + \Psi_{2px}) + \Psi_{2py} + \Psi_{2pz}$



(a) An sp orbital (b) Two sp orbitals (c) Two $2p$ orbitals perpendicular to the sp hybrid orbitals

Figure 1.18

Molecular orbital mixing diagram for the creation of any C—C σ bond. (a) In-phase addition of two C hybrid orbitals (albeit sp^3, sp^2, or sp orbital) forms a σ orbital that is lower in energy than the two starting orbitals. When the resulting orbital is populated with two electrons, a σ bond results. (b) Addition of the orbitals in an out-of-phase manner (meanin reversing the phasing of one of the starting orbitals) leads to an antibonding σ^* orbital.

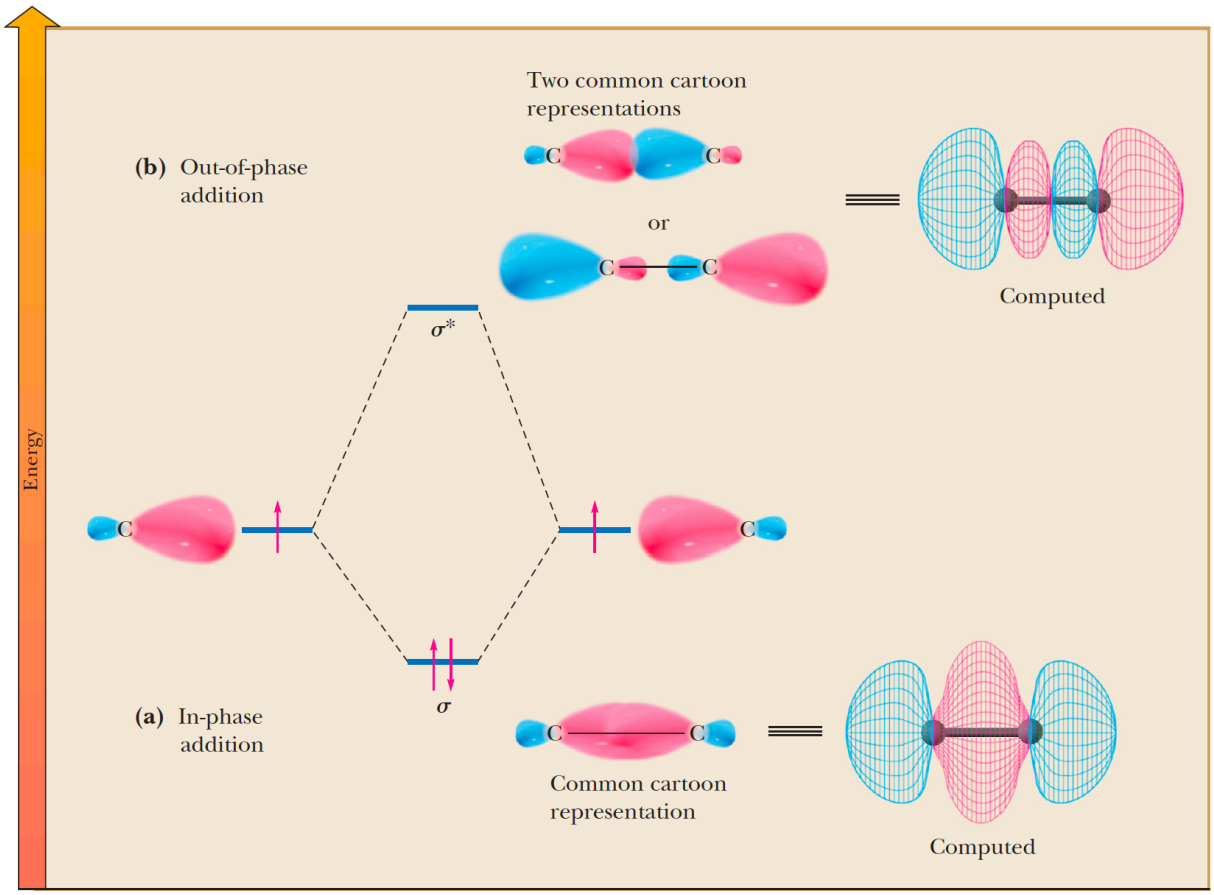
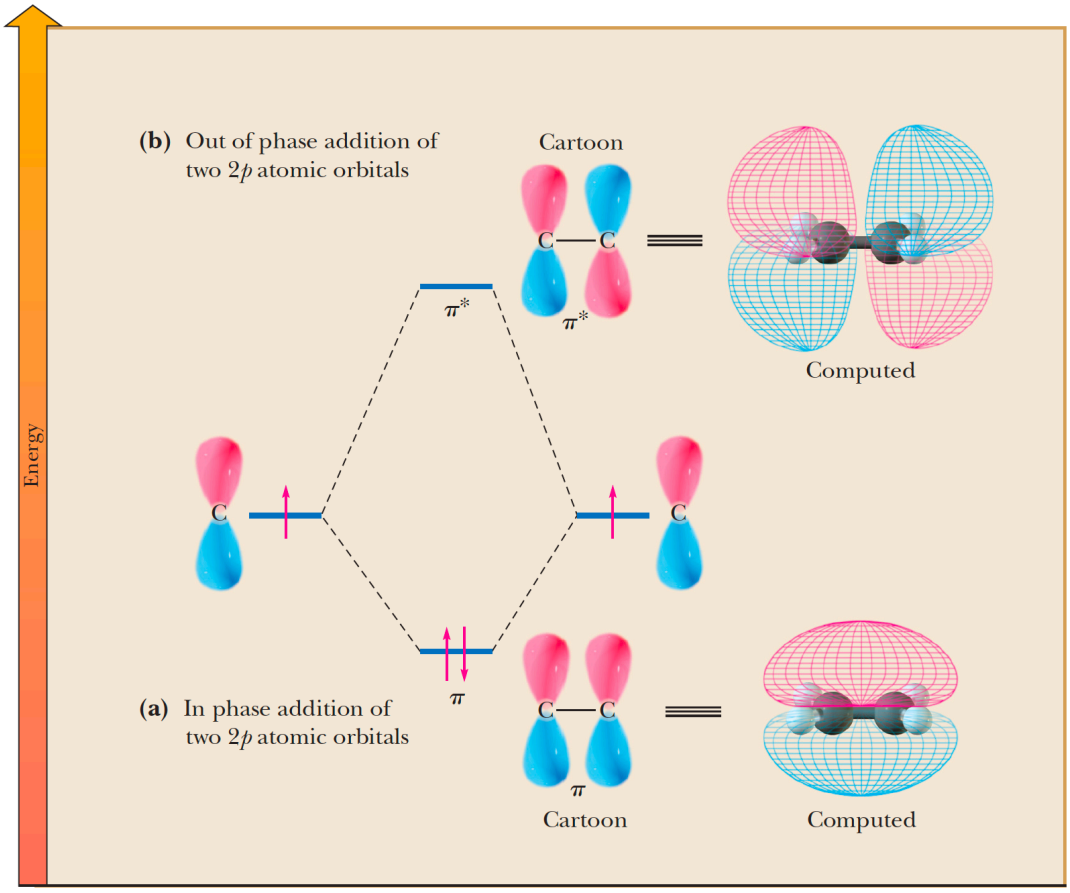
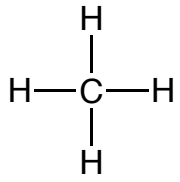


Figure 1.21
Molecular orbital mixing diagram for the creation of any C—C π bond. (a) Addition of two p atomic orbitals in-phase leads to a π orbital that is lower in energy than the two separate starting orbitals. When populated with two electrons the π orbital gives a π bond. (b) Addition of the p orbitals in an out-of-phase manner (meaning a reversal of phasing in one of the starting orbitals) leads to a π^* orbital. Population of this orbital with one or two electrons leads to weakening or cleavage of the π bond respectively.





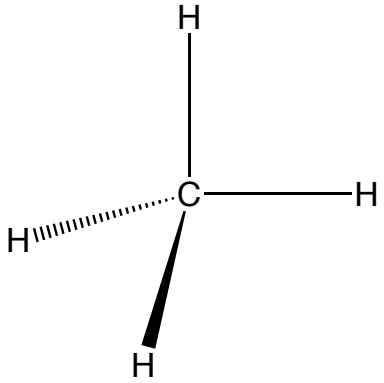
Methane

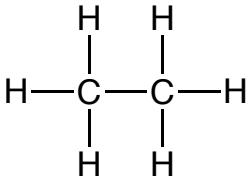
Molecular Orbital Theory approach to bonding: Just add the individual orbital wave functions:

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

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

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





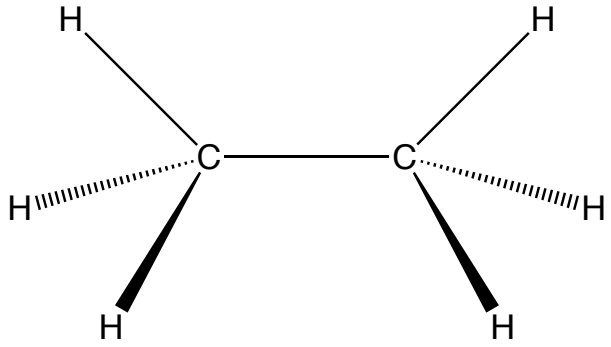
Ethane

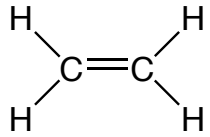
Molecular Orbital Theory approach to bonding: Just add the individual orbital wave functions:

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

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

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





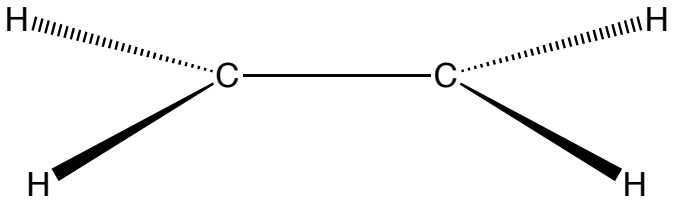
Ethene
(Ethylene)

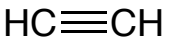
Molecular Orbital Theory approach to bonding: Just add the individual orbital wave functions:

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

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

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





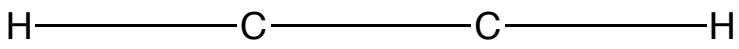
Ethyne
(Acetylene)

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:

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



Molecular Orbital Theory

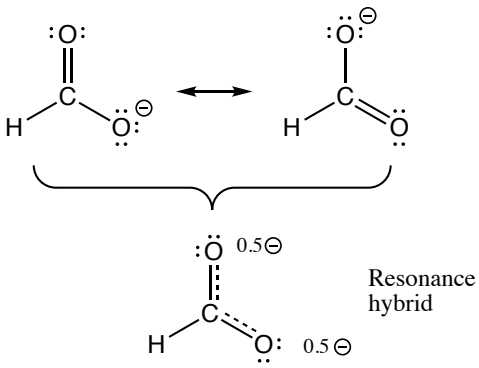
To quantify bonding in molecules we simply add all of the atomic orbital wave functions in the molecule

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

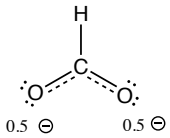
$\Rightarrow$ NEVER MORE



Carboxylate anion

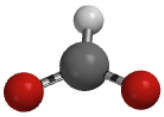
A common situation, and the one many resonance contributing structures describe, occurs when three 2p orbitals combine on adjacent atoms. A good example is the carboxylate anion. When three adjacent 2p orbitals interact (we add the three 2p orbital wave functions $\Psi_{C2pz} + \Psi_{O2pz} + \Psi_{O2pz}$),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

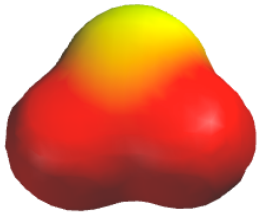
$$\Psi_{C2pz} + \Psi_{O2pz} + \Psi_{O2pz}$$

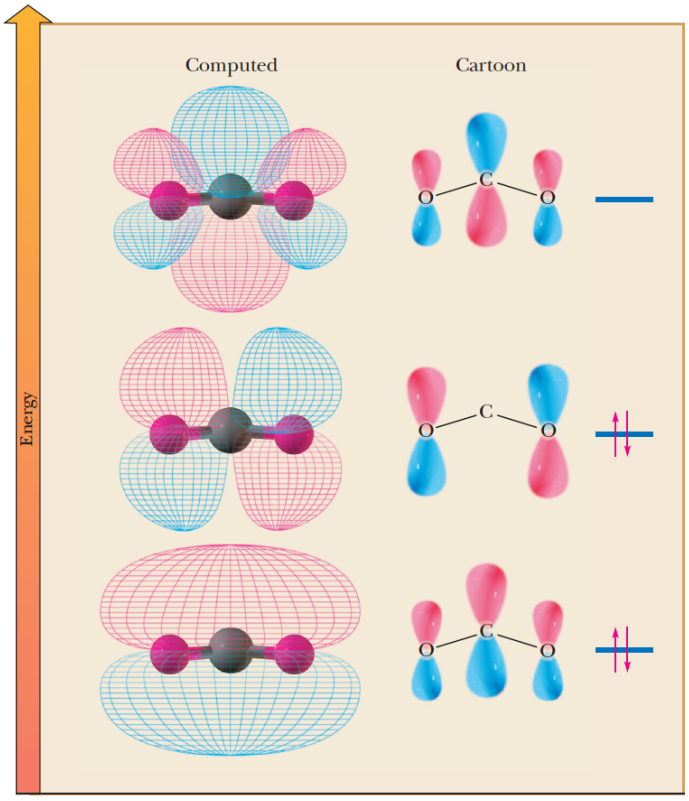


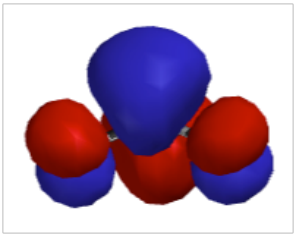
Carboxylate anion

Resonance hybrid

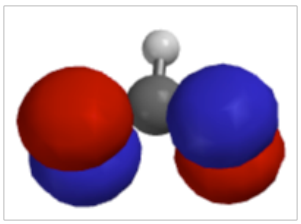




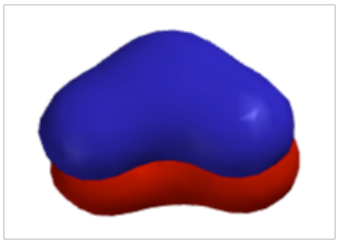




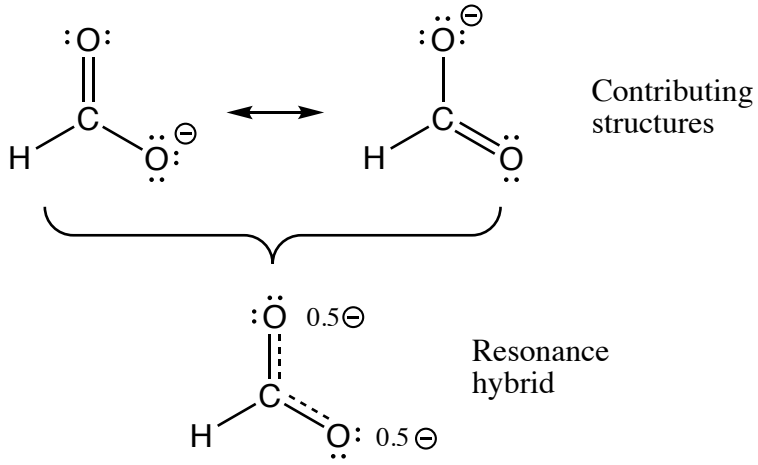
Antibonding orbital



Non-bonding orbital



"π-way" orbital



Carboxylate anion

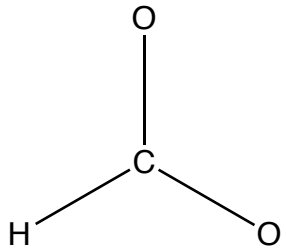
Molecular Orbital Theory approach to bonding: Just add the individual orbital wave functions:

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

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

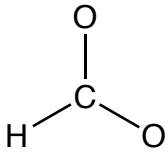
$$\Psi_{H1s} + \Psi_{C1s} + (\Psi_{C2s} + \Psi_{C2px} + \Psi_{C2py}) + \Psi_{C2pz} + \Psi_{O1s} + (\Psi_{O2s} + \Psi_{O2px} + \Psi_{O2py}) + \Psi_{O2pz} + \Psi_{O1s} + (\Psi_{O2s} + \Psi_{O2px} + \Psi_{O2py}) + \Psi_{O2pz}$$

Sigma (σ) bonding - overlap of hybridized orbitals

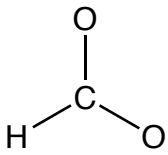


π-way bonding - overlap of 3 adjacent unhybridized 2p orbitals

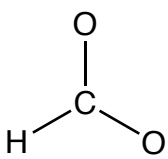
$$\Psi_{C2pz} + \Psi_{O2pz} + \Psi_{O2pz}$$



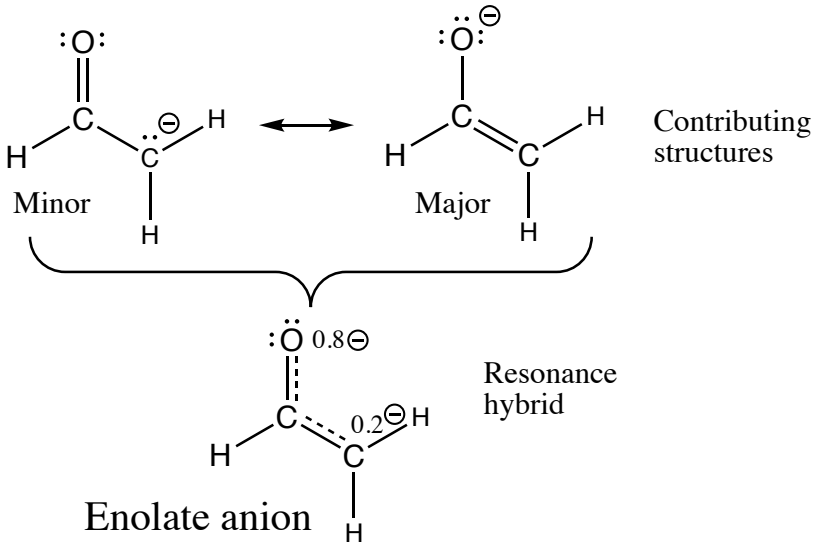
—— Antibonding



—— Non-bonding



—— Bonding



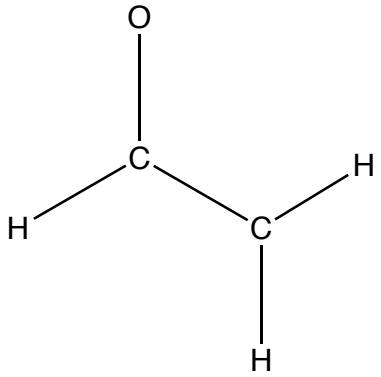
Molecular Orbital Theory approach to bonding: Just add the individual orbital wave functions:

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

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

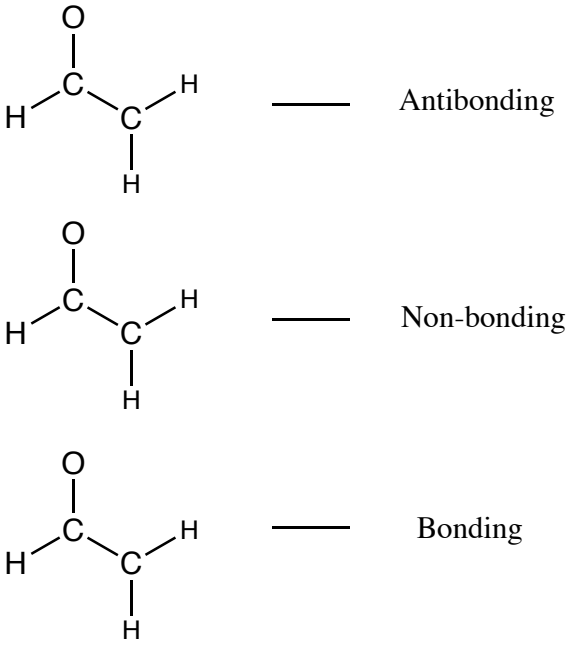
$$\Psi_{H1s} + \Psi_{H1s} + \Psi_{H1s} + \Psi_{C1s} + (\Psi_{C2s} + \Psi_{C2px} + \Psi_{C2py}) + \Psi_{C2pz} + \Psi_{C1s} + (\Psi_{C2s} + \Psi_{C2px} + \Psi_{C2py}) + \Psi_{C2pz} + \Psi_{O1s} + (\Psi_{O2s} + \Psi_{O2px} + \Psi_{O2py}) + \Psi_{O2pz}$$

Sigma (σ) bonding - overlap of hybridized orbitals

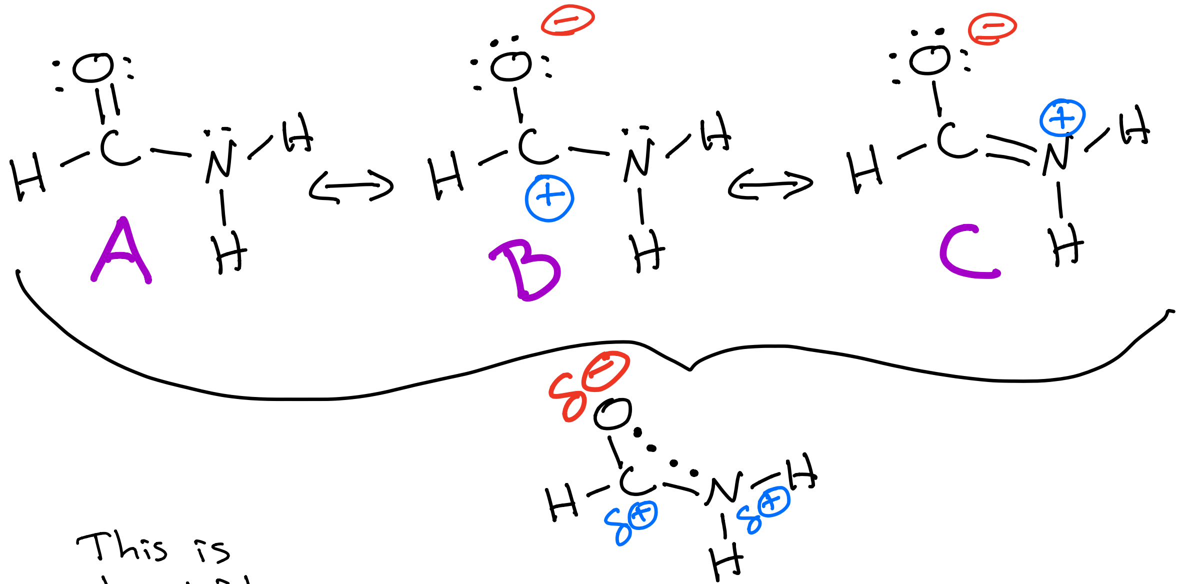


π-way bonding - overlap of 3 adjacent unhybridized 2p orbitals

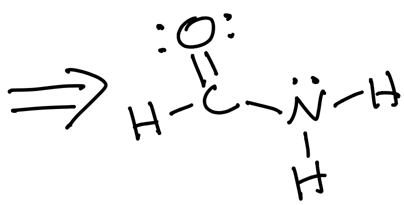
$$\Psi_{C2pz} + \Psi_{C2pz} + \Psi_{O2pz}$$



Amide contributing structures revisited



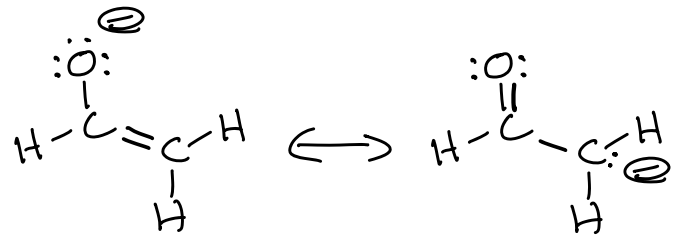
This is how it is drawn, but all 3 contributing structures must be considered



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).

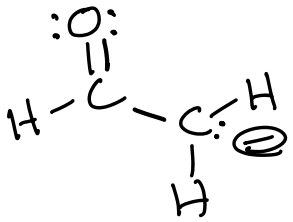
7. Delocalization of pi electron density over a larger area is stabilizing. Pi electron density delocalization occurs through overlapping 2*p* orbitals, so to take part in pi electron density delocalization atoms must be *sp2* or *sp* hybridized and reside in the same plane. Pi electron delocalization 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.

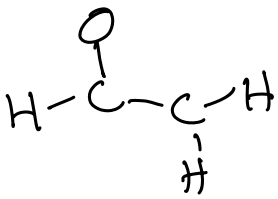
Enolate ion contributing structures



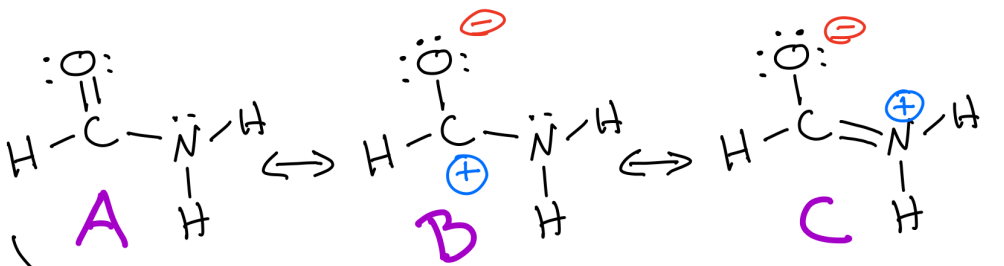
Major

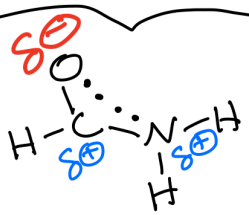
Minor
(but still important)

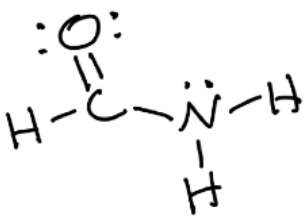




Amide contributing structures







Survival skill in O Chem

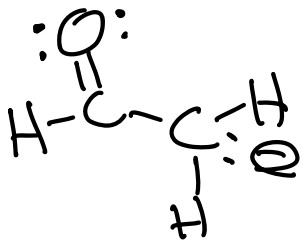
↳ Identify hybridization state of atoms in molecules

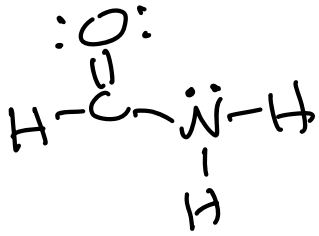
1) sp^3

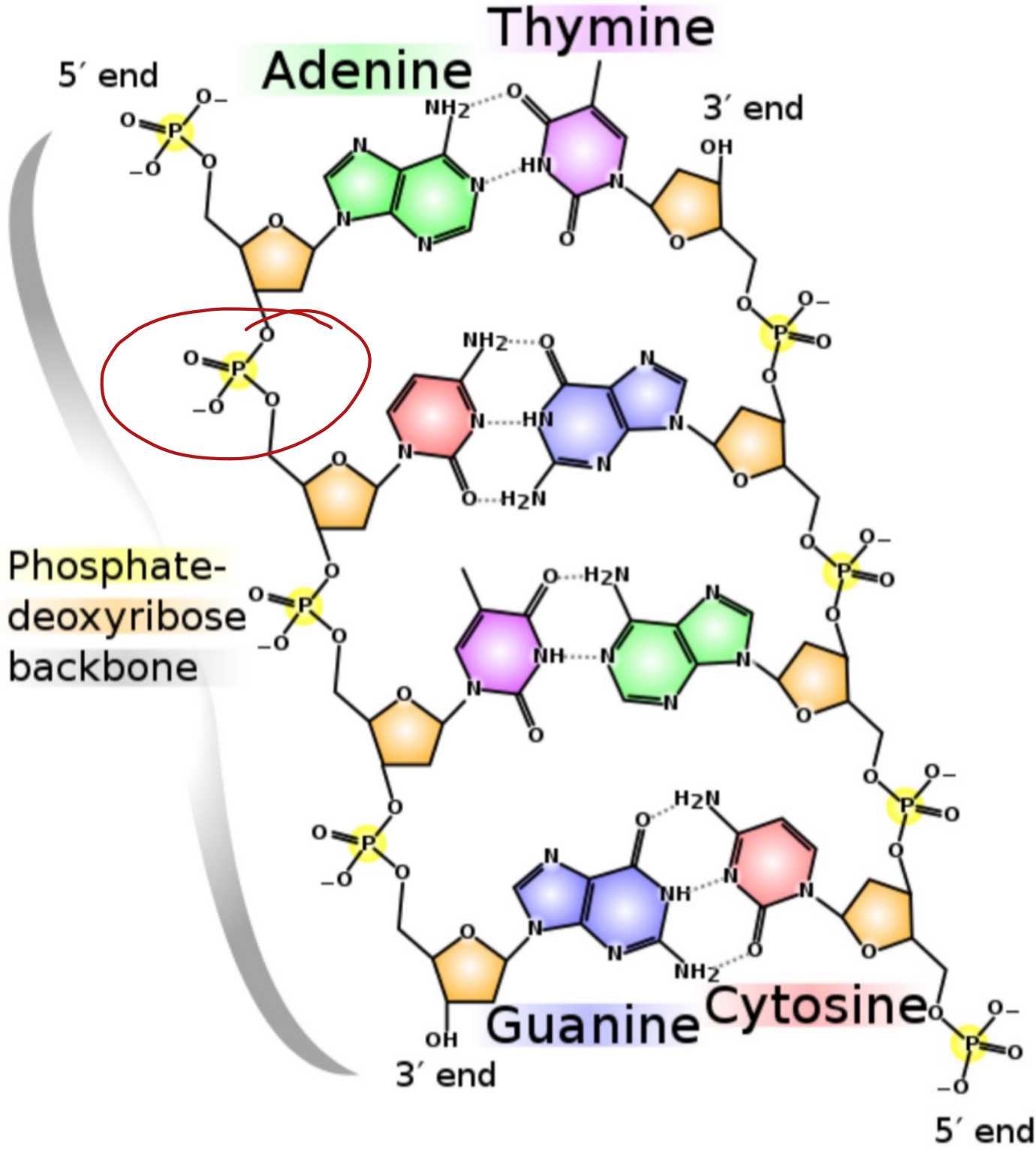
2) sp^2

3) sp

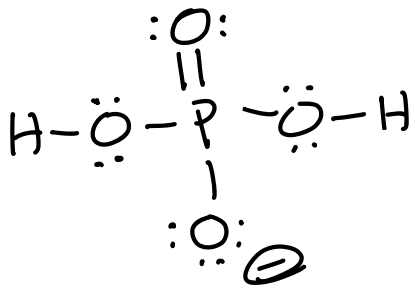
⇒ An atom counts as having a π bond



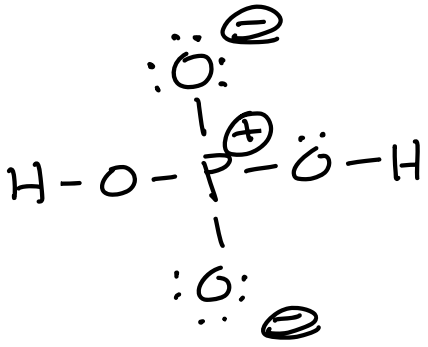


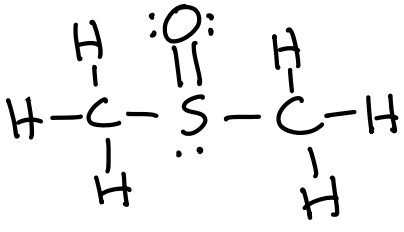


Chemical structure of DNA; hydrogen bonds shown as dotted lines



vs.





vs.