Organic Chemistry is the study of carbon-containing molecules.

This class has two points.

The first point of the class is to understand the organic chemistry of living systems. We will teach you how to think about and understand the most amazing things on the planet!!

Water is essential for life, you will learn why water has such special properties.

You will learn the secret structural reason proteins, the most important molecular machines in our bodies, can support the chemistry of life.

You will learn why when you take Advil for pain, exactly half of what you take works, and the other half does nothing.

You will learn how toothpaste works.

You will learn how a single chlorofluorocarbon refrigerant molecule released into the atmosphere can destroy many, many ozone molecules of the critical ozone layer surrounding our planet.

You will learn how medicines like Benadryl, Seldane, and Lipitor work.

You will learn how Naloxone is an antidote for an opioid overdose.

You will learn why Magic Johnson is still alive, decades after contracting HIV.

You will learn how MRI scans work.

The second point of organic chemistry is the synthesis of complex molecules from simpler ones by making and breaking specific bonds.

You will learn how to understand movies of reaction mechanisms like alkene hydration.

You will learn reactions that once begun, will continue reacting such that each product molecule created starts a new reaction until all the starting material is used up.

You will learn reactions that can make antifreeze from vodka.

You will learn a reaction that can make nail polish remover from rubbing alcohol.

You will learn how to look at a molecule and accurately predict which atoms will react to make new bonds, and which bonds will break during reactions.

You will learn how to analyze a complex molecule's structure so that you can predict ways to make it via multiple reactions starting with less complex starting molecules.

The ability to rationally synthesize new molecules changed human destiny and drives the economies of the world by enabling:

1. The synthesis of new drugs to cure disease and dramatically increase human life span
2. The development of lubricants and components for virtually all machines
3. The creation of new methods for integrated circuit production enabling faster computation
4. The creation of new materials for millions of uses including 3d printing and biodegradable plastics
5. The synthesis of new pigments for dyes, paints, cosmetics and digital displays
6. The synthesis of all synthetic clothing fibers
7. The production of highly refined and cleaner burning fuels
8. The production of rechargeable batteries
9. …to name just a FEW applications.

In other words, essentially everything that we associate with what makes modern life so incredible.

> “You can’t stop the waves, but you can learn to surf”
>
> Jon Kabat-Zinn


Alkanes
Alkenes
Alkynes
Haloalkanes
Vicinal dihaloalkanes
Ketones and Aldehydes
Carboxylic Acids
Alcohols
Where Electrons Are
Mechanisms
Roadmaps
Stereochemistry
Regiochemistry
ROTD
NIRRS
Motive
Opportunity
Carbocation
Radical
Pi-ways
Golden Rules
Make a Bond
Break a Bond
Add a Proton
Take a Proton
Nucleophiles and Electrophiles
Charge Delocalization
Hyperconjugation
Steric strain
Angle and Torsional Strain
Epoxides
Vicinal Diols
Radical Chain
SN2 vs. E2
SN1 and E1
Anti-periplanar
Markovnikov
Zaitsev

*A stepwise approach to perfect Lewis structures**

Step 1: Arrange atoms in space based on connectivity given in molecular formula.

Step 2: Add single bonds to all atoms that are connected to each other.

Step 3: Identify all carbon atoms without a filled valence shell. For each such carbon atom, look for an adjacent atom that is also without a filled valence and connect with one or two multiple bonds.

Step 4: Add lone pairs to fill all remaining unfilled valence shells.

Step 5: Add any formal charges as identified by the table presented during the first lecture.

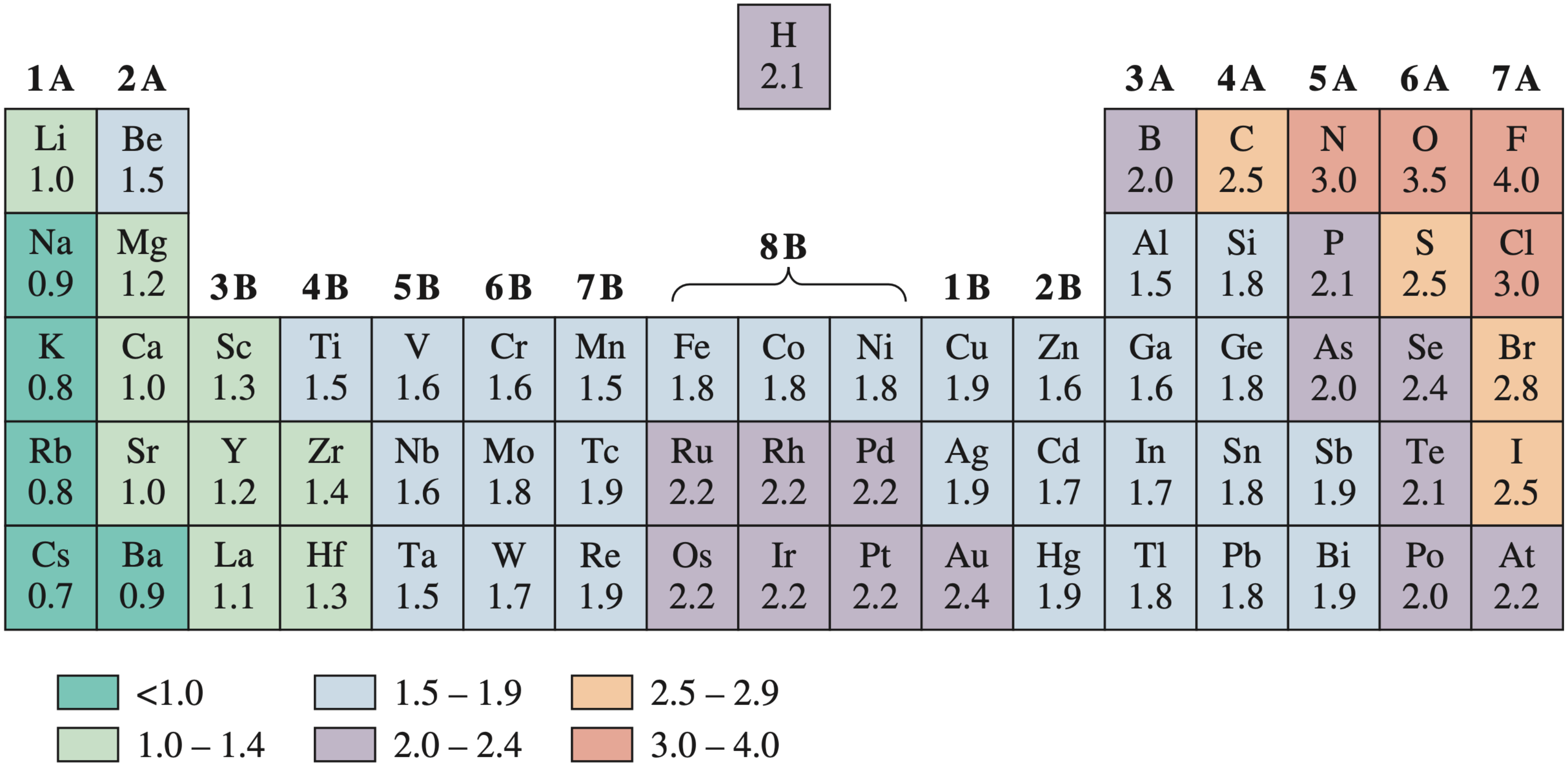
*This works for all but molecules with a carbocation. Do not worry about those at this time.

Valence Electrons in Neutral Atoms:

H	C	N	O	F,Cl,Br,I
1	4	5	6	7

Formal Charge Identification:

		Neutral		Positive Charge		Negative Charge	
Atom	# electrons in the valence shell	Bonds	Lone Pairs	Bonds	Lone Pairs	Bonds	Lone Pairs
H	2	1	0	0	0	0	1 (rare)
C	8	4	0	3	0	3	1
N	8	3	1	4	0	2	2
O	8	2	2	3	1	1	3
F,Cl,Br,I	8	1	3	-	-	0	4



1A	2A	3B	4B	5B	6B	7B	8B			1B	2B	3A	4A	5A	6A	7A
								H 2.1								
Li 1.0	Be 1.5											B 2.0	C 2.5	N 3.0	O 3.5	F 4.0
Na 0.9	Mg 1.2											Al 1.5	Si 1.8	P 2.1	S 2.5	Cl 3.0
K 0.8	Ca 1.0	Sc 1.3	Ti 1.5	V 1.6	Cr 1.6	Mn 1.5	Fe 1.8	Co 1.8	Ni 1.8	Cu 1.9	Zn 1.6	Ga 1.6	Ge 1.8	As 2.0	Se 2.4	Br 2.8
Rb 0.8	Sr 1.0	Y 1.2	Zr 1.4	Nb 1.6	Mo 1.8	Tc 1.9	Ru 2.2	Rh 2.2	Pd 2.2	Ag 1.9	Cd 1.7	In 1.7	Sn 1.8	Sb 1.9	Te 2.1	I 2.5
Cs 0.7	Ba 0.9	La 1.1	Hf 1.3	Ta 1.5	W 1.7	Re 1.9	Os 2.2	Ir 2.2	Pt 2.2	Au 2.4	Hg 1.9	Tl 1.8	Pb 1.8	Bi 1.9	Po 2.0	At 2.2

🟩 <1.0	🟦 1.5 – 1.9	🟧 2.5 – 2.9
🟩 1.0 – 1.4	🟪 2.0 – 2.4	🟥 3.0 – 4.0

Solutions to the Schrodinger equation – atomic orbitals

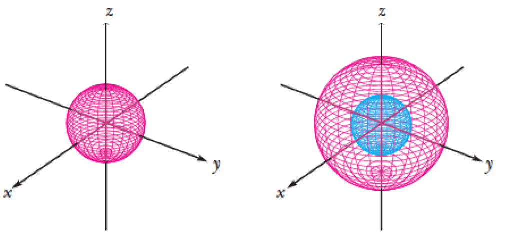
$$\psi_{n\ell m}(r,\theta,\phi)=\sqrt{\left(\frac{2}{na_0}\right)^3\frac{(n-\ell-1)!}{2n[(n+\ell)!]}}\,e^{-r/na_0}\left(\frac{2r}{na_0}\right)^{\ell}L^{2\ell+1}_{n-\ell-1}\left(\frac{2r}{na_0}\right)\cdot Y_\ell^m(\theta,\phi)$$

where:

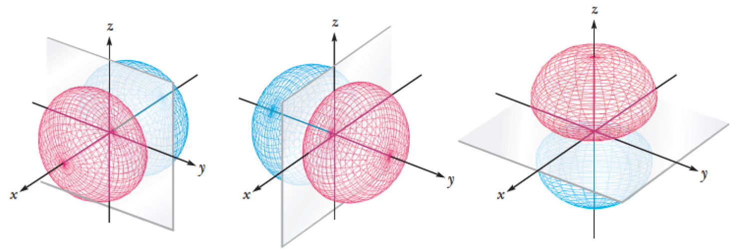
- $a_0=\dfrac{4\pi\varepsilon_0\hbar^2}{m_e e^2}$ is the Bohr radius,
- $L^{2\ell+1}_{n-\ell-1}(\cdots)$ are the generalized Laguerre polynomials of degree $n-\ell-1$.
- n, ℓ, m are the principal, azimuthal, and magnetic quantum numbers respectively: which take the values:

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

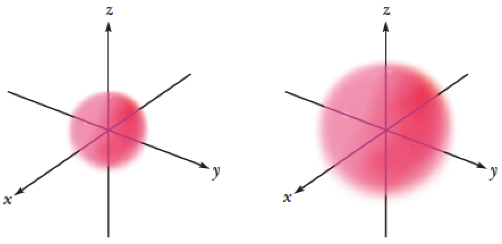
Ψ_{1s} Ψ_{2s} Ψ_{2px} Ψ_{2py} Ψ_{2pz}



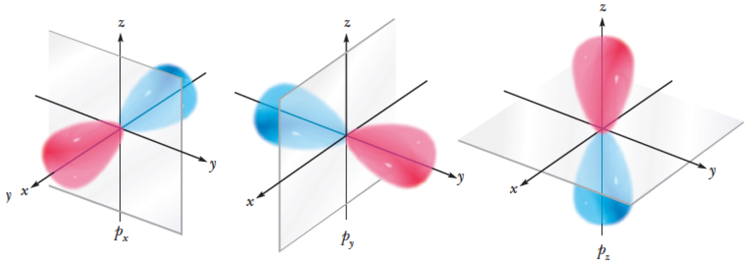
(a) 1*s* and 2*s* orbitals computed using the Schrödinger equation



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



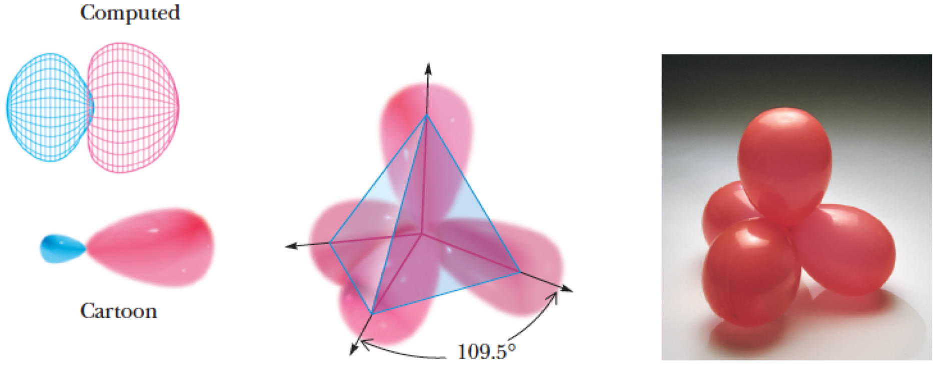
(b) Cartoon representations of 1*s* and 2*s* orbitals



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

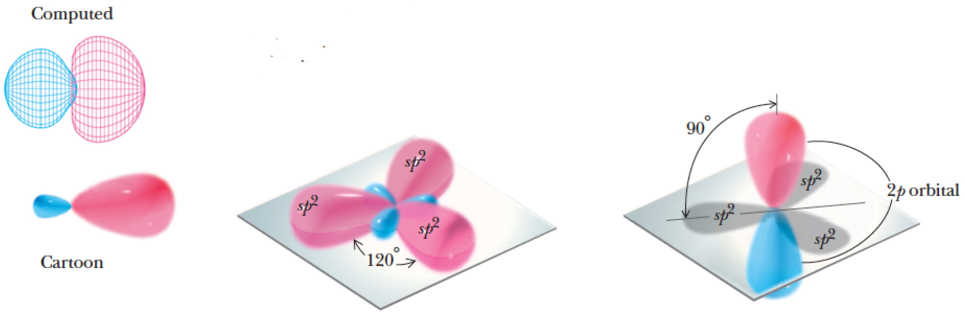
Hybridization – Valence Bond Approach to bonding

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



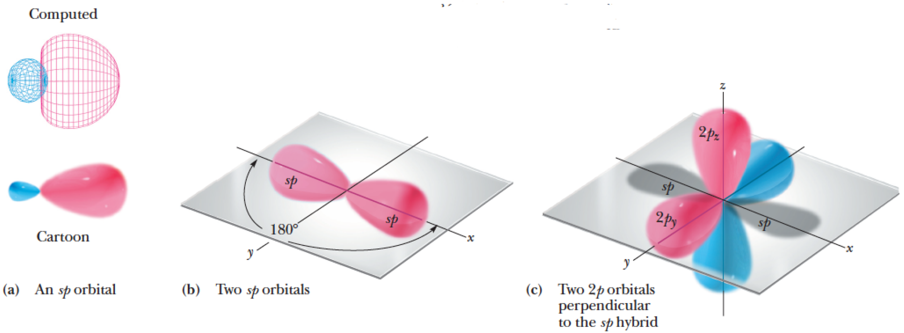
(a) An *sp*³ orbital **(b)** Four *sp*³ orbitals in a tetrahedral arrangement **(c)**

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



(a) An *sp*² orbital (b) Three *sp*² orbitals (c) A 2*p* 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 2*p* 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.

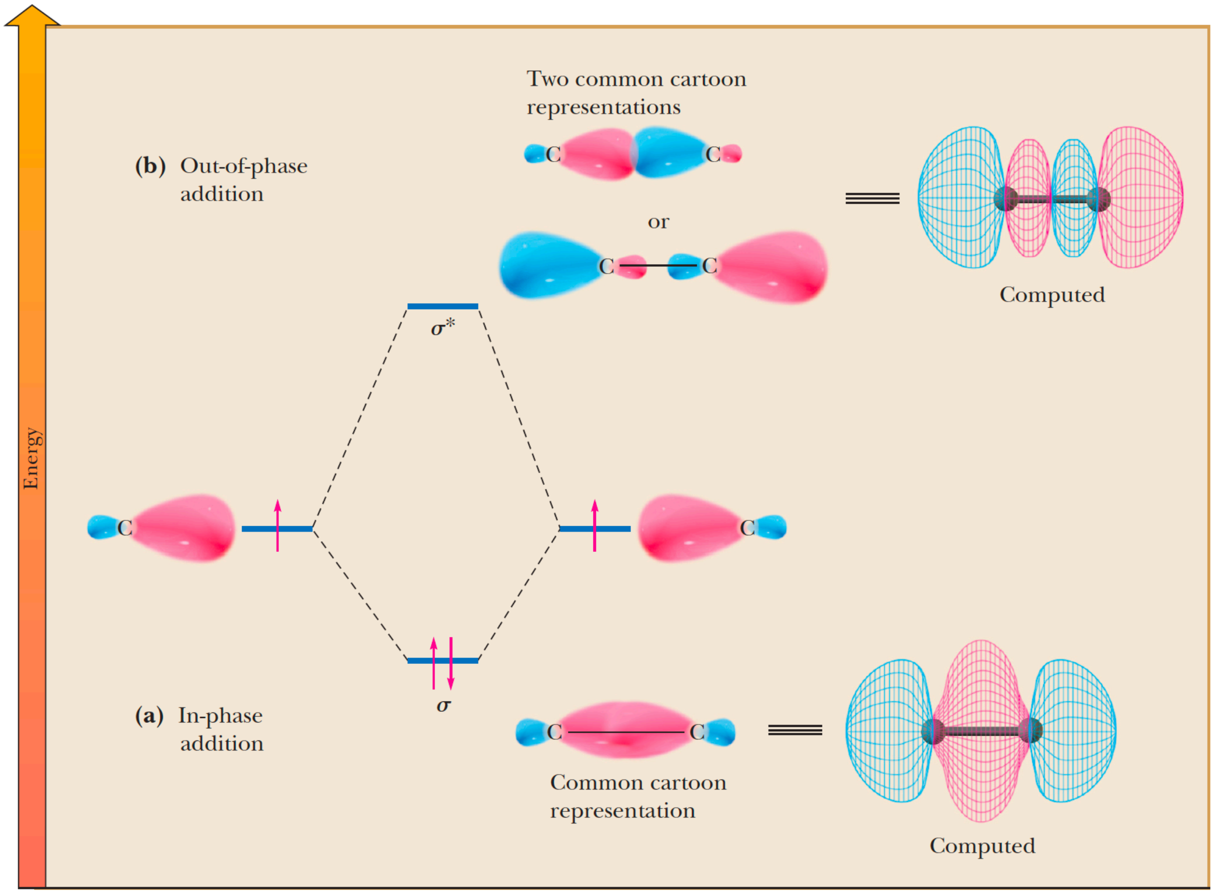
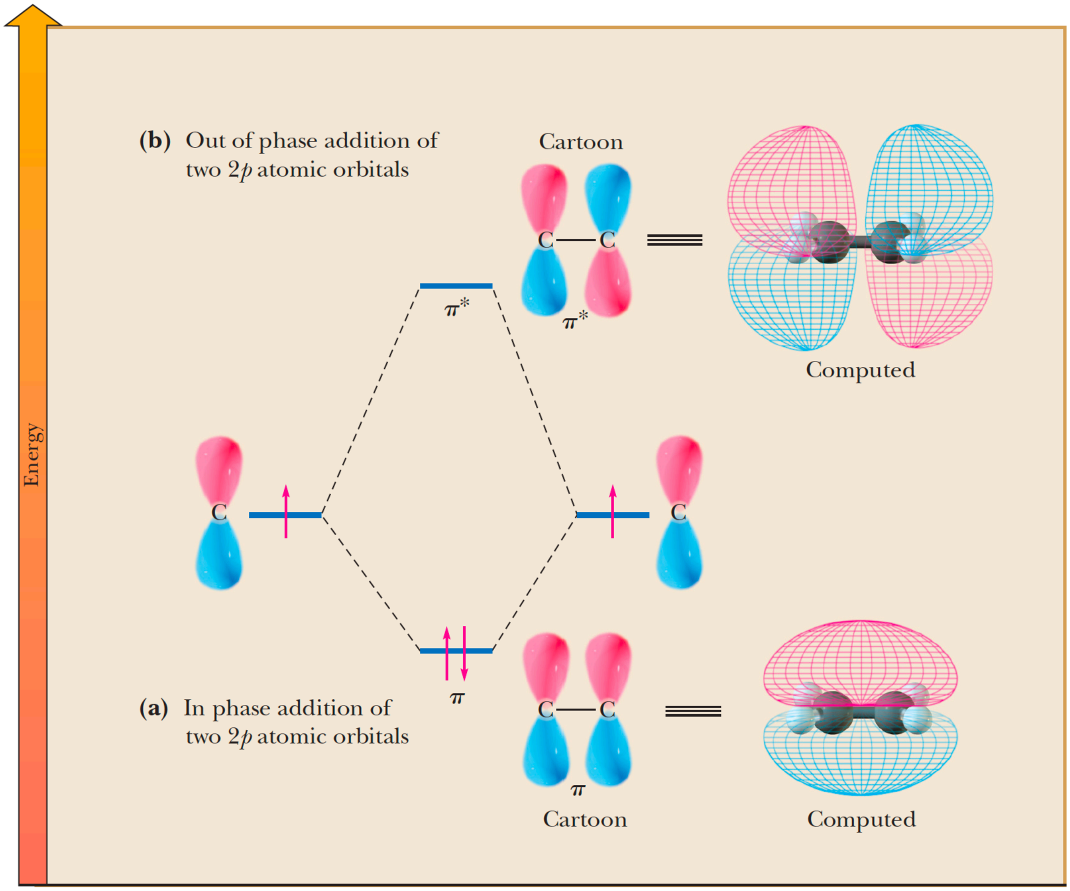
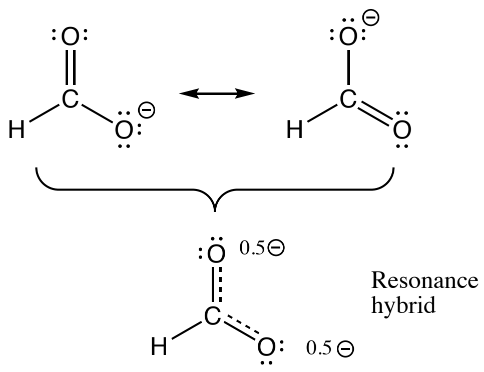


Figure 1.21 Molecular orbital mixing diagram for the creation of any C—C π bond. (a) Addition of two p atomic orbitals in-phase leads to a π orbital that is lower in energy than the two separate starting orbitals. When populated with two electrons the π orbital gives a π bond. (b) Addition of the p orbitals 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.

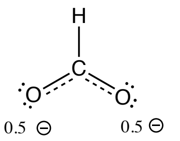




Carboxylate anion

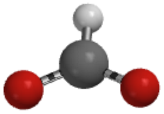
A common situation, and the one many resonance contributing structures describe, occurs when three 2p orbitals combine on adjacent atoms. A good example is the carboxylate anion. When three adjacent 2p orbitals interact (we add the three 2p orbital wave functions $\Psi_{C2pz} + \Psi_{O2pz} + \Psi_{O2pz}$),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

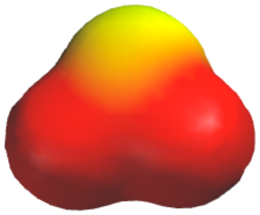
$$\Psi_{C2pz} + \Psi_{O2pz} + \Psi_{O2pz}$$

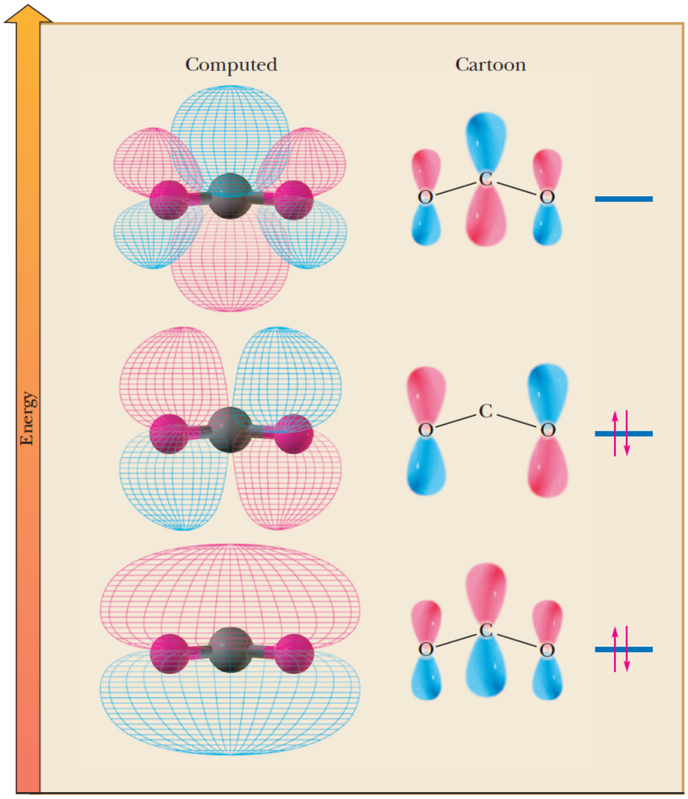


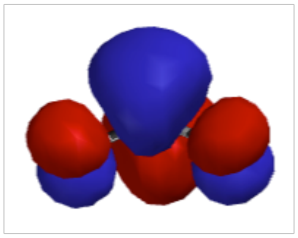
Carboxylate anion

Resonance
hybrid

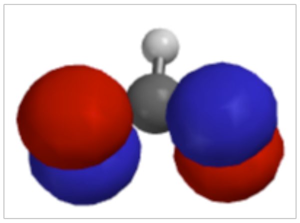




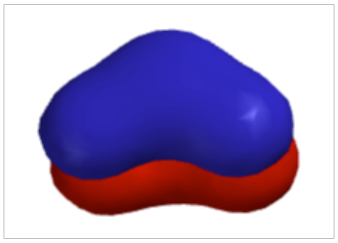




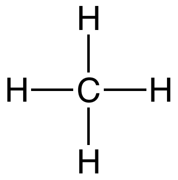
Antibonding orbital



Non-bonding orbital



“π-way” orbital



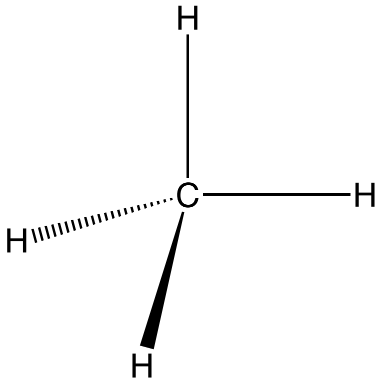
Methane

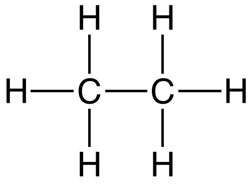
Molecular Orbital Theory approach to bonding: Just add the individual orbital wave functions:

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

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

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





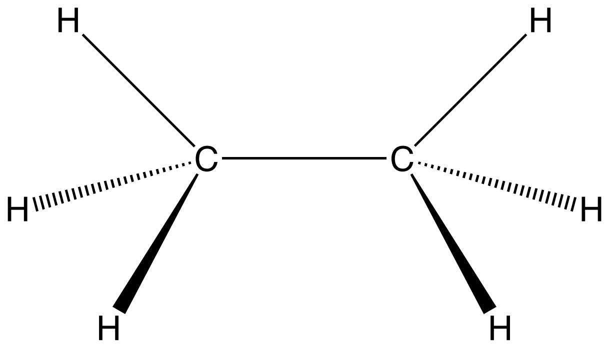
Ethane

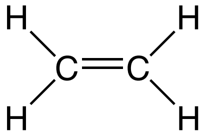
Molecular Orbital Theory approach to bonding: Just add the individual orbital wave functions:

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

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

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





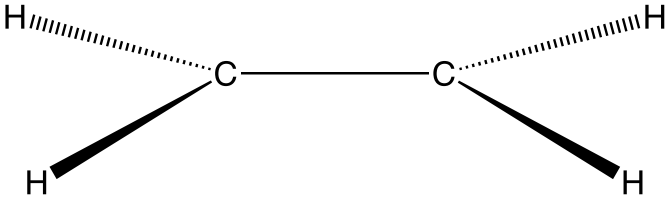
Ethene
(Ethylene)

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:

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



$HC\equiv CH$

Ethyne
(Acetylene)

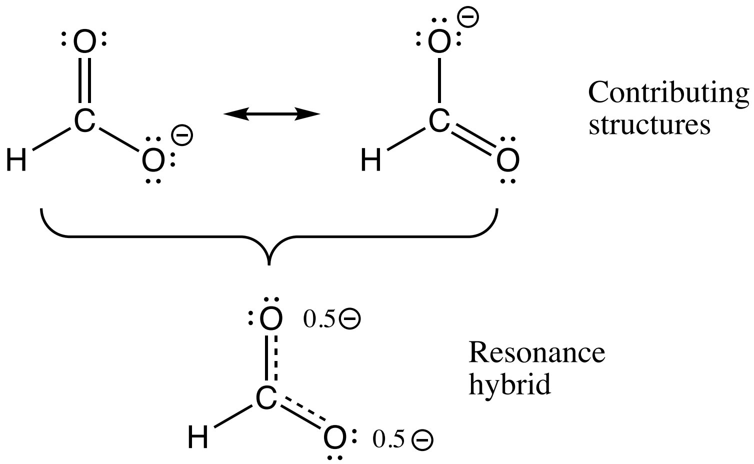
Molecular Orbital Theory approach to bonding: Just add the individual orbital wave functions:

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

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

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

$$H\text{———}C\text{———}C\text{———}H$$



Carboxylate anion

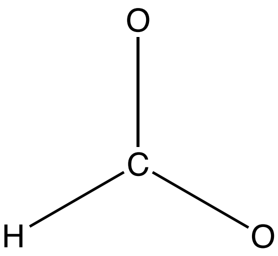
Molecular Orbital Theory approach to bonding: Just add the individual orbital wave functions:

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

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

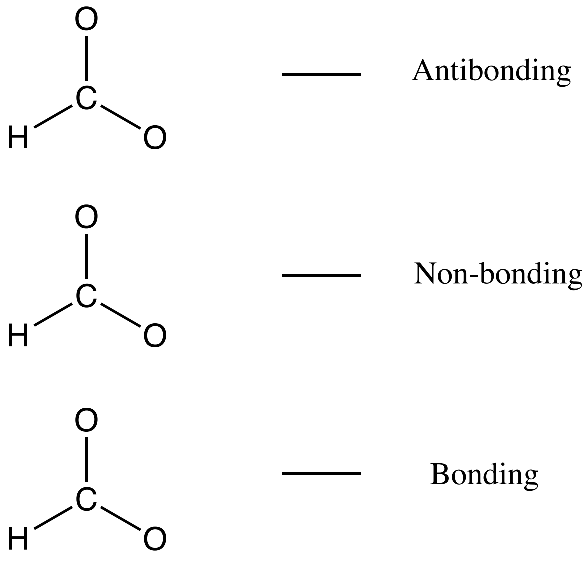
$$\Psi_{H1s} + \Psi_{C1s} + (\Psi_{C2s} + \Psi_{C2px} + \Psi_{C2py}) + \Psi_{C2pz} + \Psi_{O1s} + (\Psi_{O2s} + \Psi_{O2px} + \Psi_{O2py}) + \Psi_{O2pz} + \Psi_{O1s} + (\Psi_{O2s} + \Psi_{O2px} + \Psi_{O2py}) + \Psi_{O2pz}$$

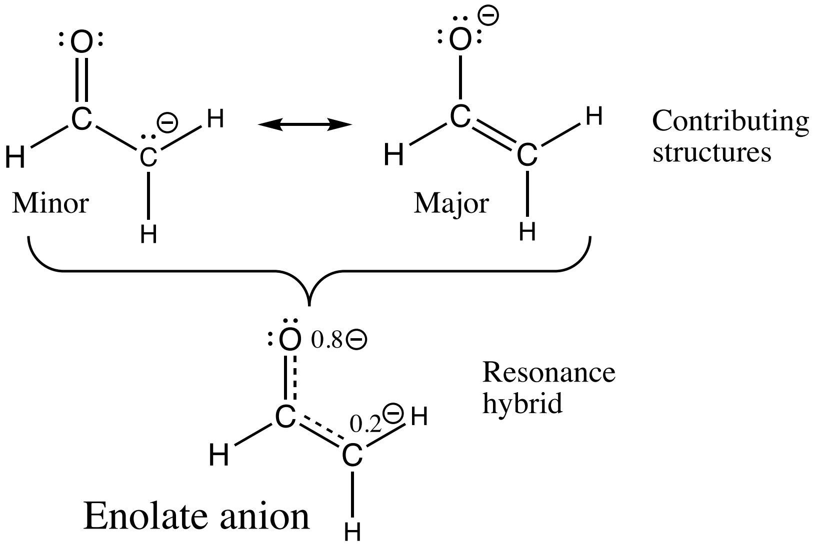
Sigma (σ) bonding - overlap of hybridized orbitals



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

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





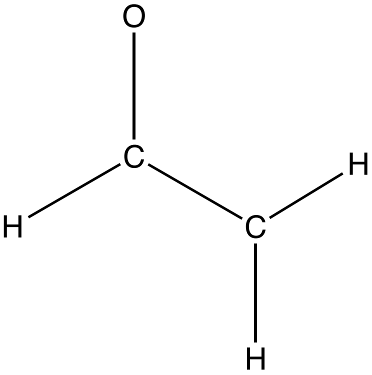
Molecular Orbital Theory approach to bonding: Just add the individual orbital wave functions:

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

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

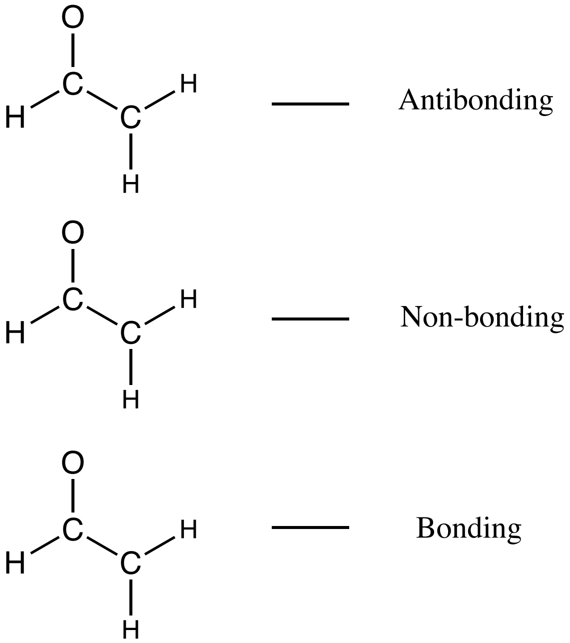
$$\Psi_{H1s} + \Psi_{H1s} + \Psi_{H1s} + \Psi_{C1s} + (\Psi_{C2s} + \Psi_{C2px} + \Psi_{C2py}) + \Psi_{C2pz} + \Psi_{C1s} + (\Psi_{C2s} + \Psi_{C2px} + \Psi_{C2py}) + \Psi_{C2pz} + \Psi_{O1s} + (\Psi_{O2s} + \Psi_{O2px} + \Psi_{O2py}) + \Psi_{O2pz}$$

Sigma (σ) bonding - overlap of hybridized orbitals

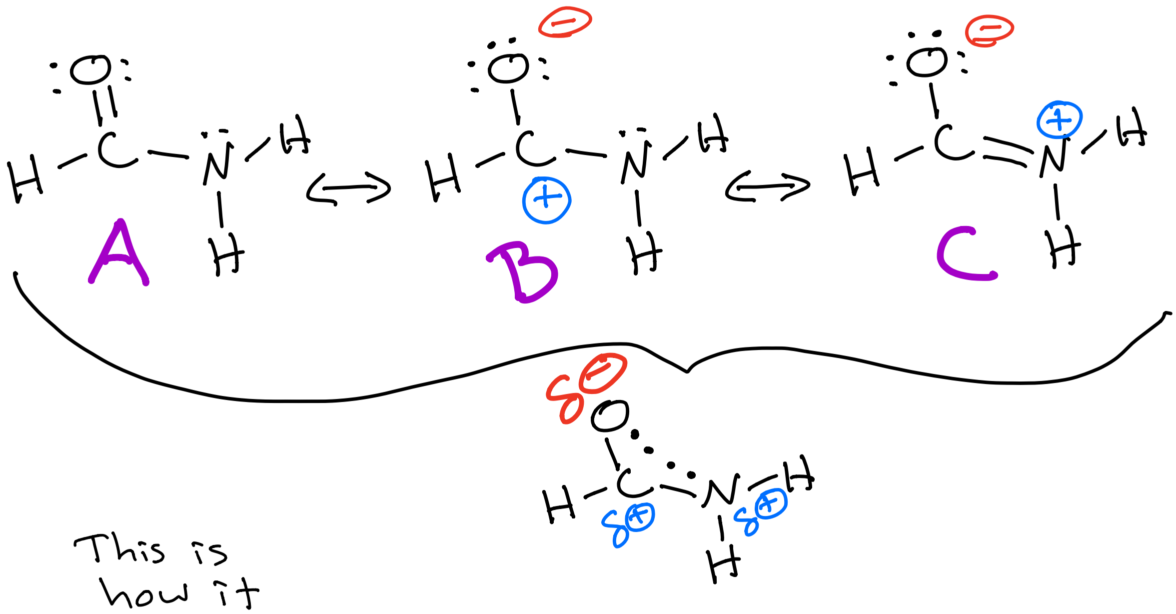


π-way bonding - overlap of 3 adjacent unhybridized 2p orbitals

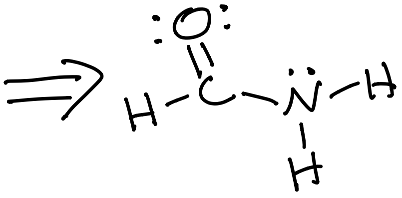
$$\Psi_{C2pz} + \Psi_{C2pz} + \Psi_{O2pz}$$



Amide contributing structures revisited



This is how it is drawn, but all 3 contributing structures <u>must</u> 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.