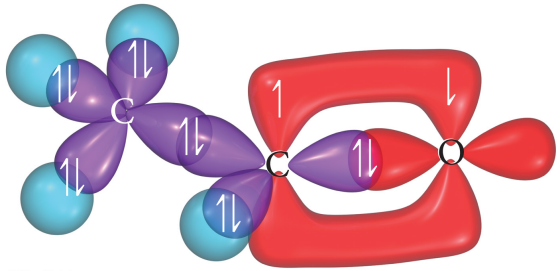
Ch10

Quantum Molecules

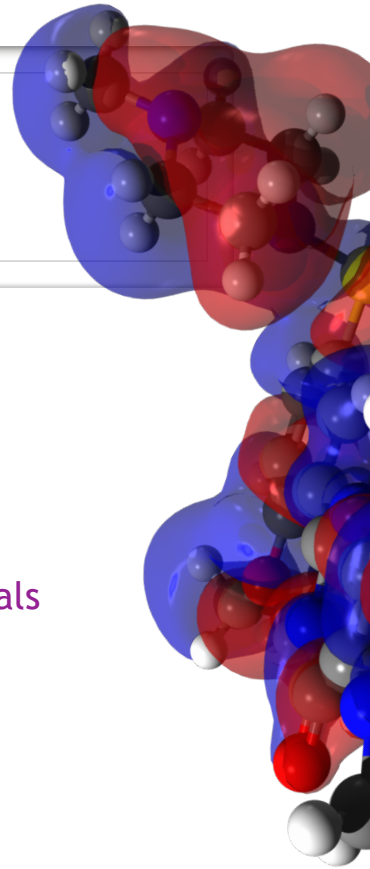
Two way's to apply quantum theory to the whole molecule.

Valence Bond Theory & Molecular Orbital Theory.

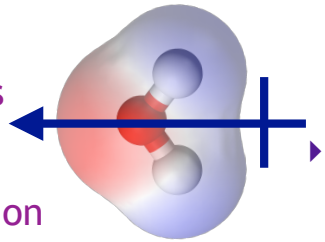


version 1.5

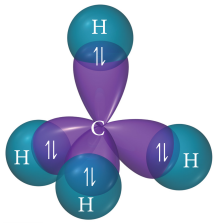
Valence Bond & MO Theories



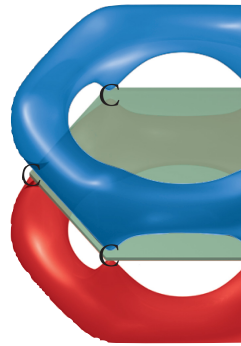
- Molecular Shape and Polarity
  - Polar Bond & Polar Molecules
  - Net Dipole Moment
  - Adding dipoles: vector addition
    - in one dimension
    - two & three dimensions
    - try some examples

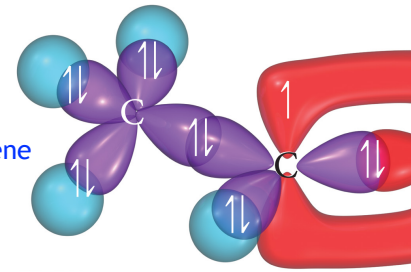


- Valence Bond Theory
  - Quantum View of Covalent Bonds
    - Bonding with Schrödinger's Quantum Atom
    - Orbital Overlap is a Covalent Bond
  - Forming Molecules w/ Quantum Atoms
    - H_2S & H_2C
  - Hybridization of Atomic Orbitals
    - Atomic Orbitals inside a molecule are not the same as the atom by itself.
    - sp3 orbitals
    - Sigma & Pi bonding: sp2 & sp orbitals
    - d-Orbital Hybridization: sp3d & sp3d2



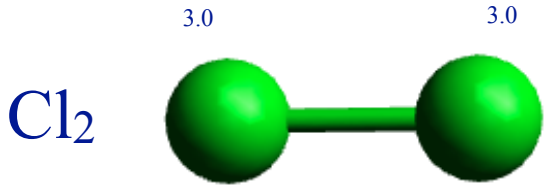
- Determining Hybridization
  - Look at electronic shape of the atom
- Molecular Orbital Theory
  - Electron Delocalization
  - Linear combinations of atomic s orbitals
    - constructive: bonding
    - destructive: antibonding
    - Molecular orbital diagrams
      - H2, He2, He2+
      - bond order
  - Linear combinations of atomic p orbitals
    - shapes of bonding and antibonding orbitals
    - Period 2 homonuclear diatomics
    - 2s-2p mixing
      - paramagnetism and diamagnetism
      - liquid oxygen
    - Period 2 heteronuclear diatomic molecules
    - Polyatomic molecules
      - electron delocalization in ozone, benzene



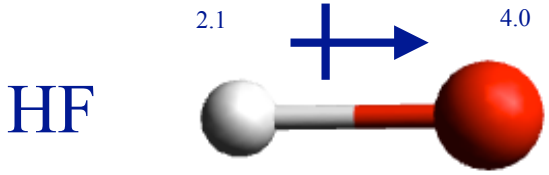


Polar Molecules

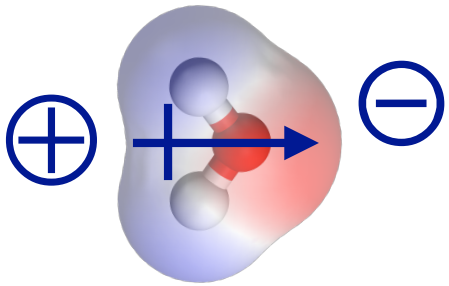
- Bonds can have a dipole moment.
  - A bond dipole is how balanced the electrons in a bond are between two atoms.
  - Bonds that have a dipole moment are said to be polar bonds.
- A molecule can have a net dipole moment.
- The net dipole moment is how balanced the electrons are overall in the entire molecule.
- Molecules that have a net dipole are said to be polar molecules.
- Polar molecules have a “north pole” and “south pole”.
- They interact with electromagnetic fields.
- Including electromagnetic fields of other polar molecules.
- They also have other physical properties unique to polar molecules.
- For example:
  - Polar molecules have higher boiling points.
  - Polar molecules can solvate ions.
  - Polar substances don’t mix with non-polar substances (oil and water).
  - Polar molecules can be affected by magnetic fields (how liquid crystal displays work).

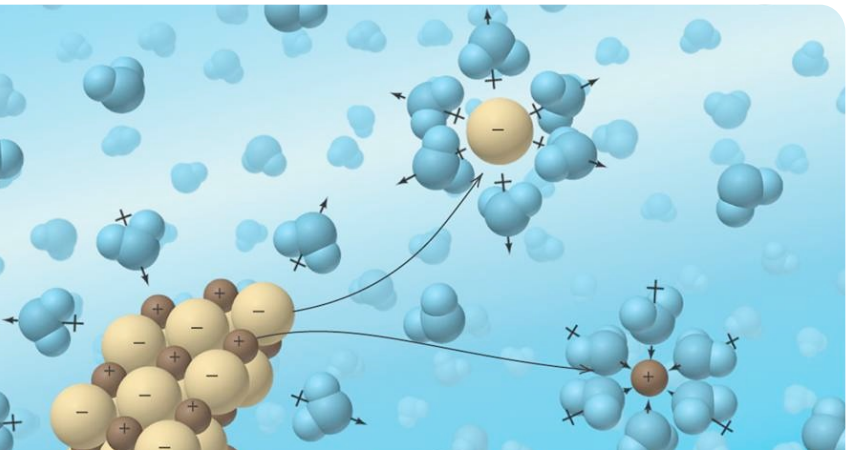


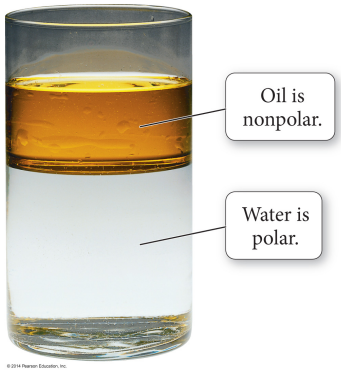
$\Delta EN = 0$

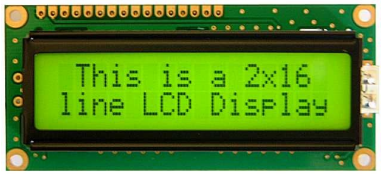


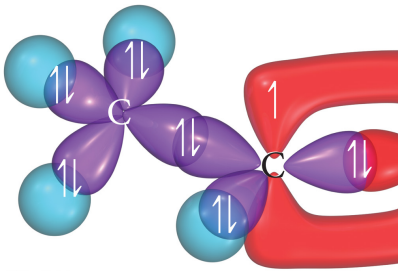
$\Delta EN = 1.9$





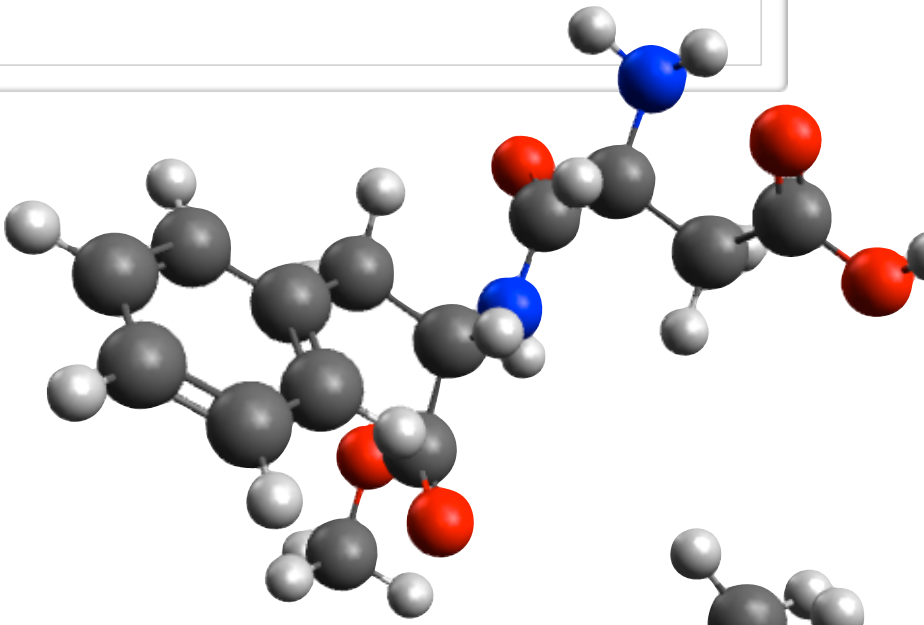


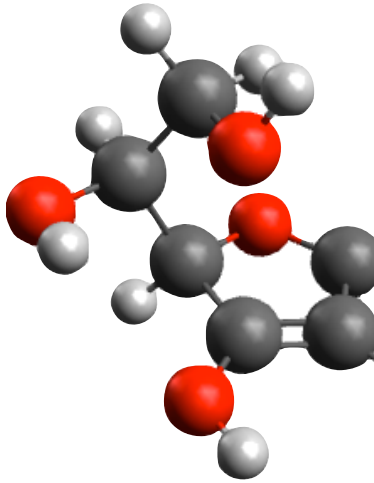


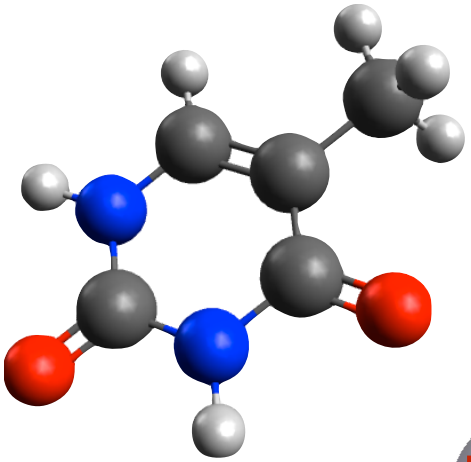


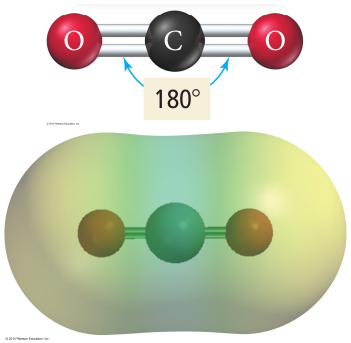
Polar Molecules

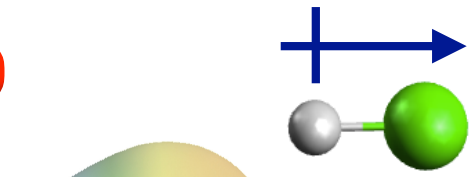
- If there are many bonds, how do you decide if the molecule is polar or non-polar?
- You add up all the bond dipoles in the molecule to create a net dipole.
- Bond dipoles are vectors, we need to talk about vector addition.

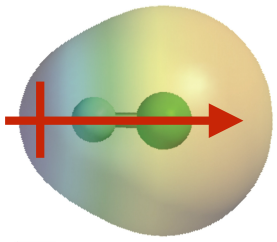


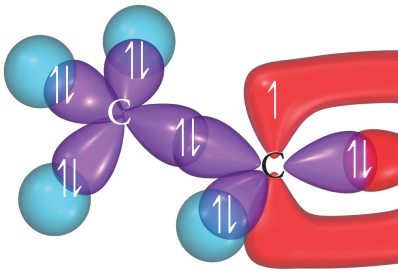






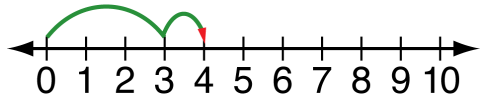


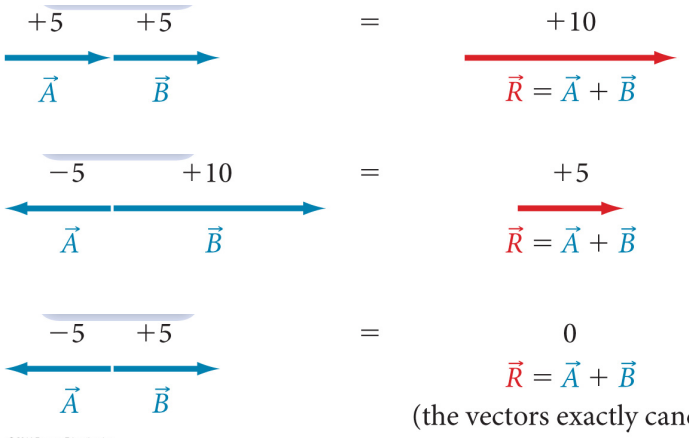




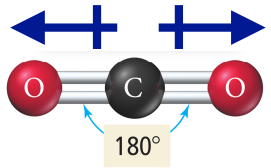
Vector Addition in 1D

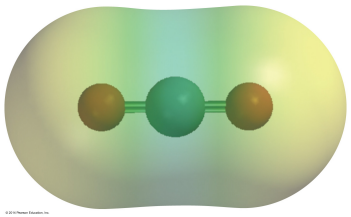
3 + 1 = **4**



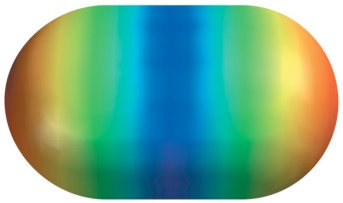


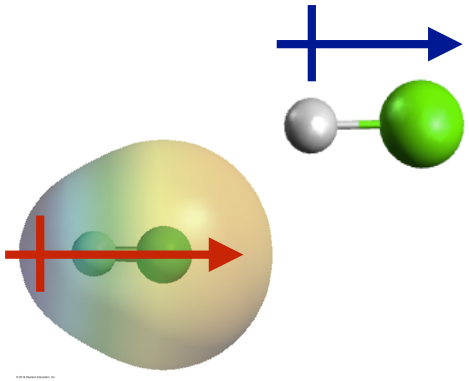
- Dipoles are vectors.
- Vectors have direction and magnitude.
- In grade school, arithmetic is taught using a number line.
- Combining vectors, vector addition, is the same as number line arithmetic.
  - A force of 5 with another force of 5 pointed the same way is a force of 10.
  - A force of 5 with a force of 5 pointed opposite it is 0.
  - A force of 10 with a force of 5 pointed the opposite is a force of 5.
- The individual dipole moments in a molecule contribute to the net dipole moment of the molecule the same way.
  - Dipoles can cooperate or they can cancel.

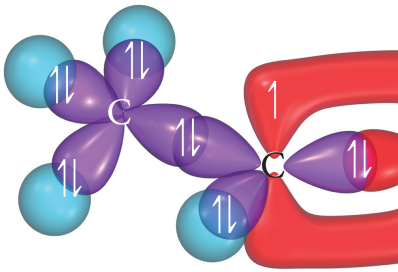




Zero Net Dipole

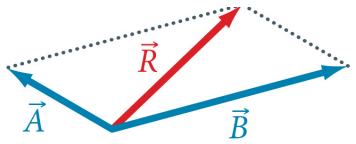




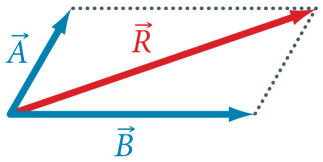


Vectors in 2D Have x and y Components

- When vectors are not on the same number line, it's more challenging to combine them.

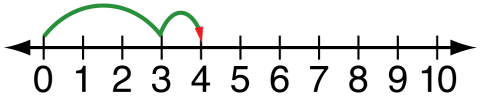


$\vec{R} = \vec{A} + \vec{B}$

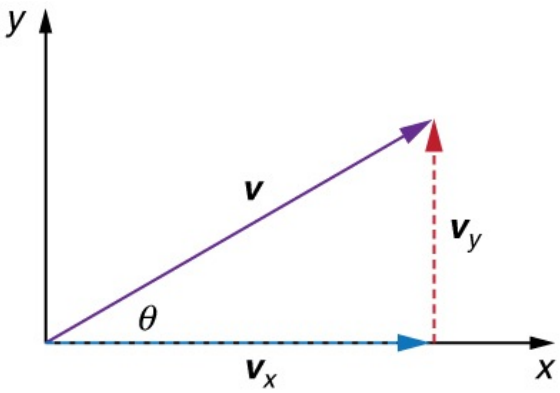


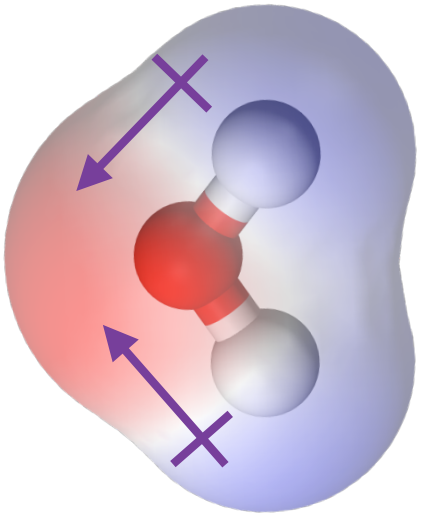
$\vec{R} = \vec{A} + \vec{B}$

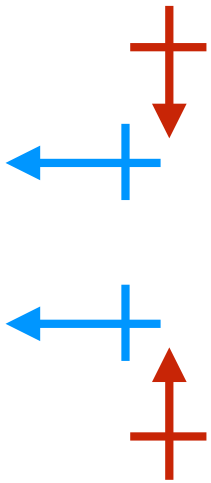
3 + 1 = **4**

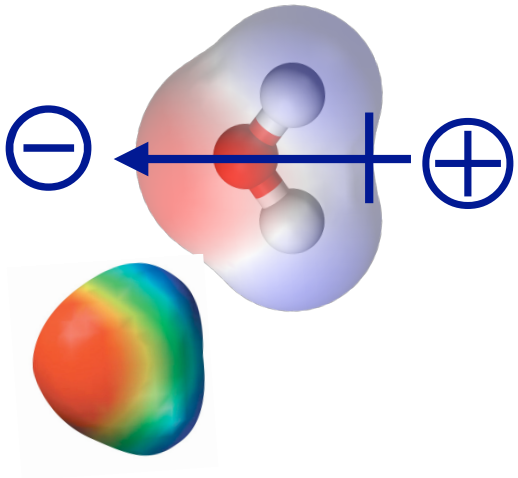


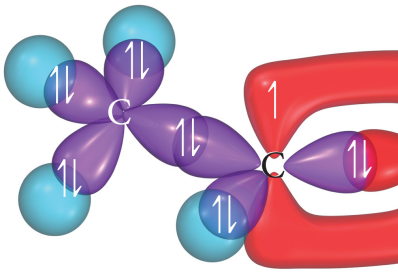
- You need to consider what part of each vector is on the x axis and what part is on the y.
- You can then add each part, just like number line arithmetic.





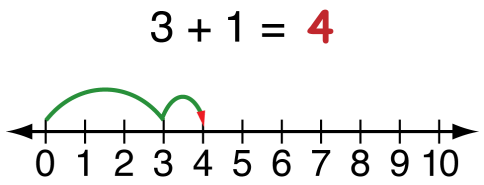


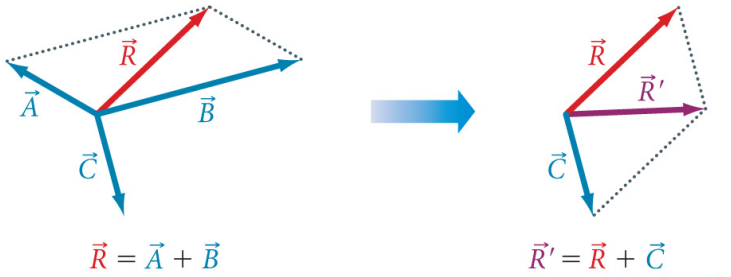


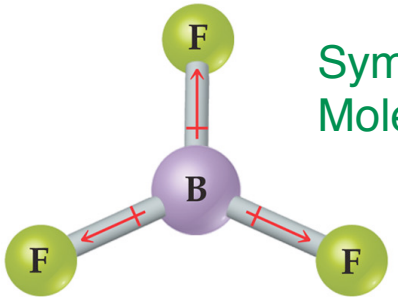


Vectors in 2D Have x and y Components

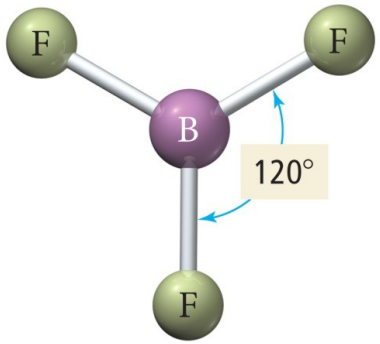
- When vectors are not on the same number line, it's more challenging to combine them.
- If you have 3 or more vectors, sometimes it helps to add two together, then add a third to it, and so on.

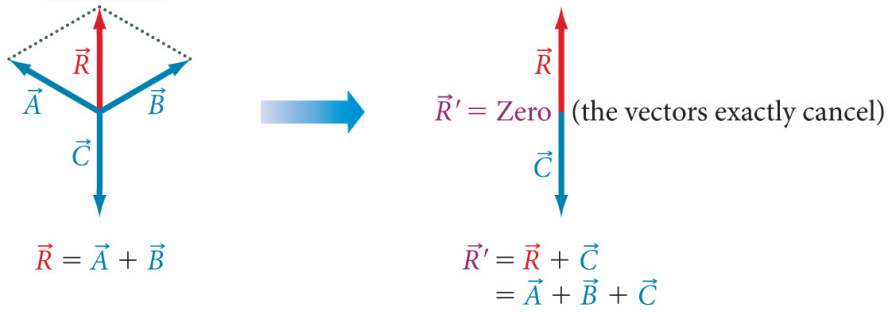


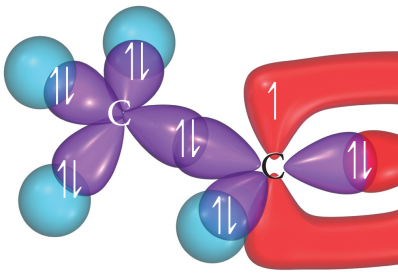




Symmetric Trigonal Planar
Molecules are non-polar

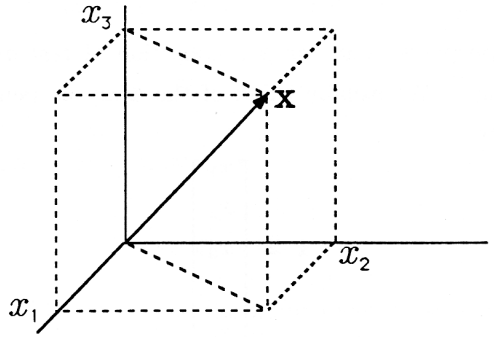


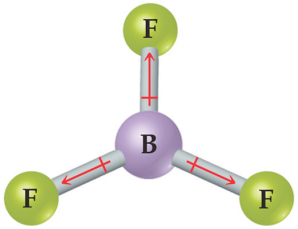




Molecules Exist in 3D Space

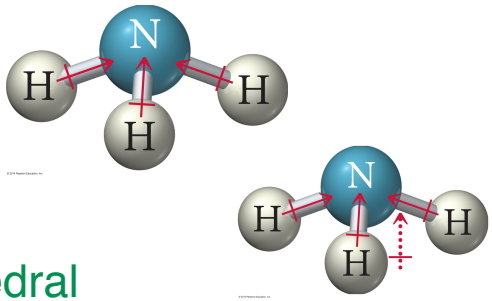
- Molecules are 3D objects.
- We have to consider x, y, and z dimensions of bond dipoles, to understand the net dipole.

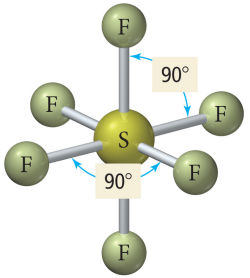


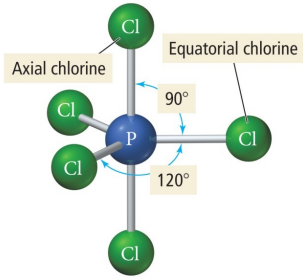


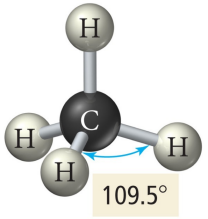
Symmetric Trigonal Planar
Molecules are Non-Polar

Symmetric Trigonal Pyramidal
Molecules are Polar

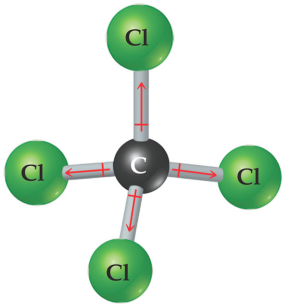


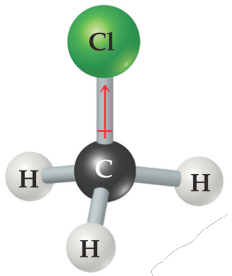




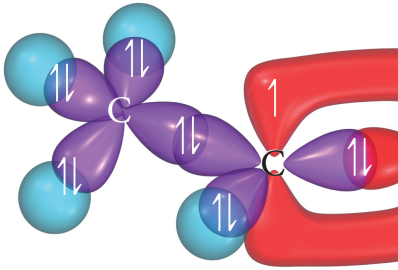


Symmetric Tetrahedral
Molecules are Non-Polar





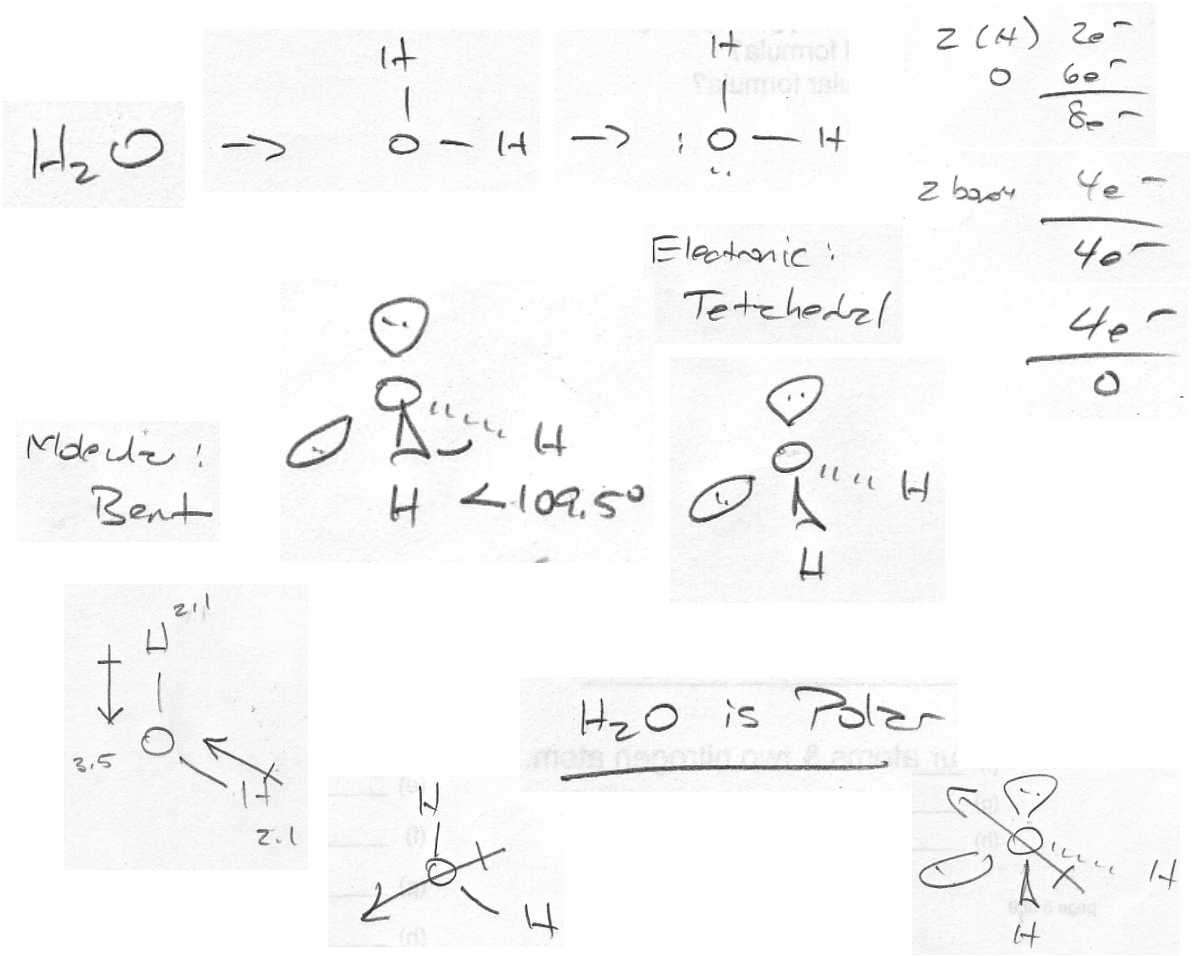
Asymmetric Molecules are
usually Polar.



	Electronic Geometry	Molecular Geometry	Bond Angles
1 e pair	Linear	Linear	180˚
2 e pair	Linear 	Linear	180˚
		Linear	
3 e pair	Trigonal Planar 	Trigonal Planar	120˚
		Bent	
		Linear	
4 e pair	Tetrahedral 	Tetrahedral	109.5˚
		Trigonal Pyramidal	
		Bent	
		Linear	
5 e pair	Trigonal Bipyramidal 	Trigonal Bipyramidal	90˚ and 120˚
		See-saw	
		T-Shaped	
		Linear	
		Linear	
6 e pair	Octahedral 	Octahedral	90˚
		Square Pyramidal	
		Square Planar	
		T-Shaped	
		Linear	
		Linear	

Molecules Exist in 3D Space

- Which molecules or ions are polar?
- Draw the 3D structure, show bond angles, and draw the net dipole for the molecule or ion.



H_2O BrH_5

BCl_3 ClO_2^-

CH_2O

PO_4^{3-}

PCl_3 XeF_4

$SClF_5$ SF_4

SO_2

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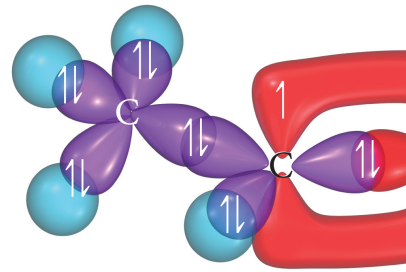

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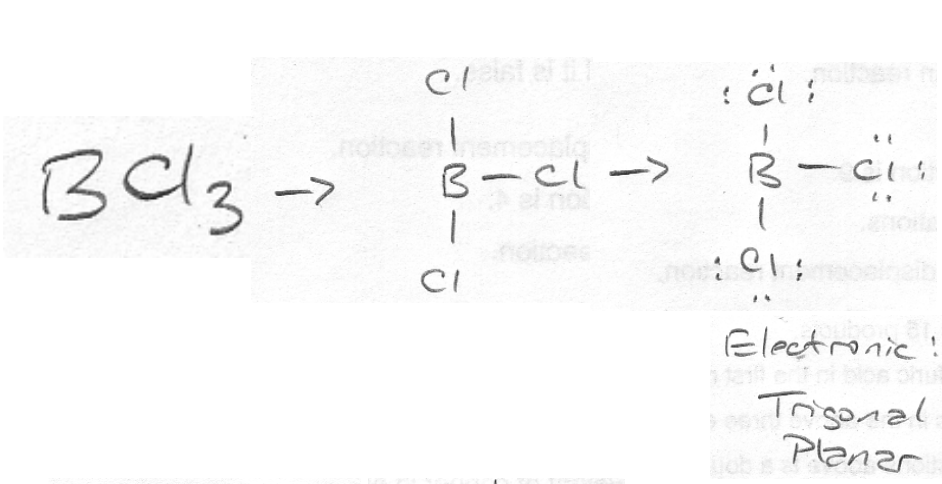

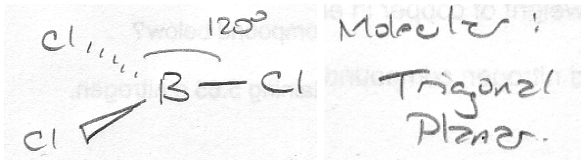

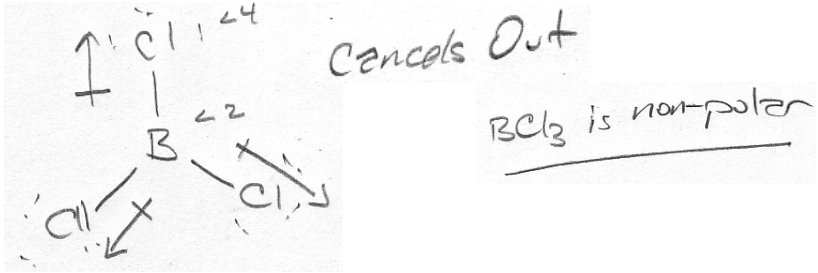

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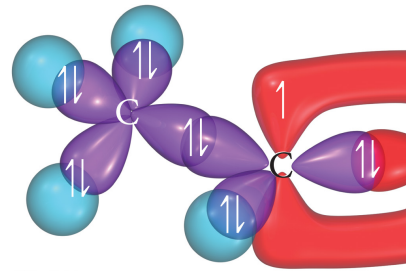

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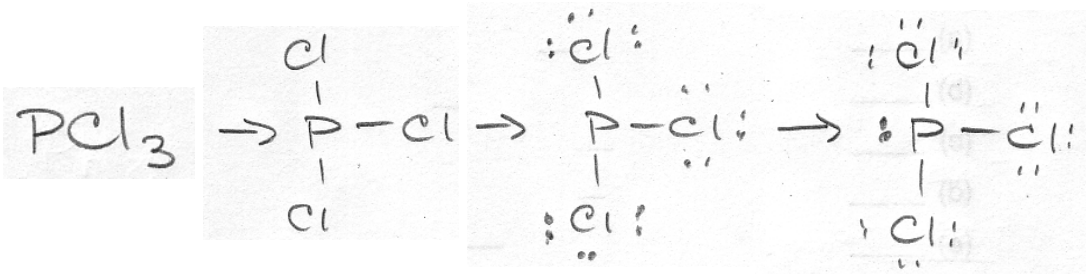

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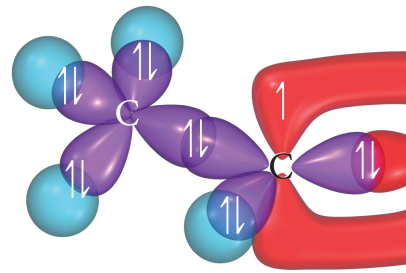

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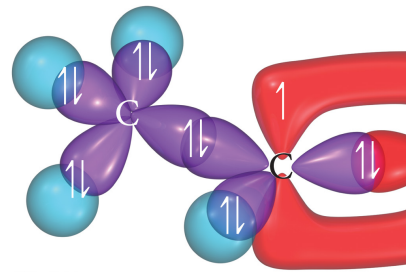
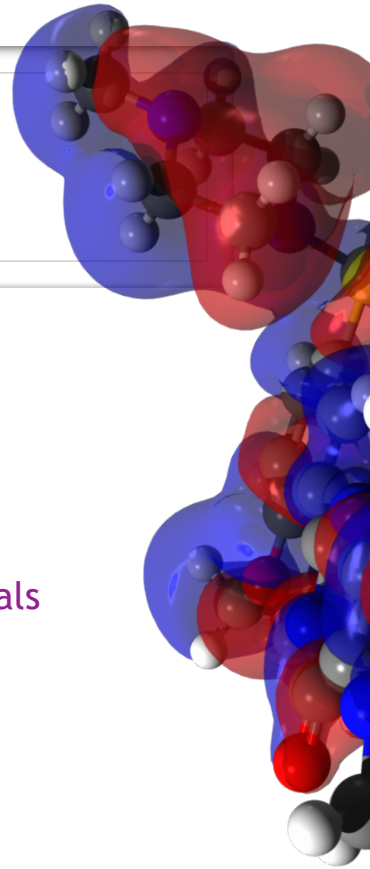


Valence Bond & MO Theories



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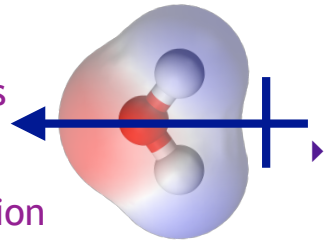

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    - Sigma & Pi bonding: sp2 & sp orbitals
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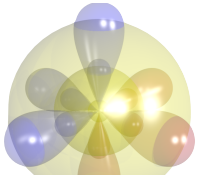

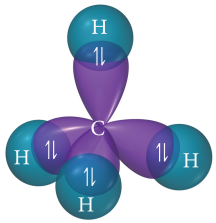

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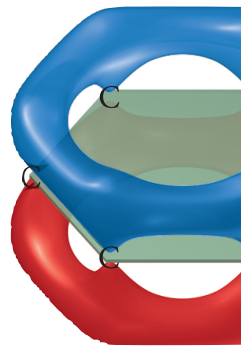
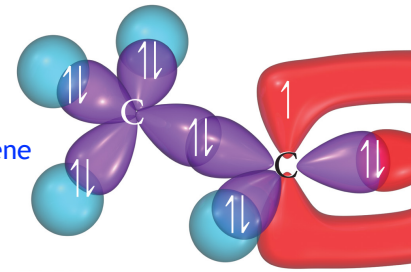
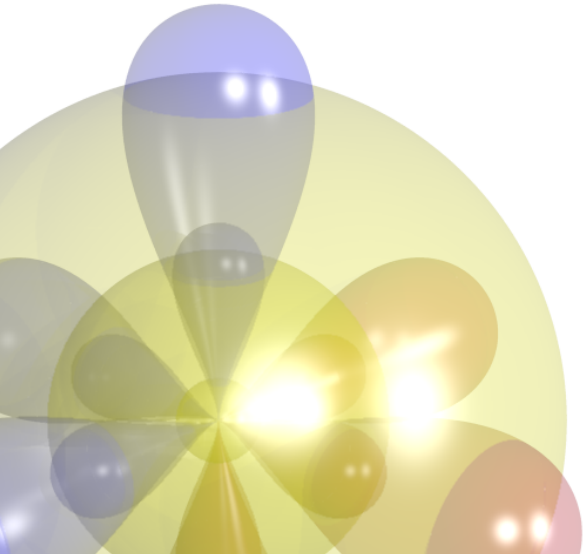


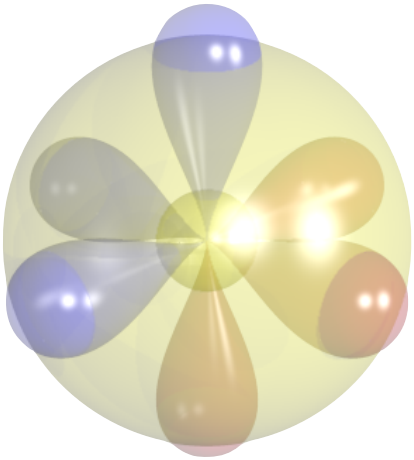


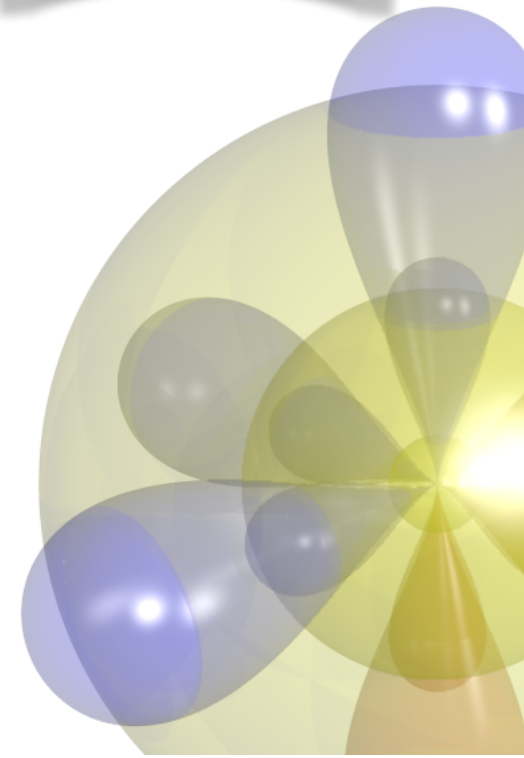
Valence Bond Theory

- Erwin Schrödinger gave us a mathematical model for predicting the behavior of electrons around atomic nuclei.
- Schrödinger's equation accurately predicts the shape of electron density (orbitals) around atoms.
- Valence Bond theory attempts to reconcile Schrödinger's model of the atom with Lewis' model of the covalent bond.
- Valence Bond theory attempts to describe and predict covalent bonding by combining valence orbitals from Schrödinger's atomic model.

$$\Psi(n,l,m_l,m_s)$$



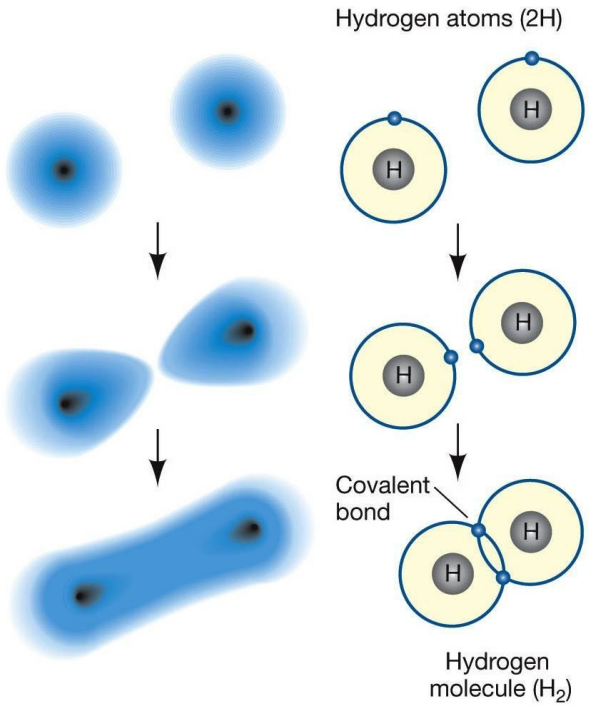




Quantum Covalent Bonds

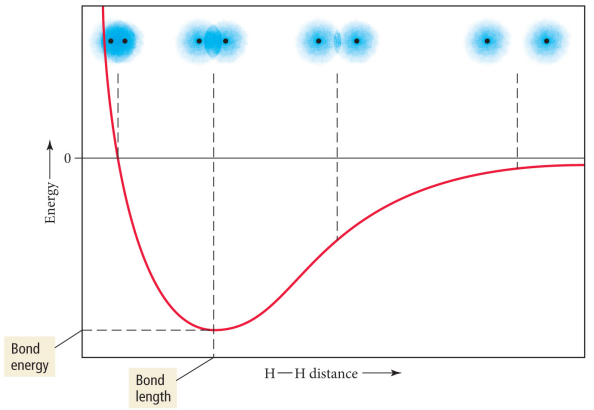
- Lewis described the covalent bond with classical mechanics.
  - Thinking of an Electron as a particle.
    - Electrostatic attraction between adjacent electrons and nuclei.
    - Electrostatic repulsion between adjacent nuclei.
  - The bond is two nuclei hanging onto a pair of electron particles.

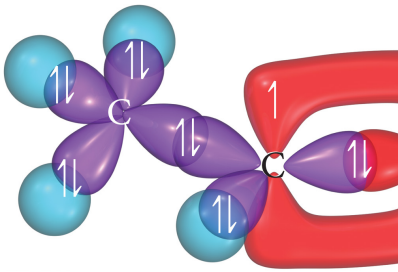
- Schrödinger's quantum model also predicts covalent bonding.
  - Thinking of Electron Density as a wave.
    - Overlap of the two orbitals allows both nuclei to stabilize the wave.
    - There is still electrostatic repulsion between the nuclei.
  - The bond is a region of electron density stabilized by both nuclei.
    - The overlap of atomic orbitals from each atom.
  - Solving Schrödinger's equation for two nuclei predicts the observed bond distance of hydrogen.



This suggests we should be able to describe a molecule by connecting adjacent atomic orbitals.

Connecting valence atomic orbitals on adjacent atoms to predict molecular shape is valence bond theory.



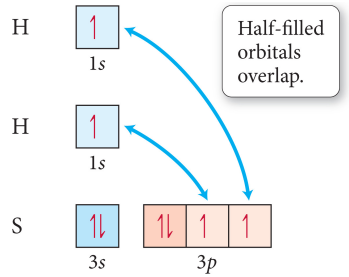


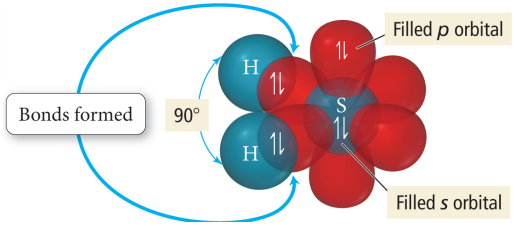
Valence Bond Theory

- Combine hydrogen and sulfur atoms:

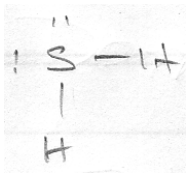
S [Ne] $3s^2 3p^4$

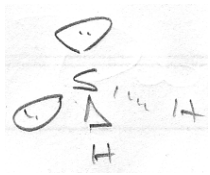
H 1s'



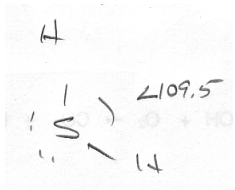


H_2S

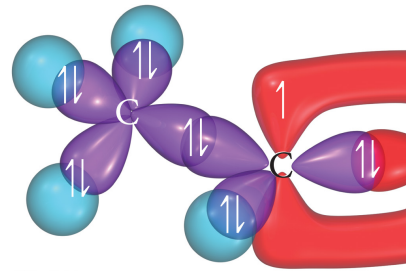




E: Tetrahedral
M: Bent

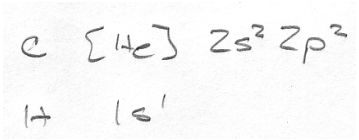


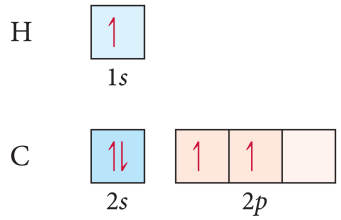
- Connecting valence orbitals works.
- Lewis & VSEPR theory predict a tetrahedral electronic structure around H_2S and therefore a H—S—H bond angle of less than 109.5°
- Valence Bond Theory predicts a 90° bond angle.
- Experiment confirms a 90° bond angle.
- Valence Bond Theory predicts molecular shape (in some cases better than VSEPR)

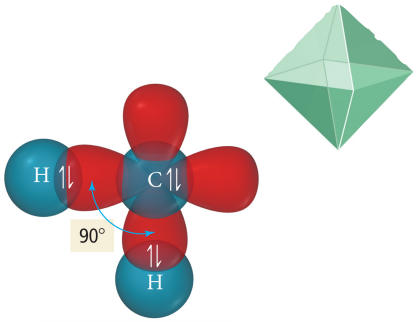


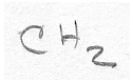
Valence Bond Theory

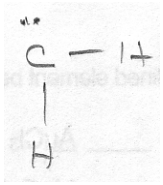
- Combine hydrogen and carbon atoms:

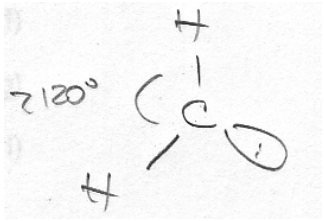


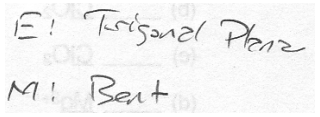




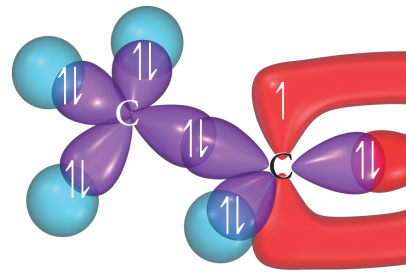




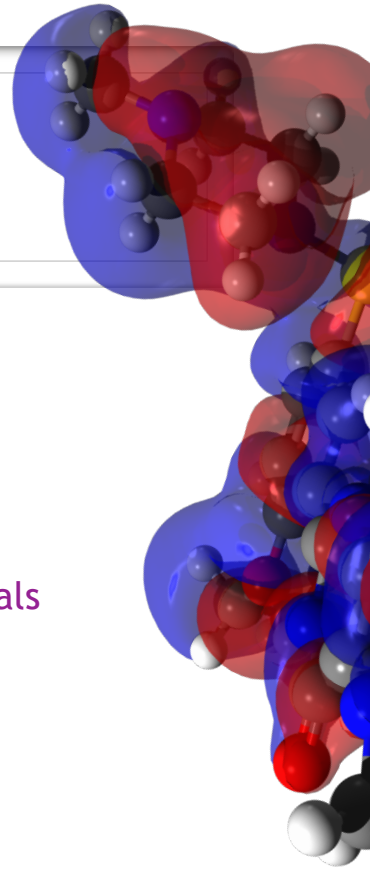




- Trying the same thing with carbon gives a bad result.
- We'd end up with CH_2:
  - Carbon couldn't fill it's octet.
  - It's $2p_z$ orbital is left entirely empty, while the molecule is double booking electrons in carbon's $2p_x$ and $2p_y$ orbitals.
  - It would predict a bent 90° structure for carbon.
- This structure does not look stable.
- Experiment does not support this result (this stuff doesn't form).
- Valence Bond theory works, but we're still missing a piece.



Valence Bond & MO Theories



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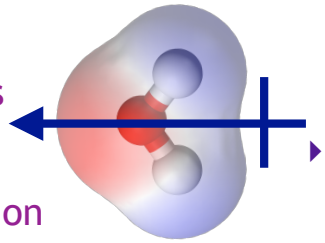

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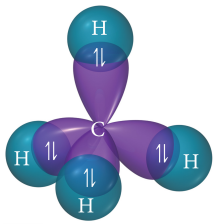

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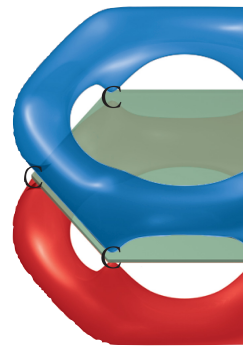
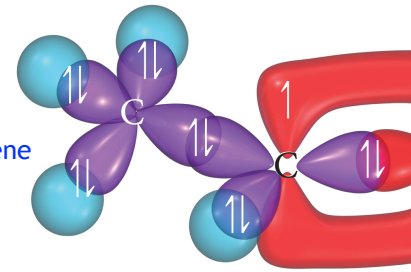
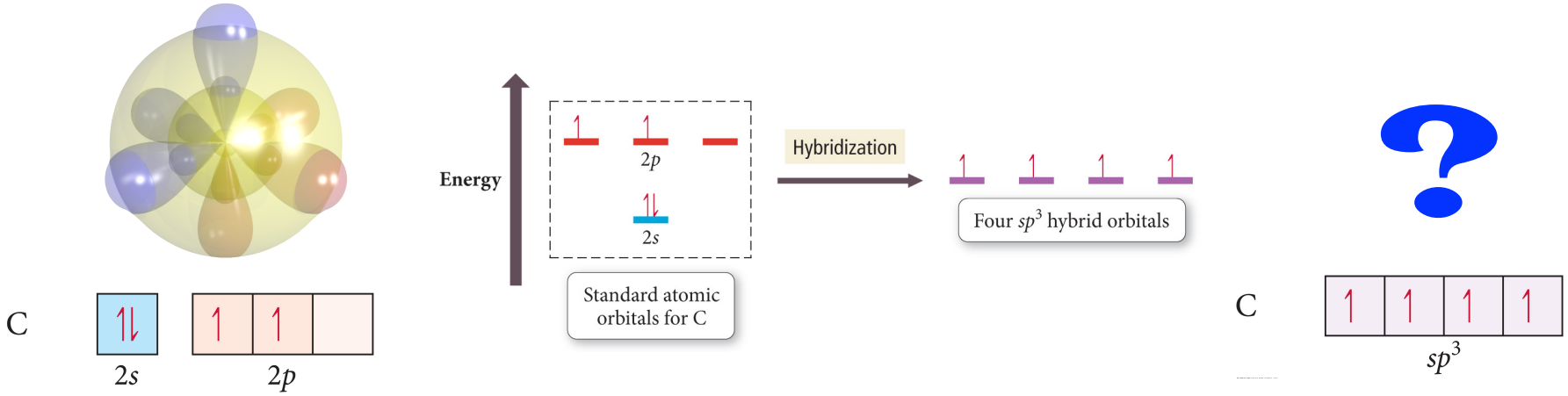




Orbital Hybridization

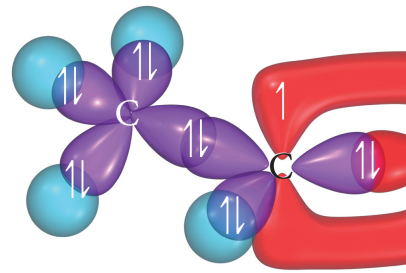


- Carbon want's to fill it's valence shell by sharing electrons with hydrogen.
- To do that it needs four unpaired electrons.
- It's ground state: [He] $2s^2$ $2p^2$ doesn't let it do that (with hydrogen).

- If carbon absorbs some energy it can have an excited state of [He] $2s^1$ $2p^3$.
  - This is not a stable state for a lone carbon atom.
  - But carbon, with those four hydrogens around it can stabilize four unpaired electrons in the n = 2 shell.

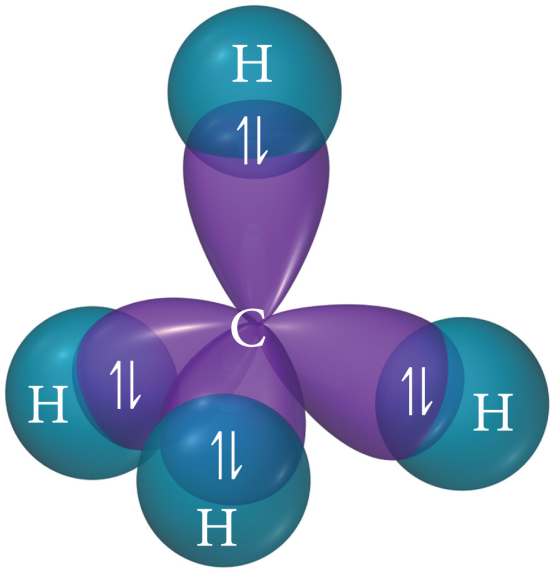
- The shape of the orbitals change, to lower the overall energy of 4 unpaired electrons in one shell.
- This changing of singly occupies orbitals to create covalent bonds with other atoms is called hybridization.

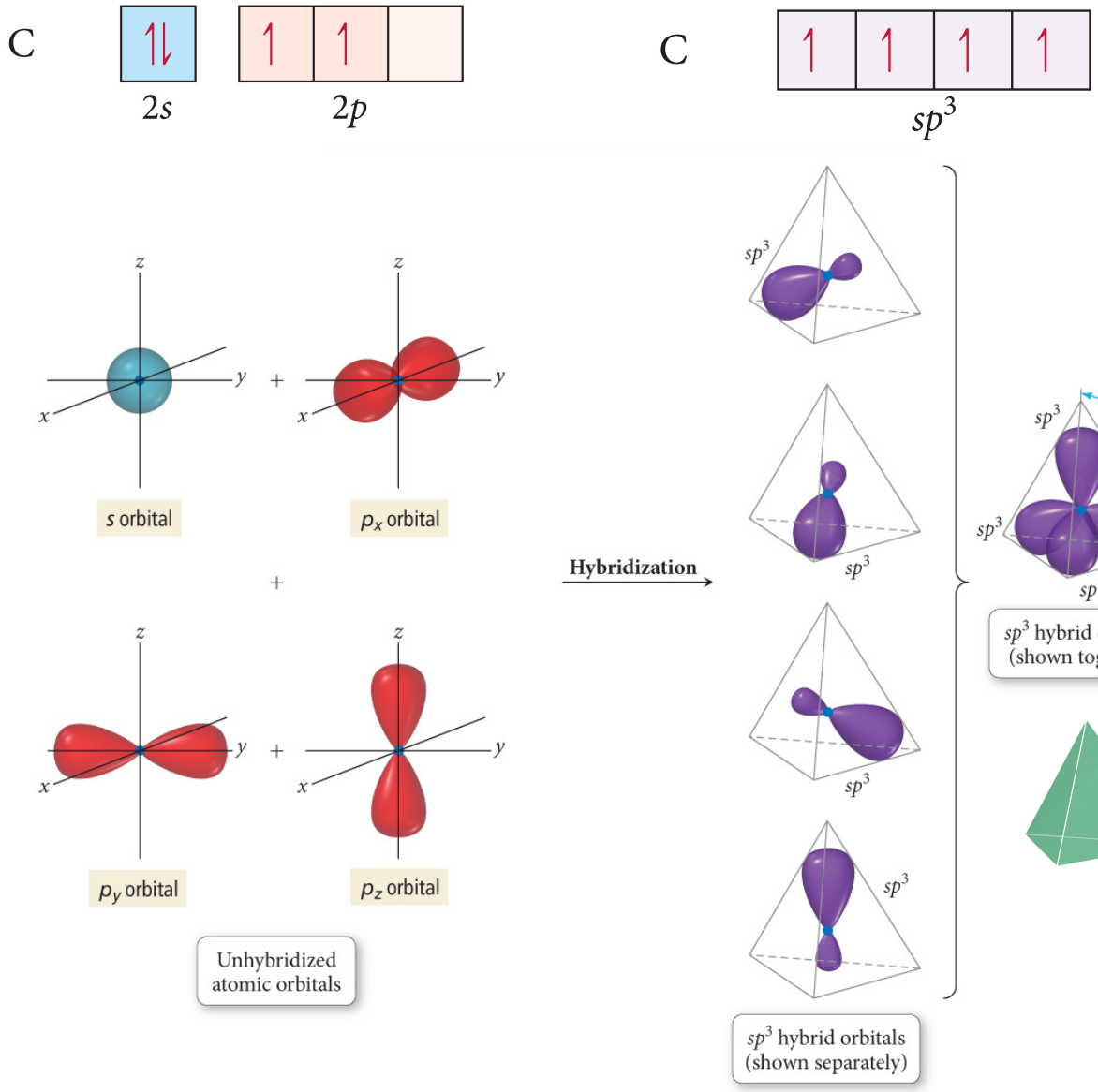
- The new hybridized orbitals are named after the type and number of atomic orbitals combined to form them.
- In this case, we used a single s orbital and three p orbitals to form four sp^3 orbitals.
- We never create or destroy orbitals, just reshape them.
  - So we always end up with the same number of orbitals we started with.



Shape of sp^3 Orbitals

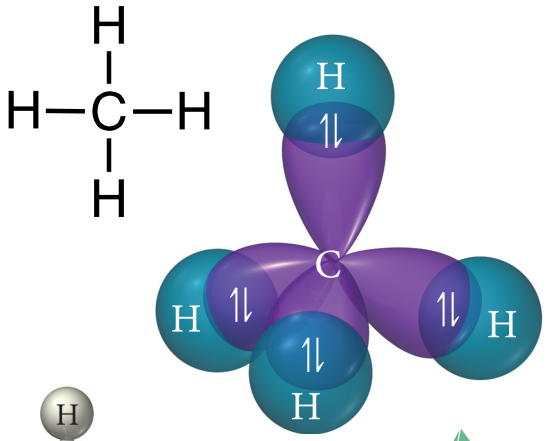
- Using the same mathematics that predicted the shape of s and p orbitals, we can predict the best shape of 4 equal orbitals around carbon.
- We find the shape defined by the four new sp^3 hybridized orbitals is a tetrahedron.
- The sp^3 orbitals are the lowest energy state for the electrons around carbon *only within the molecule*.
- The four H atoms are required to make this a lower energy configuration.

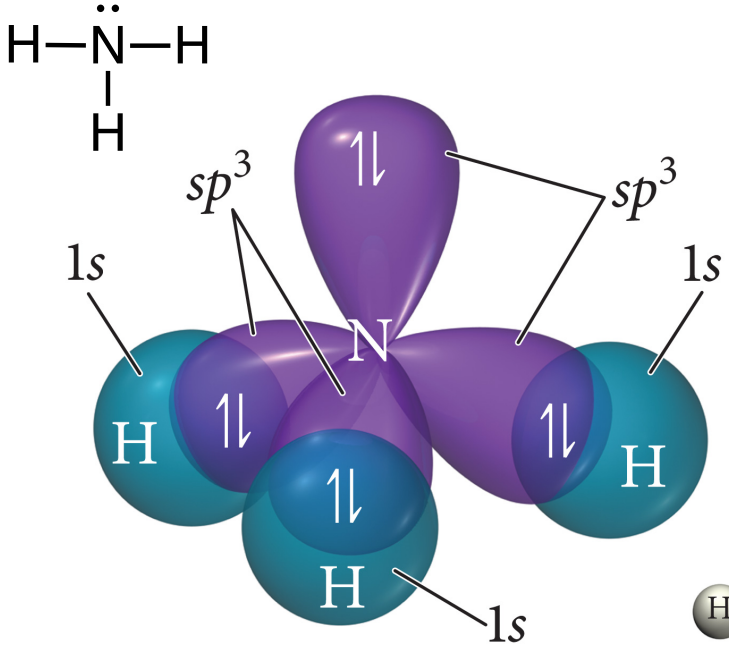


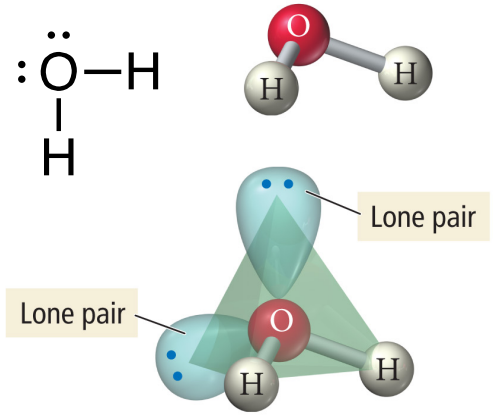


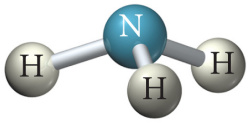
Hybrid Orbitals

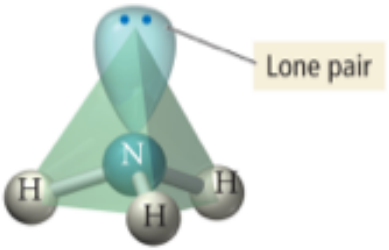
- Hybridized orbitals can be used to form covalent bonds or to contain an atoms lone pairs.

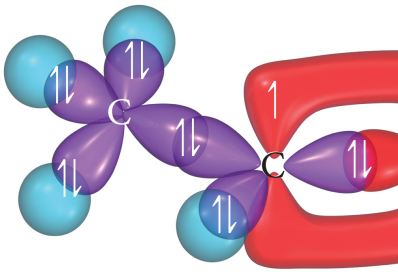






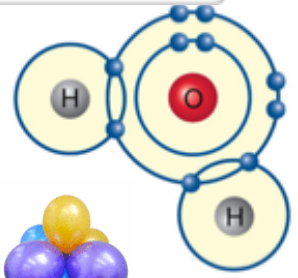


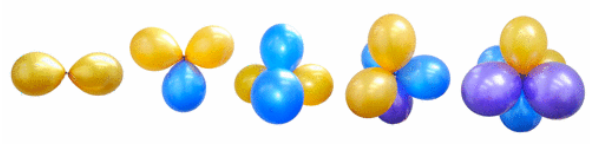


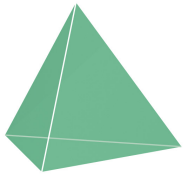


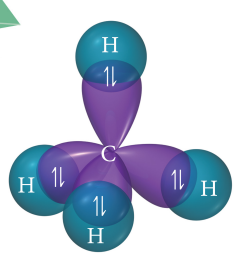
VSEPR vs Valence Bond Theory

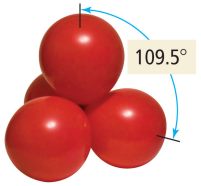
- VSEPR theory predicts how valence atoms distribute around a central atom.
  - By understanding the geometry of each atom, we can understand the geometry of the molecule.
  - VSEPR is based on classical mechanics and the Bohr atom.
    - Electrostatic attraction between opposite charges.
    - Electrostatic repulsion between like charges.
  - It's a fast, crude approach that works well for many molecules.
    - It does not consider the wave nature of electrons.
    - It does not explain multiple bonds.
    - Bond angles and distances are less precise.
- Valence Bond Theory is a different approach to understanding molecular shape.
  - Valence Bond Theory looks at how the valence orbitals of a central atom connect with orbitals of valence atoms to define shape.
  - It is based on quantum mechanics and Schrödinger's atomic model.
    - VB theory starts with atomic orbitals and remixes them based on how valence atoms effect those orbitals.
    - Atomic orbitals as
  - Valence bond theory is consistent with VSEPR.
    - You can predict the hybridization of a central atom based on the number of electron regions.
  - It's an alternative method for calculating the structure of molecules.
    - It's more accurate than VSEPR if you do the quantum math.
    - It accounts for multiple bonds.
    - It explains bond rotation and structural isomers.

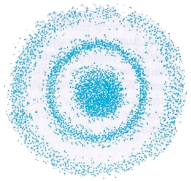


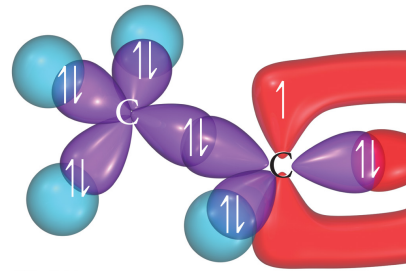




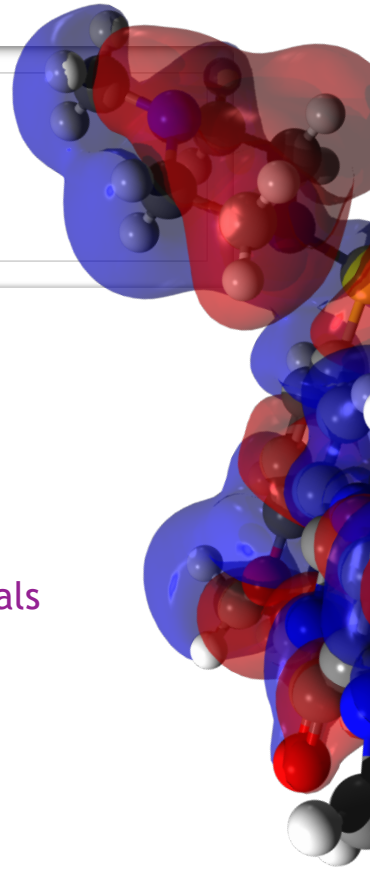




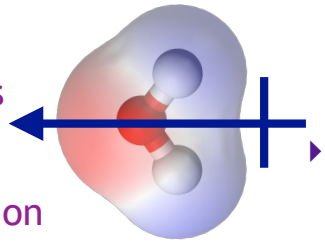




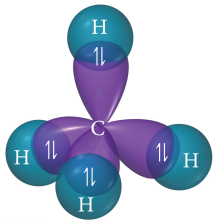
Valence Bond & MO Theories



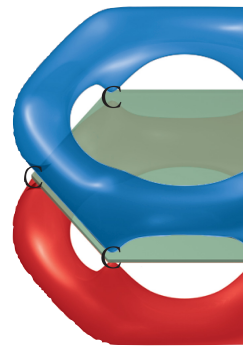
- Molecular Shape and Polarity
  - Polar Bond & Polar Molecules
  - Net Dipole Moment
  - Adding dipoles: vector addition
    - in one dimension
    - two & three dimensions
    - try some examples

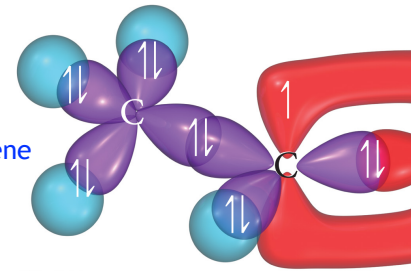


- Valence Bond Theory
  - Quantum View of Covalent Bonds
    - Bonding with Schrödinger's Quantum Atom
    - Orbital Overlap is a Covalent Bond
  - Forming Molecules w/ Quantum Atoms
    - H_2S & H_2C
  - Hybridization of Atomic Orbitals
    - Atomic Orbitals inside a molecule are not the same as the atom by itself.
    - sp3 orbitals
    - Sigma & Pi bonding: sp2 & sp orbitals
    - d-Orbital Hybridization: sp3d & sp3d2

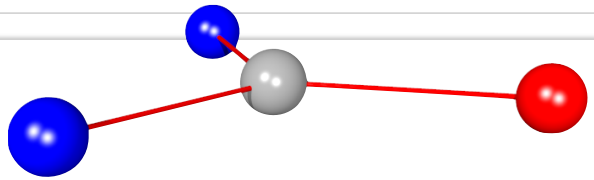


- Determining Hybridization
  - Look at electronic shape of the atom
- Molecular Orbital Theory
  - Electron Delocalization
  - Linear combinations of atomic s orbitals
    - constructive: bonding
    - destructive: antibonding
    - Molecular orbital diagrams
      - H2, He2, He2+
      - bond order
  - Linear combinations of atomic p orbitals
    - shapes of bonding and antibonding orbitals
    - Period 2 homonuclear diatomics
    - 2s-2p mixing
      - paramagnetism and diamagnetism
      - liquid oxygen
    - Period 2 heteronuclear diatomic molecules
    - Polyatomic molecules
      - electron delocalization in ozone, benzene

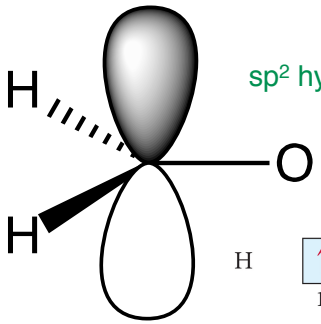




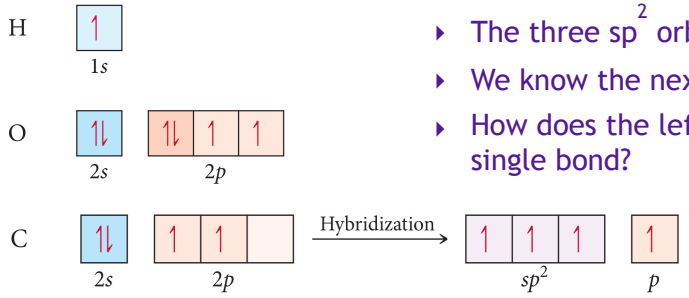
Shape of sp^2 orbitals



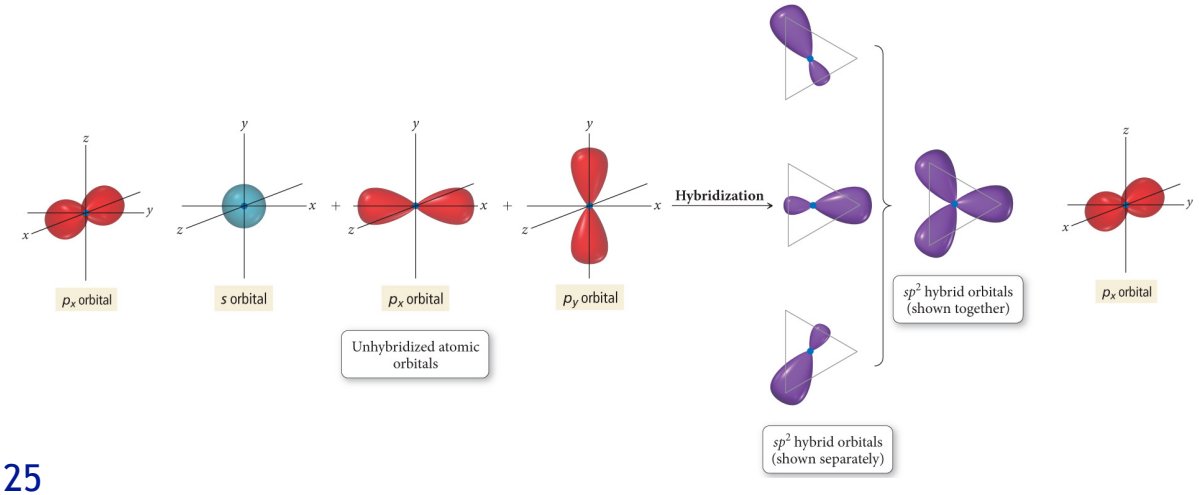
CH_2O

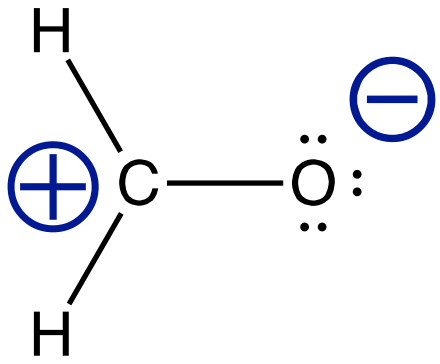


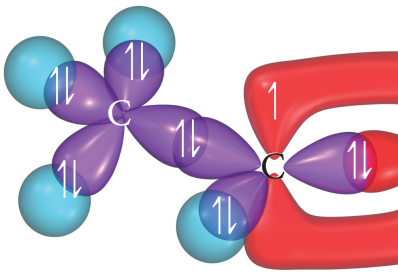
sp^2 hybridized carbon



- CH_2O is formed by three atoms coming up to a central carbon atom.
- Those three atoms will avoid each other, by approaching carbon in a trigonal planar geometry.
  - Carbon will "reach out" to these atoms with three of it's own orbitals.
- This will hybridize the three orbitals in that plane, but they don't get near the third p orbital.
- This produces three sp^2 orbitals and leaves one p orbital.
- The three sp^2 orbitals form a trigonal planar geometry.
- We know the next step is to form a double bond between oxygen and carbon.
- How does the left over p orbital make a double bond, without interfering with the existing single bond?

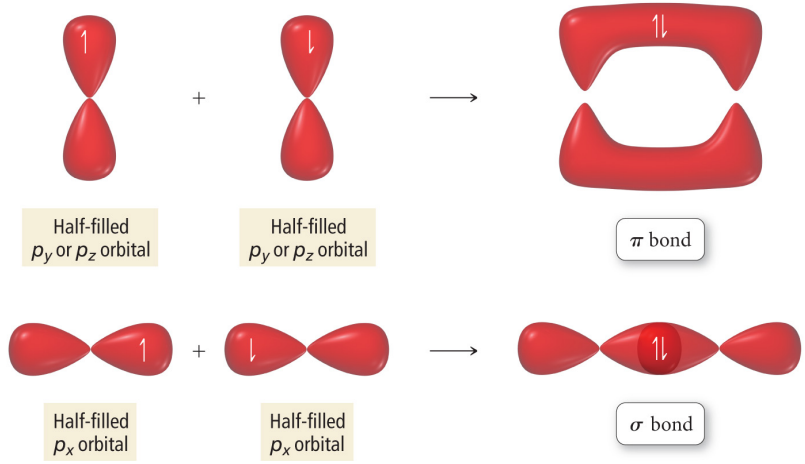


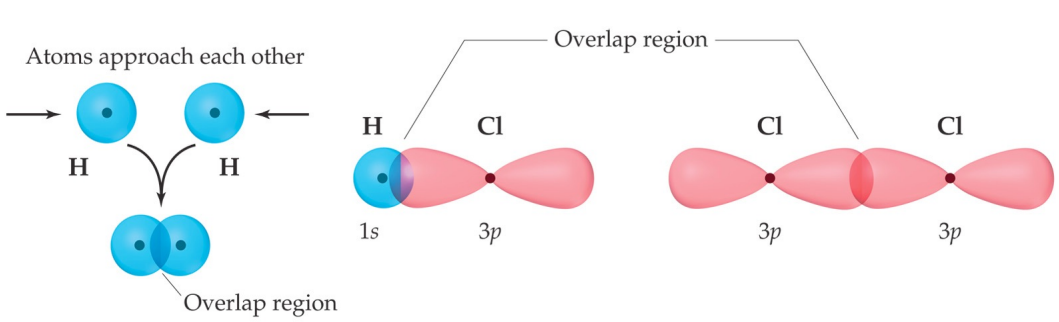


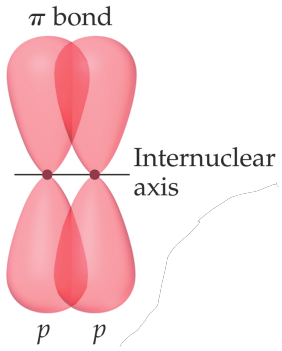


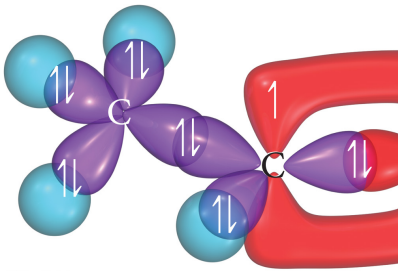
σ and π bonds

- Single bonds are accomplished by end on overlap between orbitals.
- End on overlap is called a σ bonds.
- Adding a second bond between two atoms, requires another kind of overlap.
- Edge on overlap is called a π bond.
- σ are much stronger than π bonds (better overlap).
- A double bond occurs when an atom has both σ and π overlap with another atom.
- The π bond pulls the atoms closer than they would be with just a σ bond.
- That creates better overlap, which creates a net bonding much stronger than two single bonds.



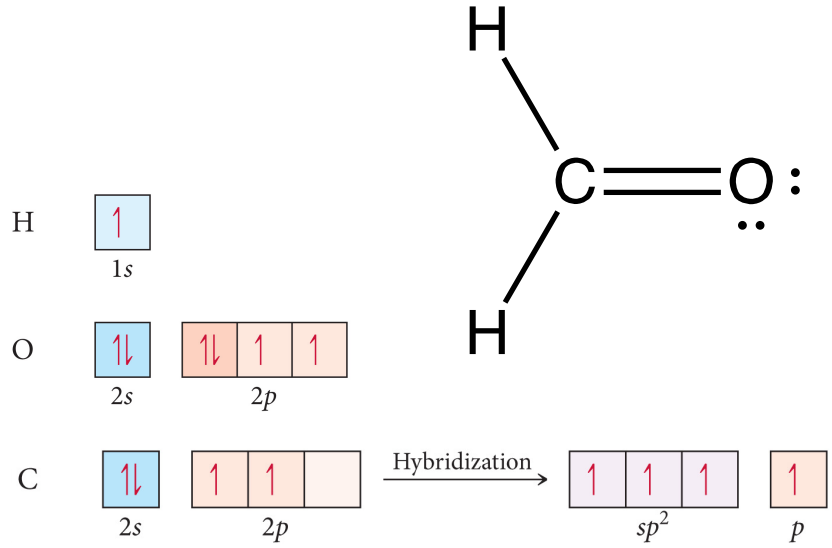


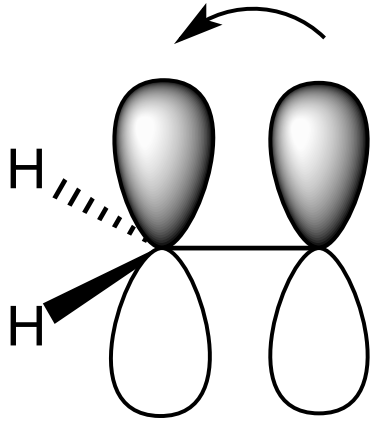


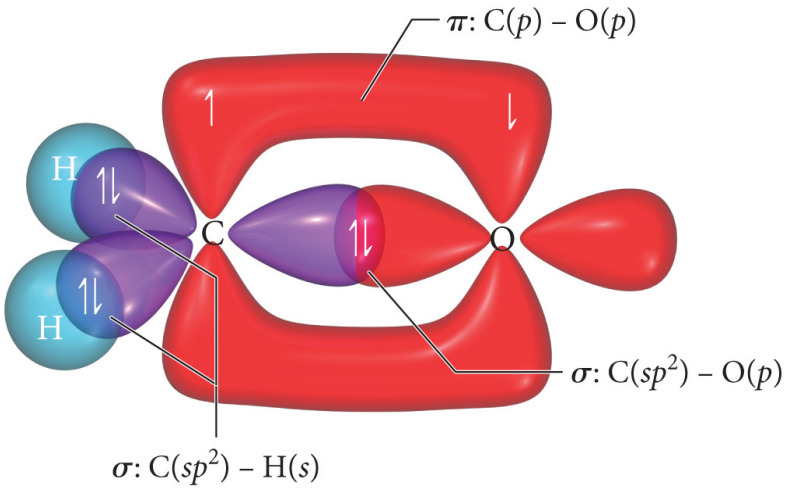


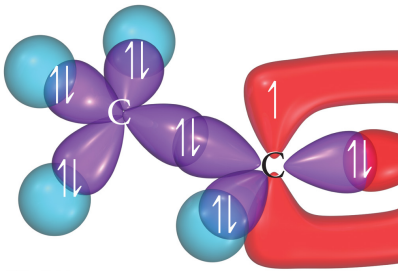
Shape of sp^2 orbitals

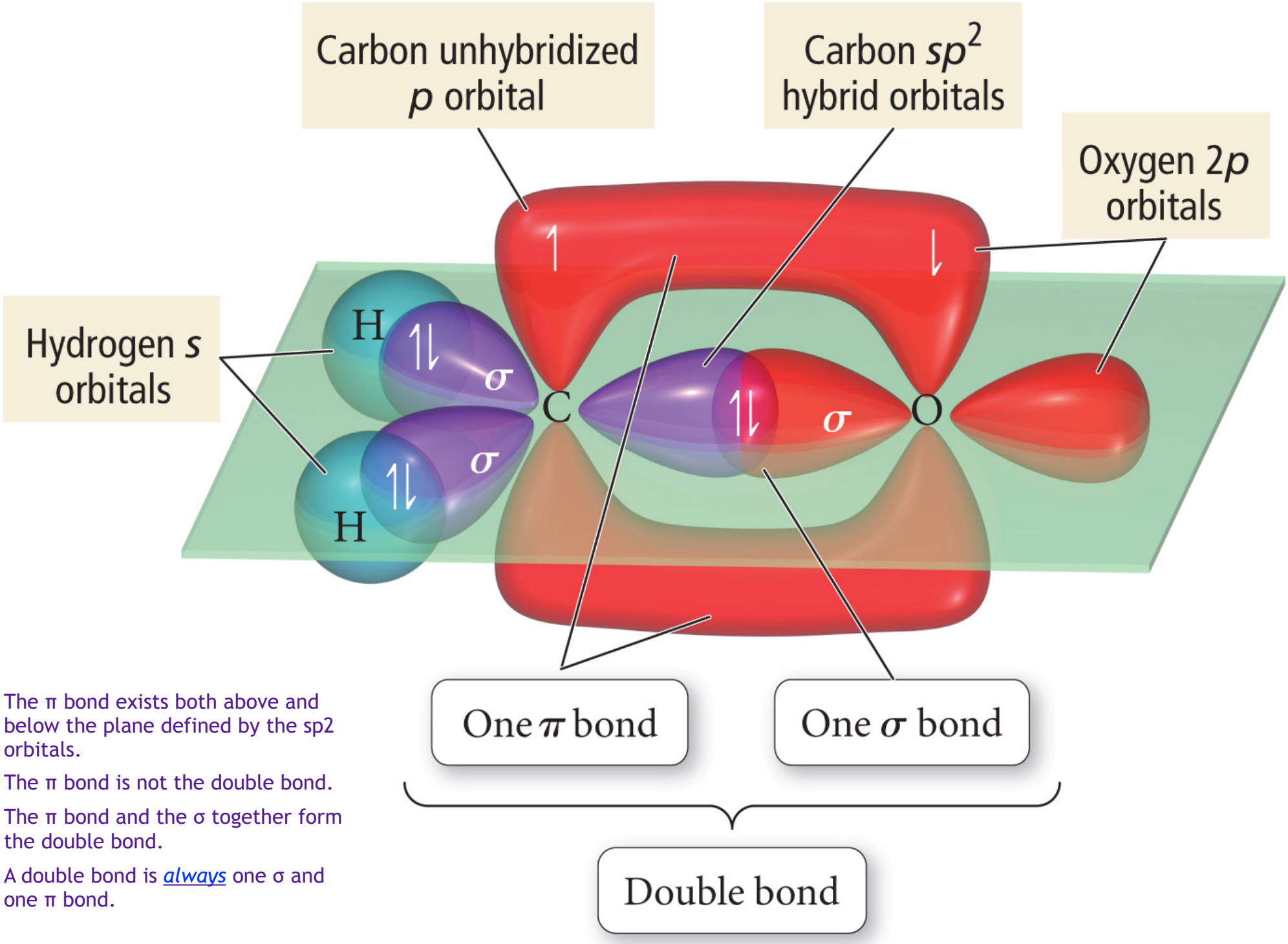
- CH_2O is formed by three atoms coming up to a central carbon atom.
- Those three atoms will avoid each other, but coming in a trigonal planar geometry.
- The will hybridize the three orbitals they touch, but they don't get near the third p orbital.
- This produces three sp2 orbitals and leaves one p orbital.
- The three sp2 orbitals form a trigonal planar geometry.
- We know the next step is to form a double bond between oxygen and carbon.
- How does the left over p orbital make a double bond, without interfering with the existing single bond?





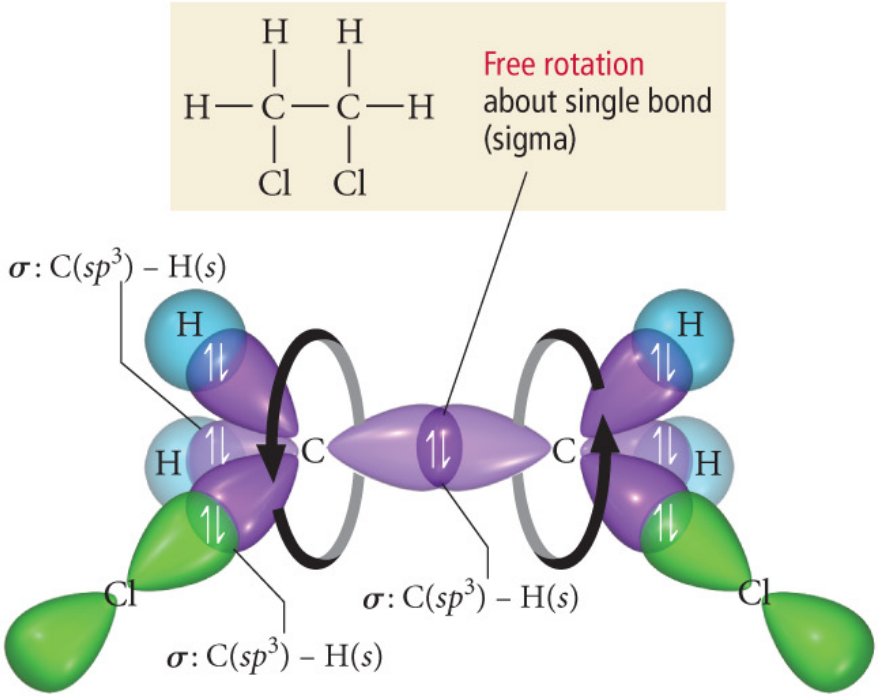


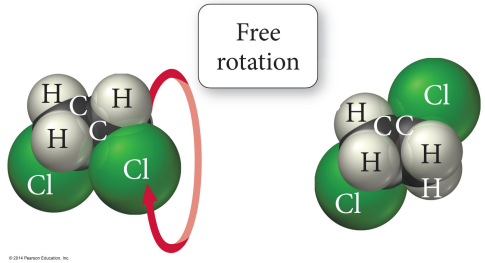


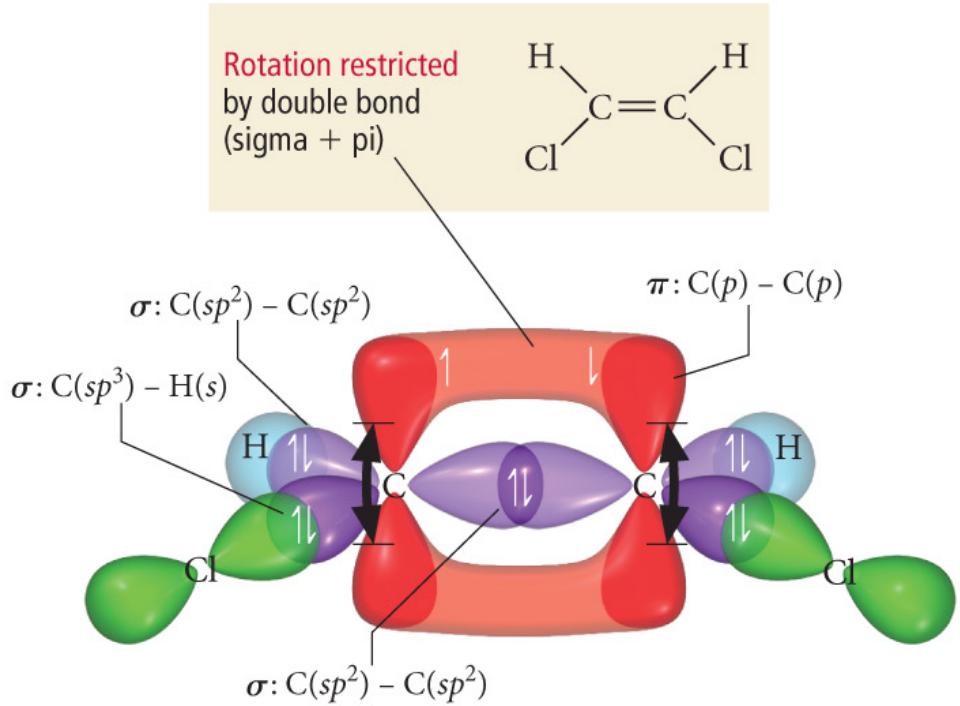


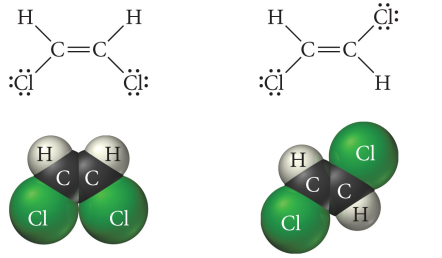
- The π bond exists both above and below the plane defined by the sp2 orbitals.
- The π bond is not the double bond.
- The π bond and the σ together form the double bond.
- A double bond is *always* one σ and one π bond.

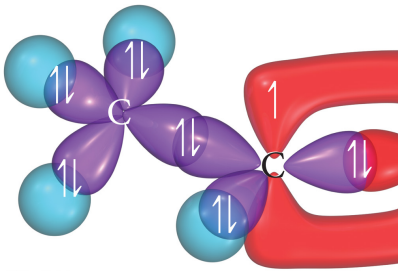
- σ bonds can rotate and still maintain orbital overlap.
  - Molecules can readjust their extended shape by rotation around σ bonds.
- π bonds cannot rotate without breaking overlap.
  - Molecules cannot readjust their shape by rotating around π bonds.
- As a result there are two structures of dichloroethene that do not interconvert.
- They are <u>different substances</u> with difference chemical properties.
- Isomers are different substances that have the same composition and connectivity, but different shapes.





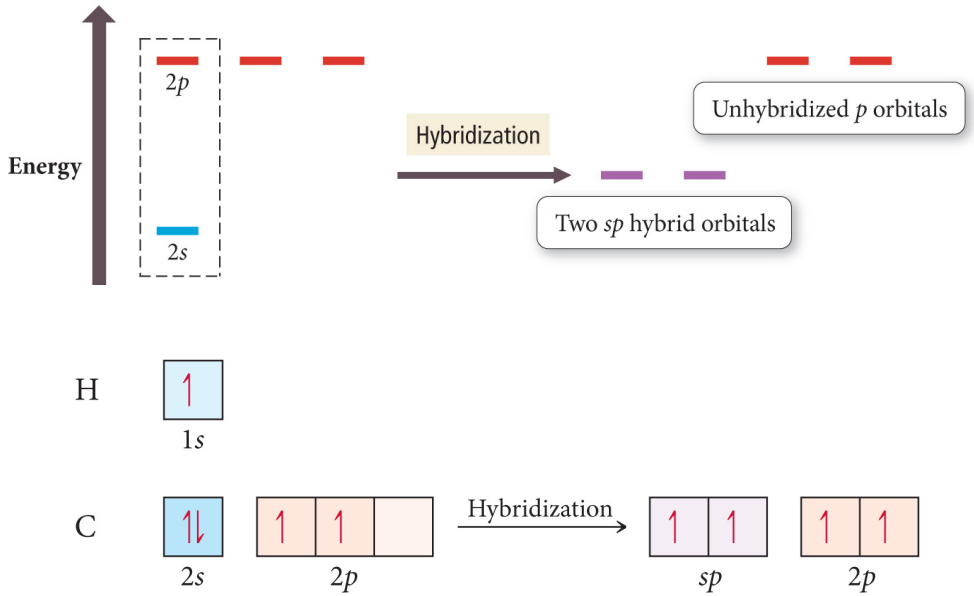


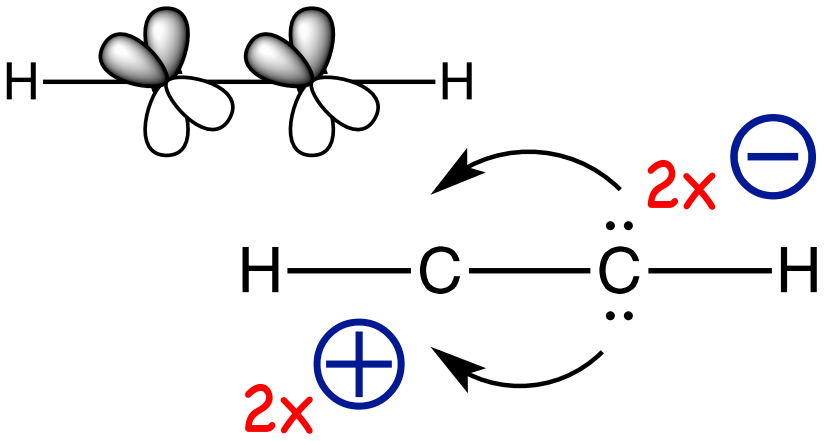


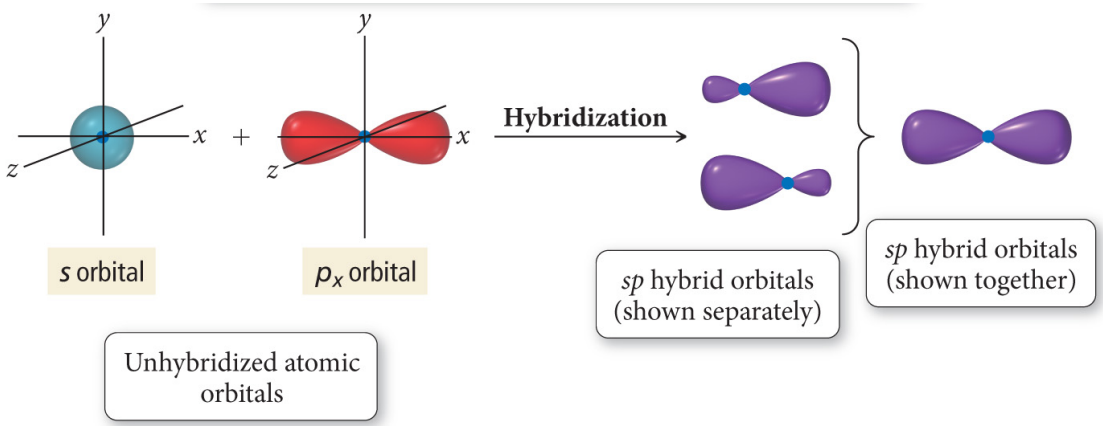


Shape of sp orbitals

- C_2H_2 is formed by two atoms coming on either side of a single carbon.
- Those two atoms will avoid each other, but coming in a linear geometry around each carbon.
- The will hybridize the two orbitals they touch, but they don't get near the two p orbital not in their path.
- This produces two sp orbitals and leaves two p orbitals.
- The two sp orbitals form a trigonal planar geometry.
- The next step is forming a double and then triple bond.

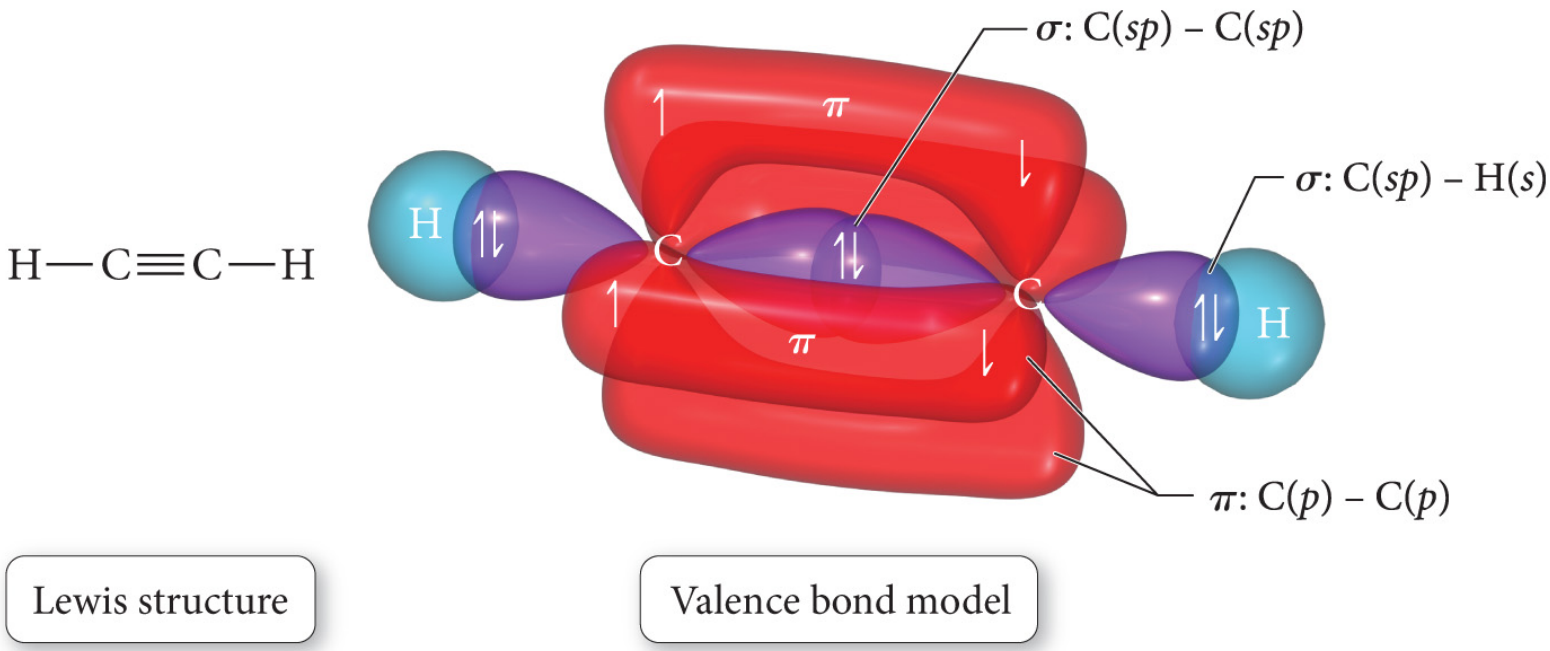






Structure of a Triple Bond

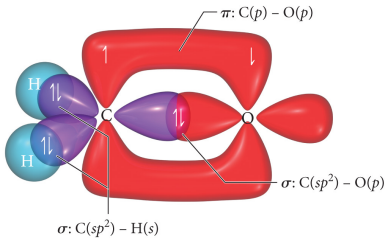
- One π bond exists both above and below the xz plane.
- One π bond exists both above and below the xy plane
- A triple bond is always composed of a σ and two π bonds.
  - (This structure explains why triple bonds need to be treated as one electron domain in VSEPR)

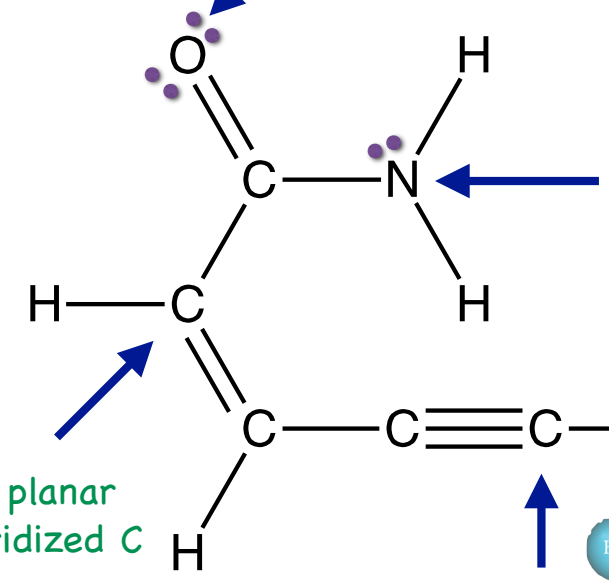


Applying Valence Bond Theory

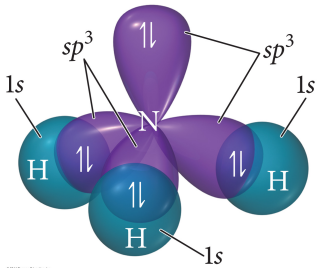
- Valence Bond theory let's you see how electrons shape the molecule.
- It explains restricted bond rotation.
- It shows you the position of exposed electron pairs (lone pairs and multiple bonds).
- You'll need this theory in 220 and beyond to understand reaction mechanisms.

3 domains
→ trigonal planar
→ sp^2 hybridized O

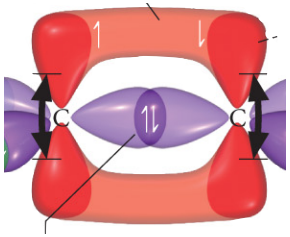




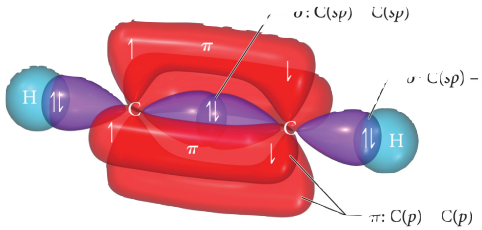
4 domains
→ tetrahedral
→ sp^3 hybridized N

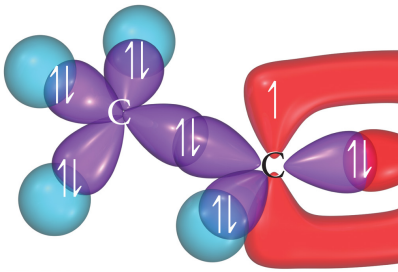


3 domains
→ trigonal planar
→ sp^2 hybridized C



2 domains
→ linear
→ sp hybridized C





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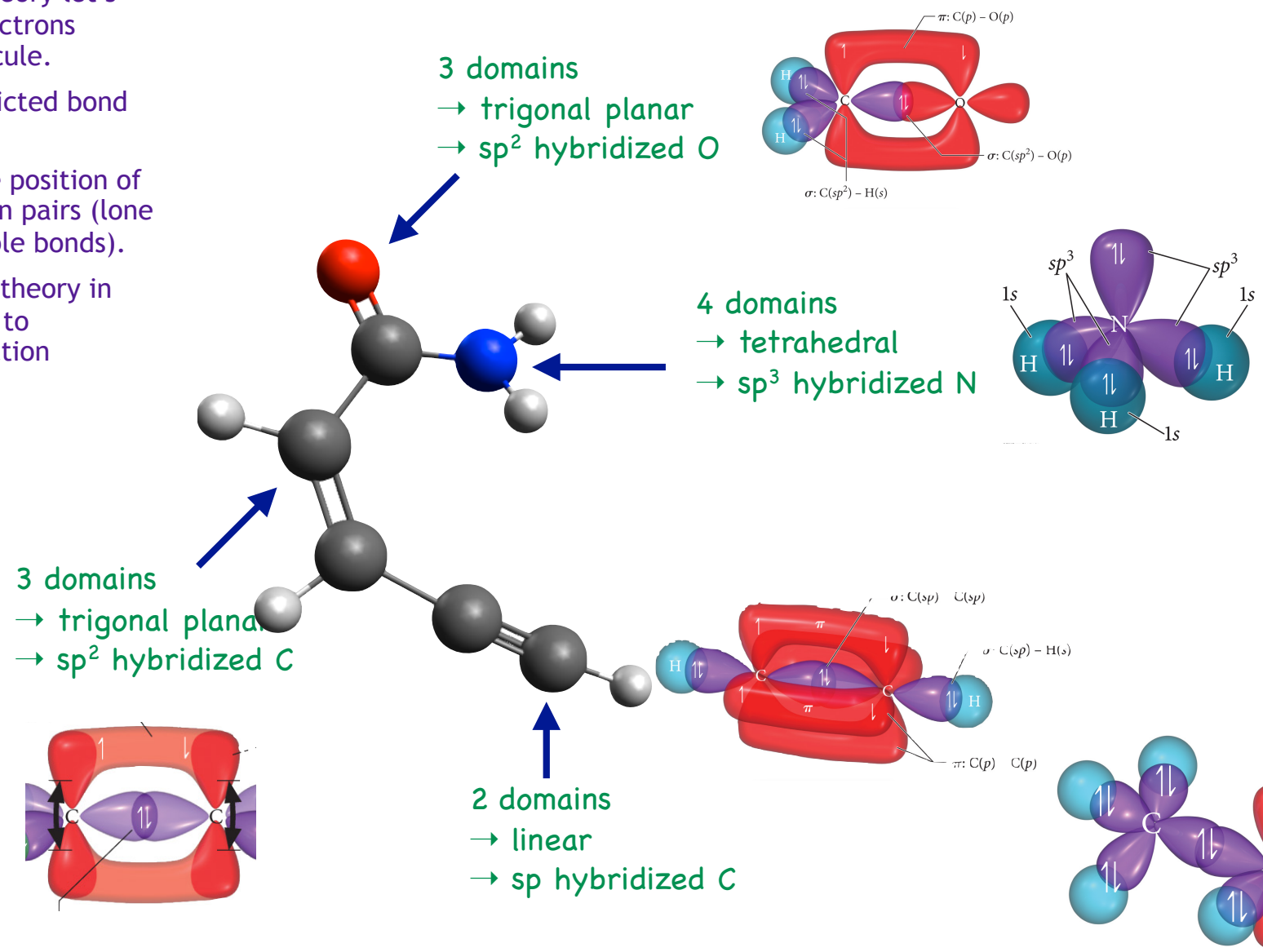
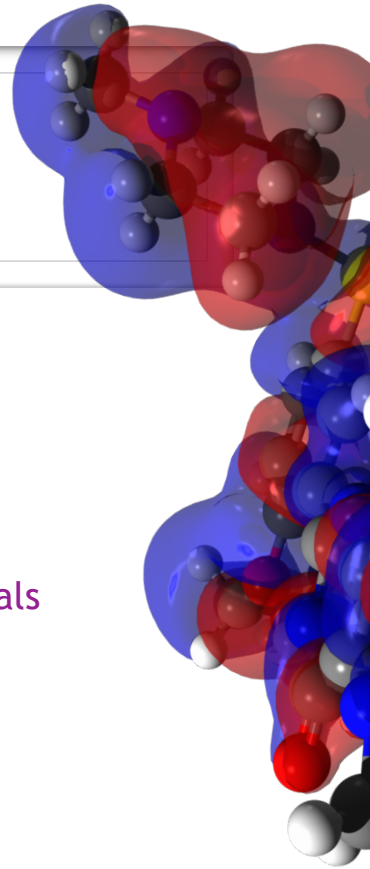


Valence Bond & MO Theories



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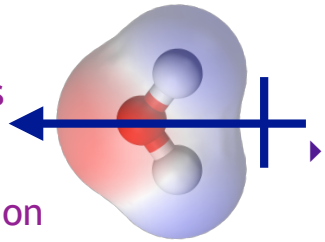

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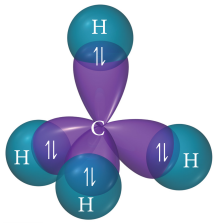

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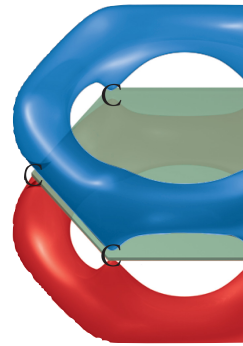
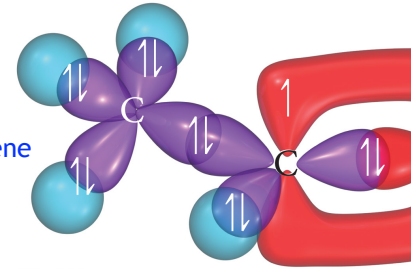
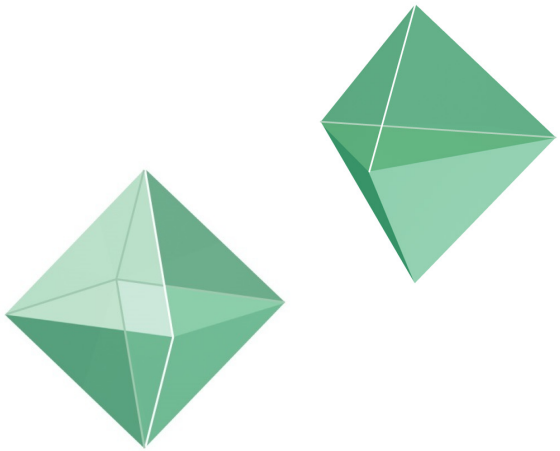
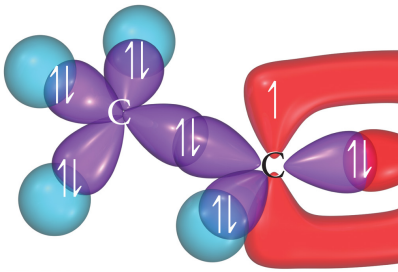




Higher Order Hybridizations

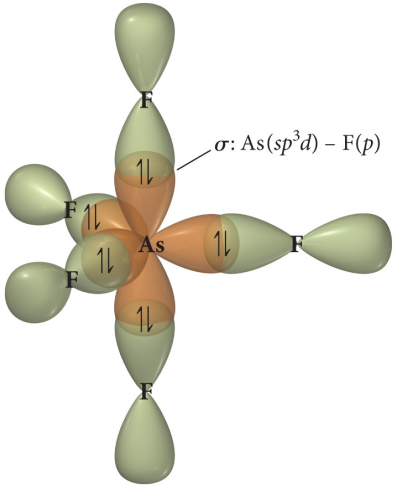
- Atoms of first and second period elements, will only be sp3, sp2 or sp hybridized.
- Third period and below elements can hybridize d orbitals as well.
- We will not be discussing d orbitals in bonding this semester, but you should be able to identify the hybridization of these atoms.
- You already know their electronic shapes.

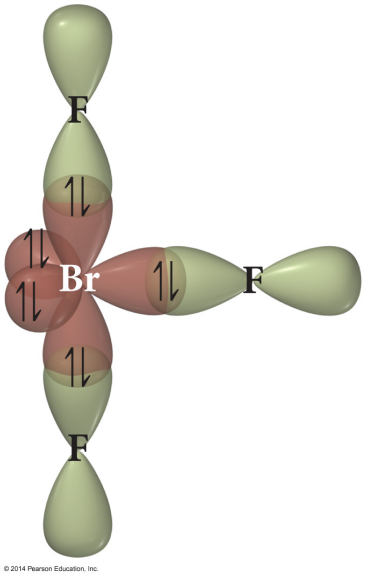


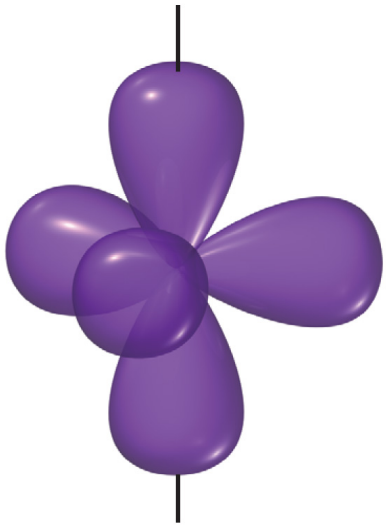


sp^3d Hybridization

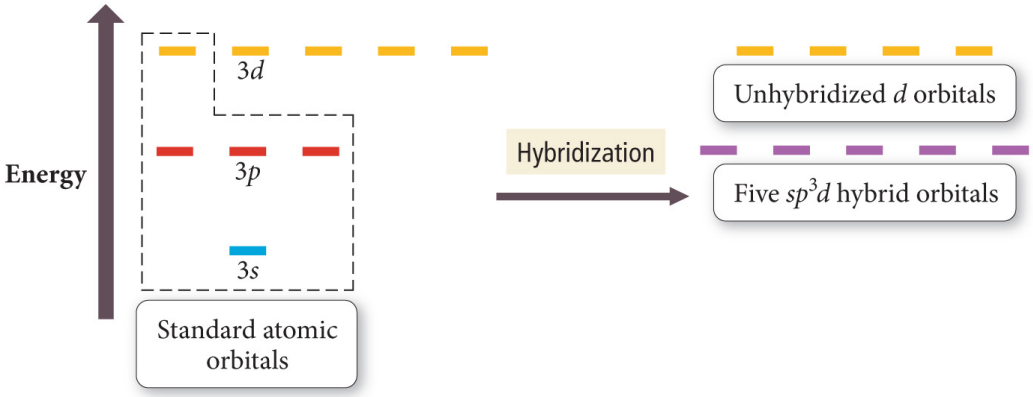
- A trigonal bipyramidal electronic structure is the result of combining:
  - one s orbital
  - three p orbitals
  - one d orbital
- Five sp^3d hybrid orbitals are produced.

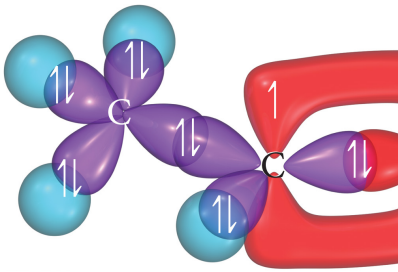






sp^3d hybrid orbitals (shown together)





sp^3d^2 Hybridization

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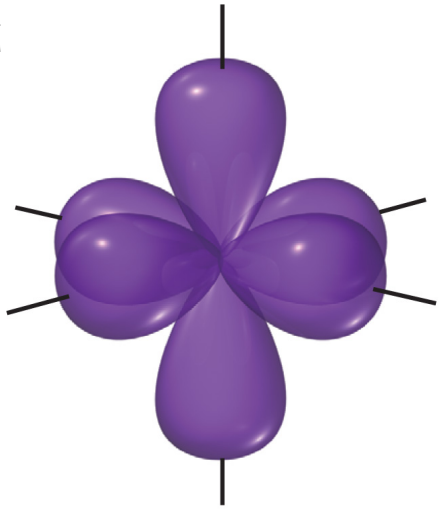
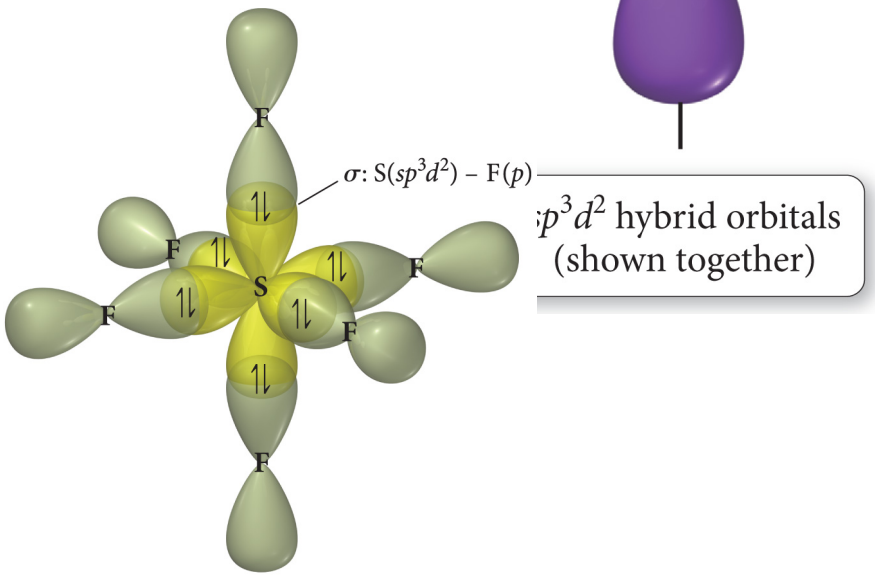
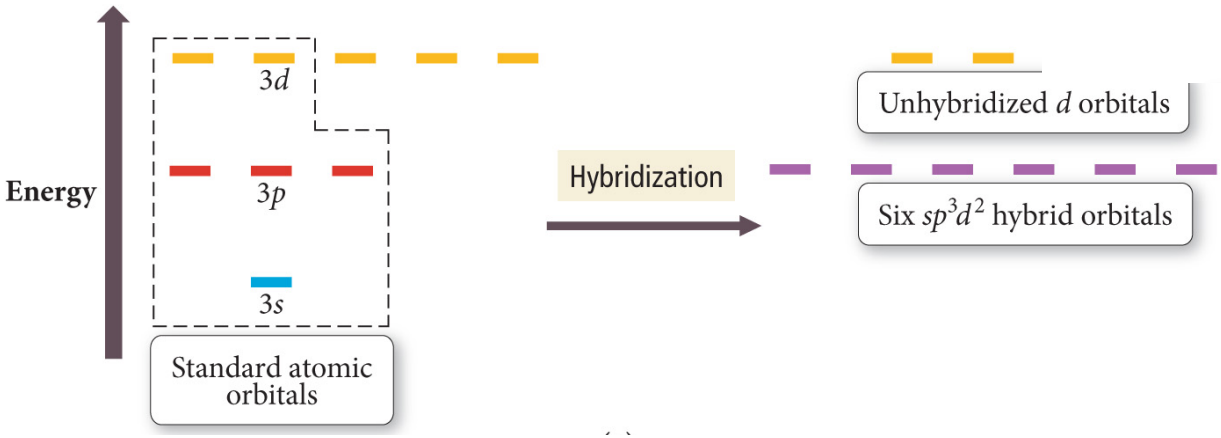
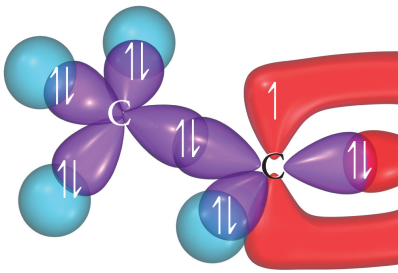
- Five sp^3d^2 hybrid orbitals are produced.









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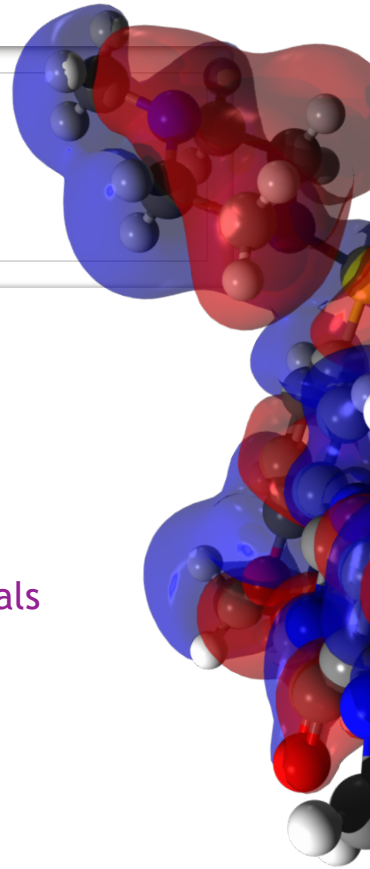

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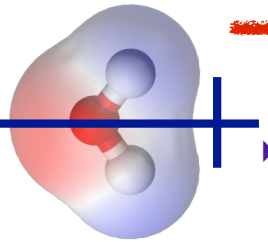

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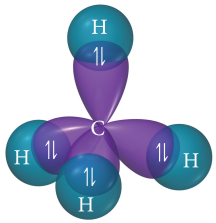

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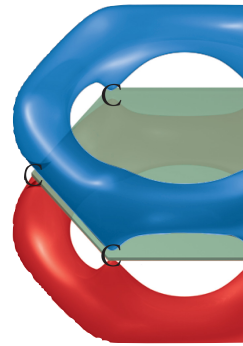
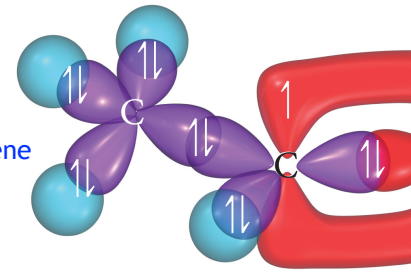
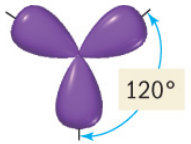
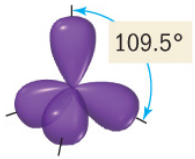
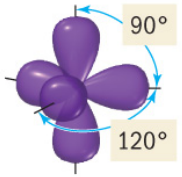
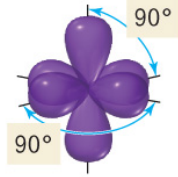
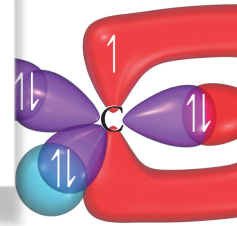




VSEPR Predicts Hybridization

- The hybridization of an atom produces it's electronic structure.
- Since you can predict the electronic structure of an atom from VSEPR, you can predict it's hybridization.

Number of Electron Groups	Electron Geometry (from VSEPR Theory)	Hybridization Scheme	
2	Linear	sp	
3	Trigonal planar	sp^2	
4	Tetrahedral	sp^3	
5	Trigonal bipyramidal	sp^3d	
6	Octahedral	sp^3d^2	



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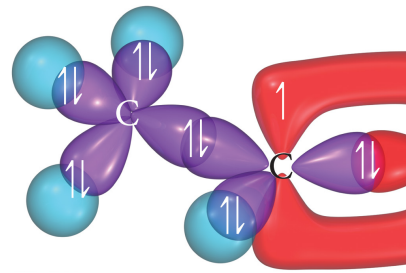
H-C≡N: → H-C≡N:

2 domains
Linear Elec Shape
N is sp hybridized



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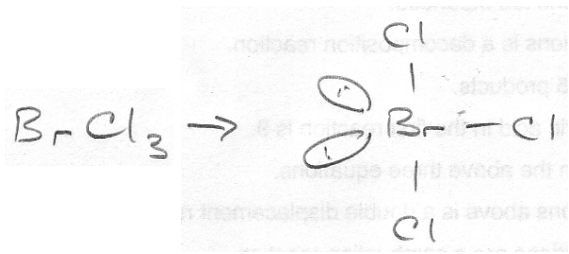

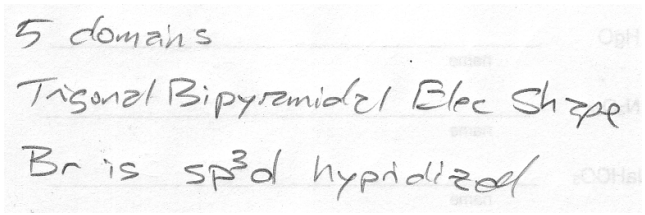

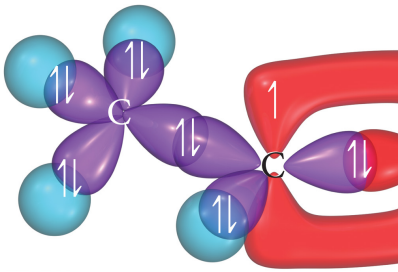

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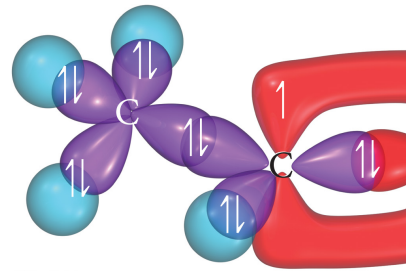

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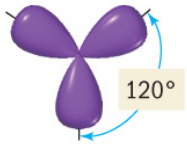
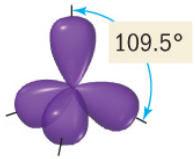
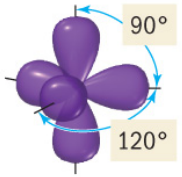
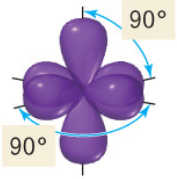
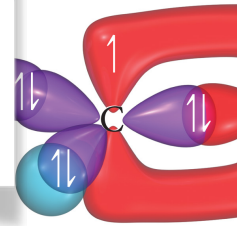
3	Trigonal planar	sp^2	
4	Tetrahedral	sp^3	
5	Trigonal bipyramidal	sp^3d	
6	Octahedral	sp^3d^2	



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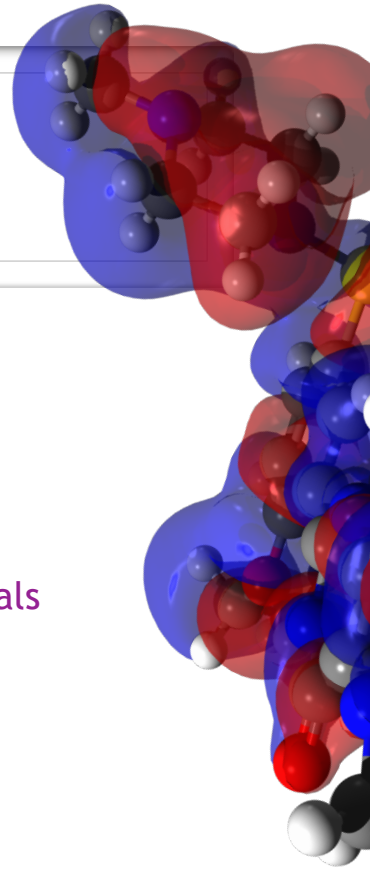

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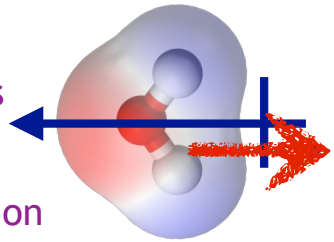

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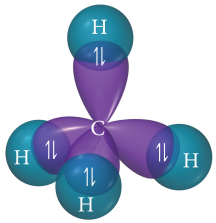

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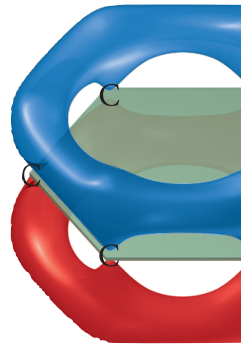
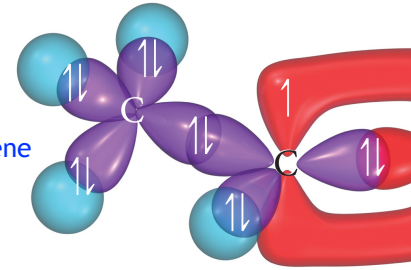
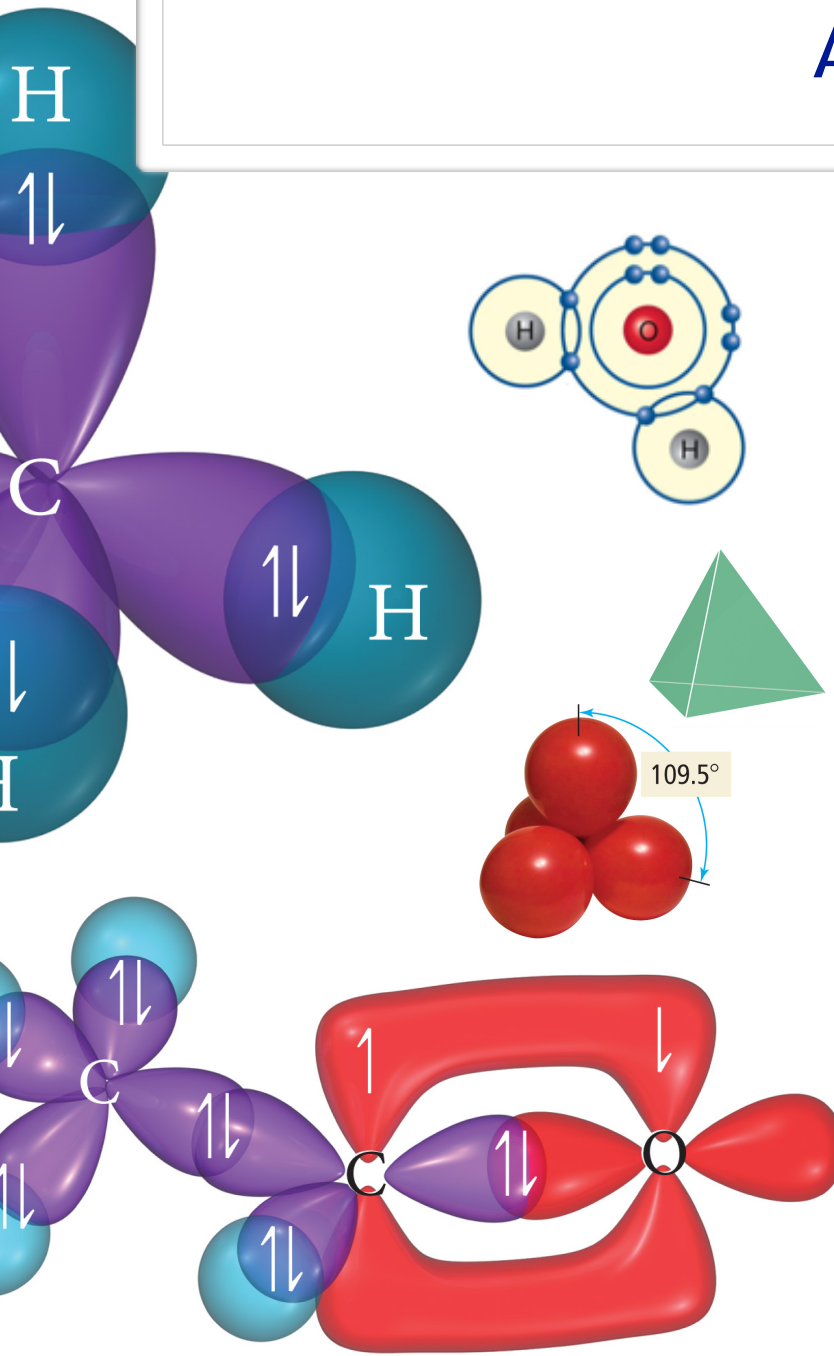
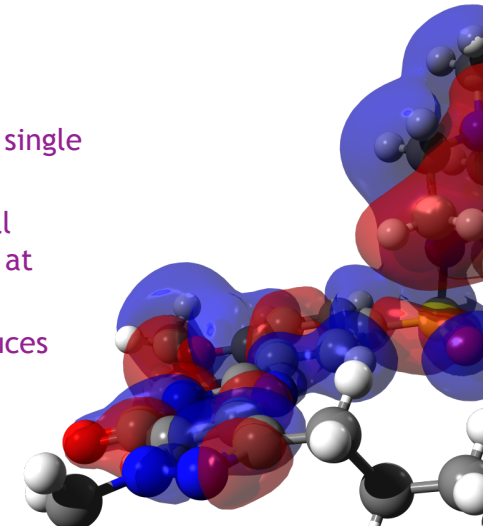




A Third Theory

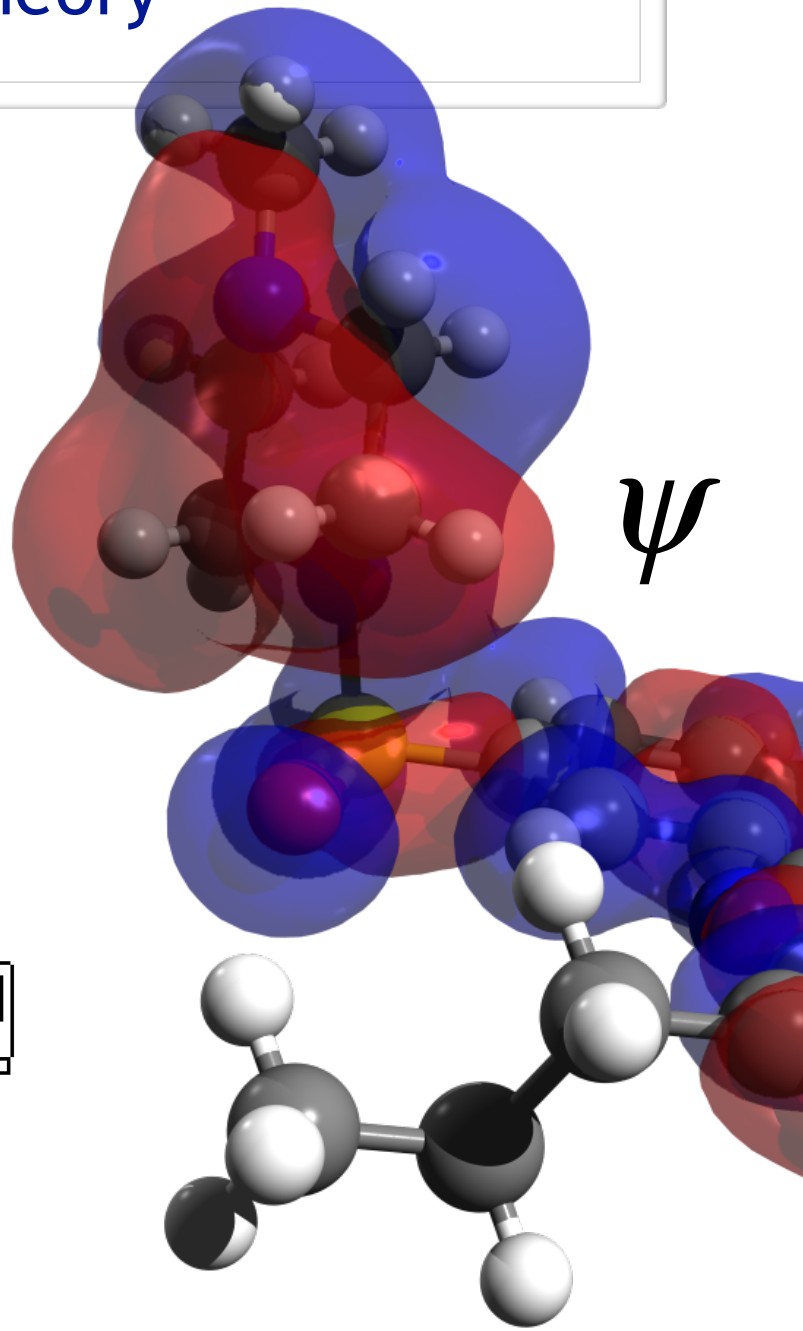


- VSEPR Theory has no quantum mechanics or any kind of calculation.
  - It's a qualitative, quick and dirty, way of estimating shape.
  - It's balloon theory.
- Valence Bond (VB) Theory starts with the QM calculated shape of **atomic** orbitals, then stretches them to make them work with other atoms in a molecule.
  - It's like calculating how a car behaves at one intersection, using that behavior to estimate how it will move through successive intersections then saying that's how it will move through a city.
  - It's better than balloons, but it's still a hack.
  - It's a hybrid approach making atomic orbitals work in a molecule.
- But when we make a molecule the valence electrons of the atoms can spread over multiple atoms.
- Molecular Orbital (MO) Theory is a third tool for understanding molecular behavior.
  - MO Theory does not limit valence electrons to a single atom.
  - It solves the Schrödinger equation considering all valence electrons and all atoms in the molecule at once.
  - Instead of working with atomic orbitals, it produces **molecular** orbitals.

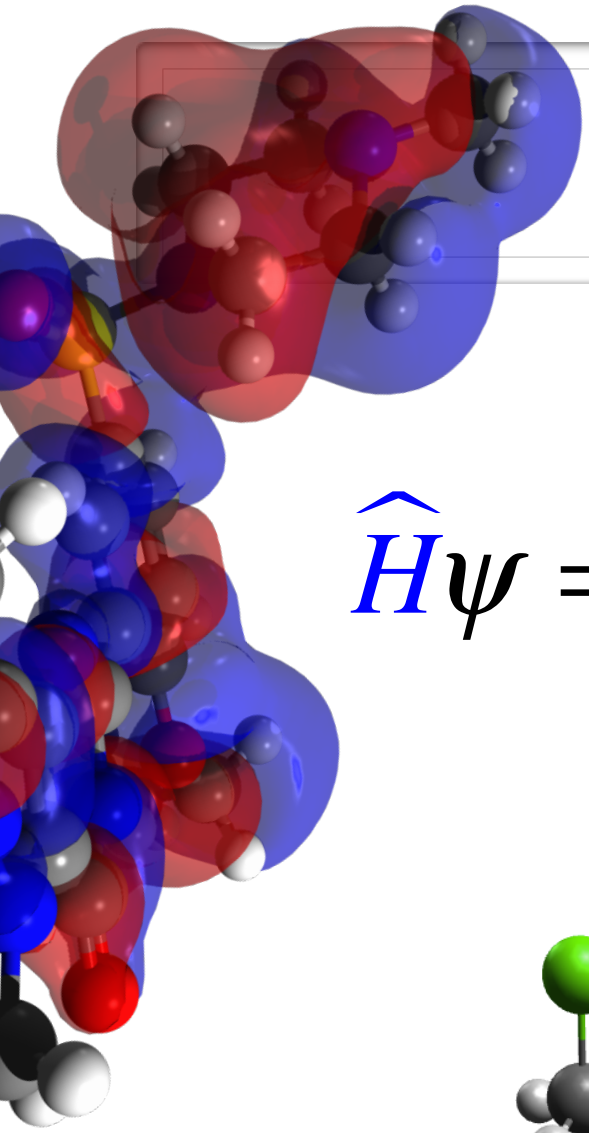


Molecular Orbital Theory

- MO Theory calculates the behavior of electrons over all atoms in the molecule at once.
  - Electrons are not confined to one atom anymore.
  - When you model how each electron moves, how it's wave function behaves, you use data from all atoms in the molecule at once.
  - It's like calculating how a car will be influenced by all the traffic lights, other cars, and street signs as it moves around a city.
  - If you can model all the things that influence the car, and know how it will react to each, you exactly predict a cars path.
    - The equations are much more complicated.
    - It produces a much more complete description of a molecule.
    - It's too complicated to solve by the method we use for atoms.
      (Even with a personal super computer like a Mac)
    - But we even if we can't solve the wave functions, we can still use them to explore the molecule.

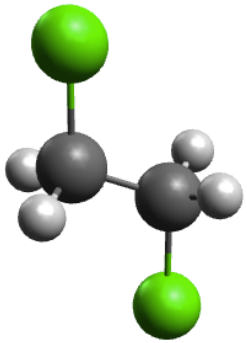


Molecular Orbital Theory

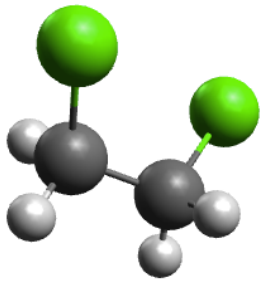


$$\hat{H}\psi = E\psi$$

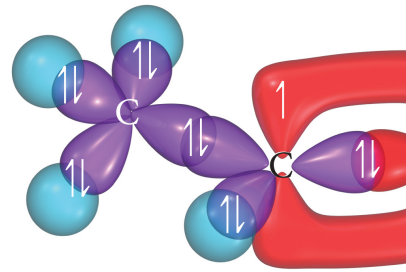
- Valence electrons spread out over multiple atoms.
- They work in pairs (one spin up; one spin down).
- They're pulled by each nucleus, and try to avoid other pairs of electrons.
- We describe their behavior with wave functions (ψ_1, ψ_2, ψ_3, …).
  - The wave functions are shaped by the 3D position of each nucleus.
- Each wave function has variables for the x, y, z position of *each* atom.
- And more variables that describe the shape of each electron orbital.
  - There are hundreds of variables for each wave function.
  - And changing one, in one wave function, changes all the other wave functions.
- It's impossible to solve for all these variables at once.
- But we can calculate the energy of any combination of variables.
- And once we know the energy of each occupied orbital, we can get the overall energy of the molecule.
  - $E_{total} = E_1 + E_2 + E_3$ …
- So we can make a guess as to a molecular shape and find out how stable that shape is relative to another guess.
- And we know nature will arrange those atoms in the most stable orientation possible.
- So we can compare any two shapes and decide which one nature would prefer.



1.37 kJ/mol

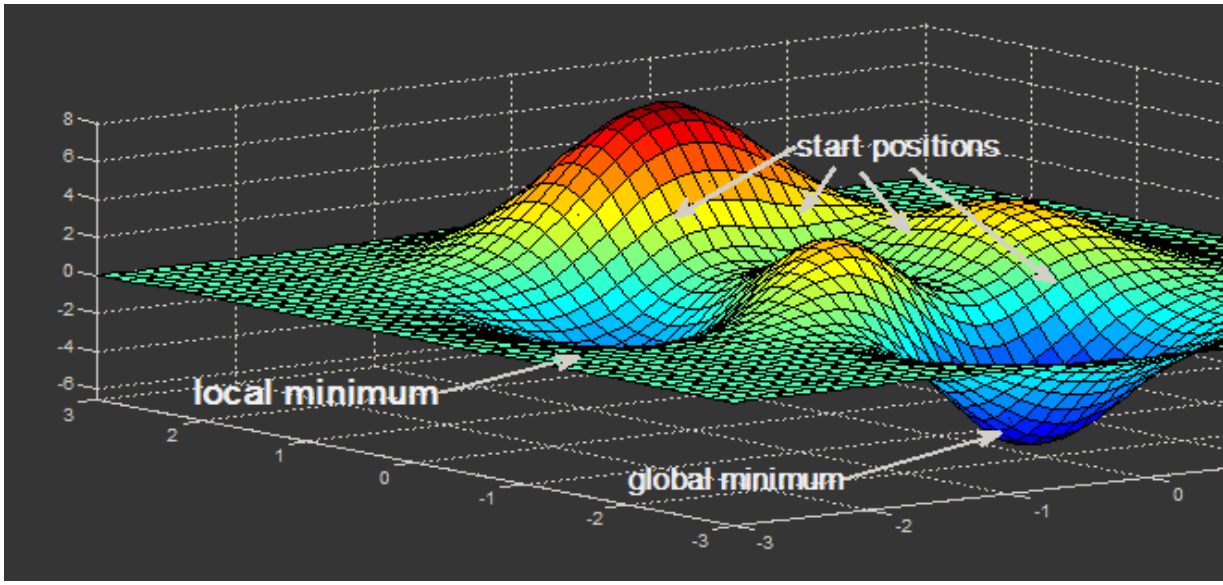


4.33 kJ/mol

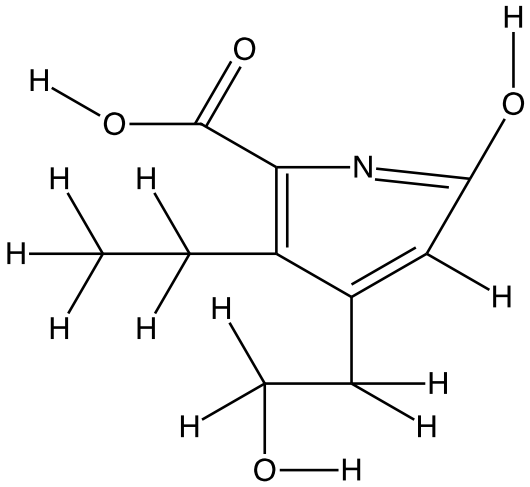


Molecular Orbital Theory

- We can make a guess as to a molecular shape and find out how stable that shape is relative to another one.
  - We can start with a "good guess" for the right position of nuclei (based on knowledge of it's connectivity from Lewis analysis or other methods).
    - And a good guess for the right shape of the electron orbitals.
  - We optimize the orbitals to find out what the total energy of orbitals and thus the structure is.
    - The shape of the orbitals we find, helps us understand how the molecule will behave.
    - We see where it want's electrons, where it has a build up of them.
    - Where it's strong and where it's weak.
    - Where it can bend or twist.
  - Then we twist the molecule a touch, recalculate the position of the nuclei and do it again.
  - Each optimized adjustment is another step along a map.
  - The deepest valley in that map is the lowest possible energy structure.
  - That's the structure nature has already found.



$C_{10}H_{13}NO_3$



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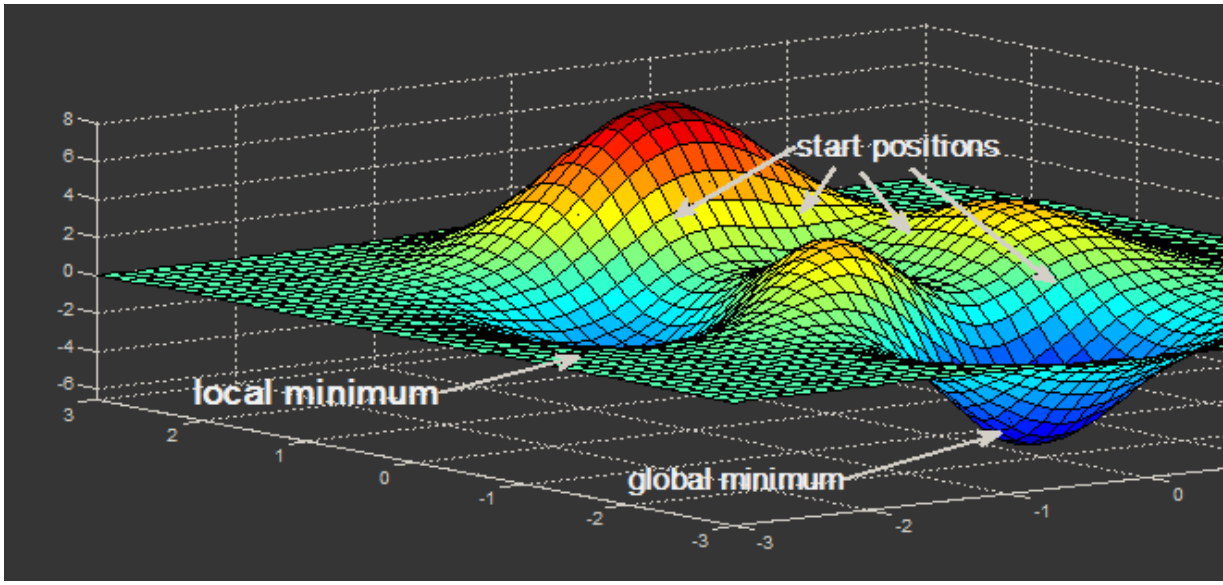

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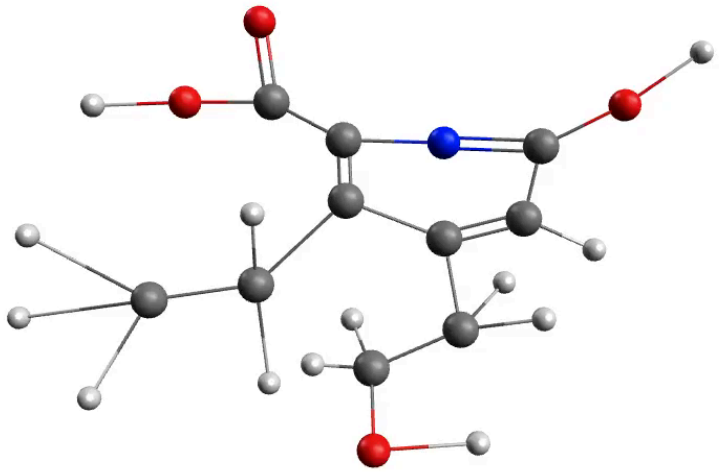
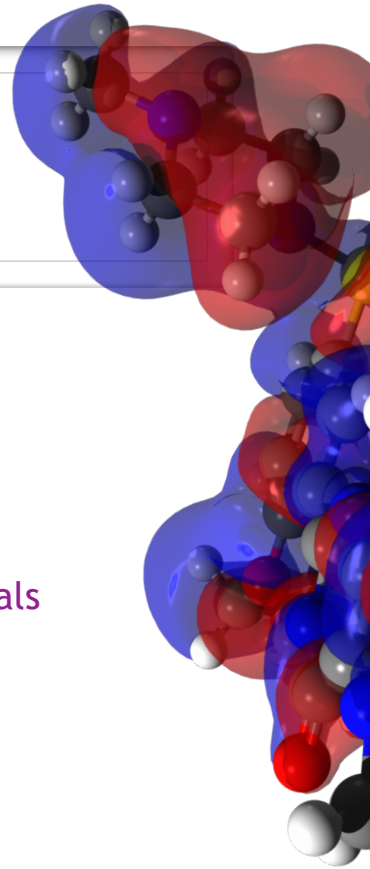
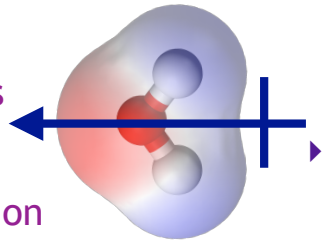


Valence Bond & MO Theories



- Molecular Shape and Polarity
  - Polar Bond & Polar Molecules
  - Net Dipole Moment
  - Adding dipoles: vector addition
    - in one dimension
    - two & three dimensions
    - try some examples



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  - Forming Molecules w/ Quantum Atoms
    - H_2S & H_2C
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    - sp3 orbitals
    - Sigma & Pi bonding: sp2 & sp orbitals
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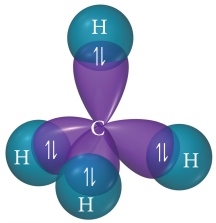

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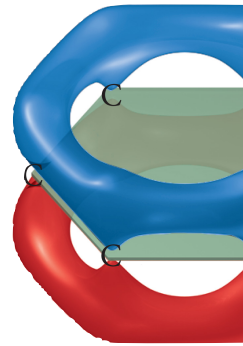
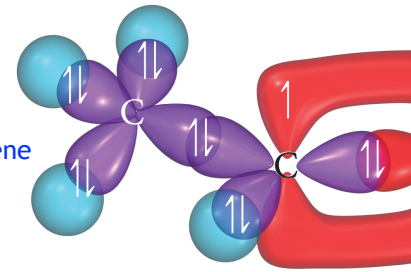
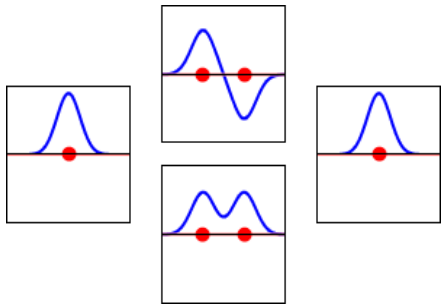
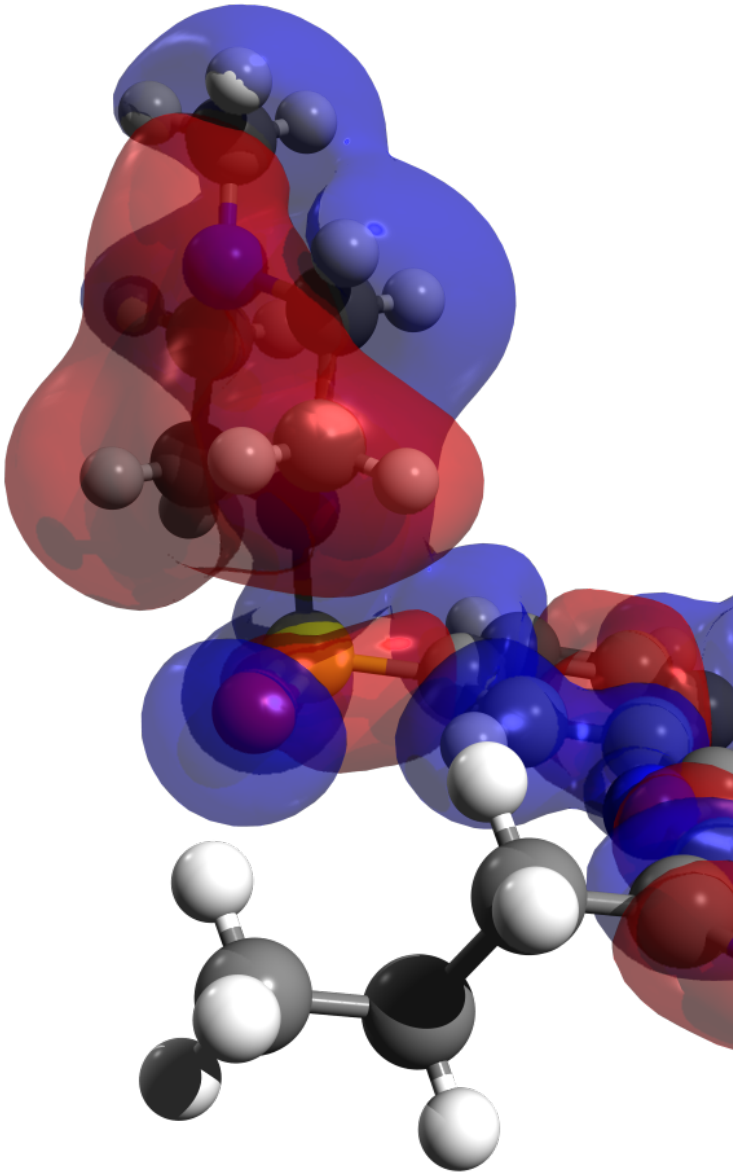




MO Theory, LCAO Strategy

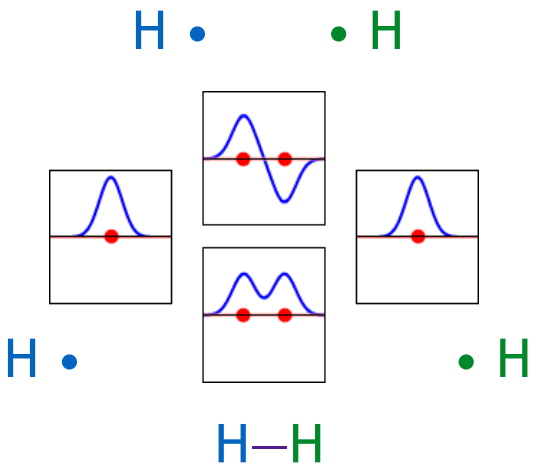
- Getting good energies for each shape starts with guessing how electron orbitals might be smeared over a molecule.
- How do we make a good guess for molecular orbitals?
- Different strategies use different initial guesses for the molecular wave functions.
- The simplest MO model involves combining orbitals from adjacent atoms.
  - Like when we mixed orbitals on the same atom, to create hybrid orbitals.
- LCAO (linear combination of atomic orbitals) just adds to adjacent orbitals to form two new molecular orbitals.
  - First add them in phase.
    - Constructive addition (interference)
  - Then add the with opposite phase.
    - Destructive addition (interference)
- This works really well.
- When you combine orbitals, you always end up with the same number of orbitals and same net energy.
- But depending on the electron configuration within those orbitals, the atoms might end up in a lower energy state.

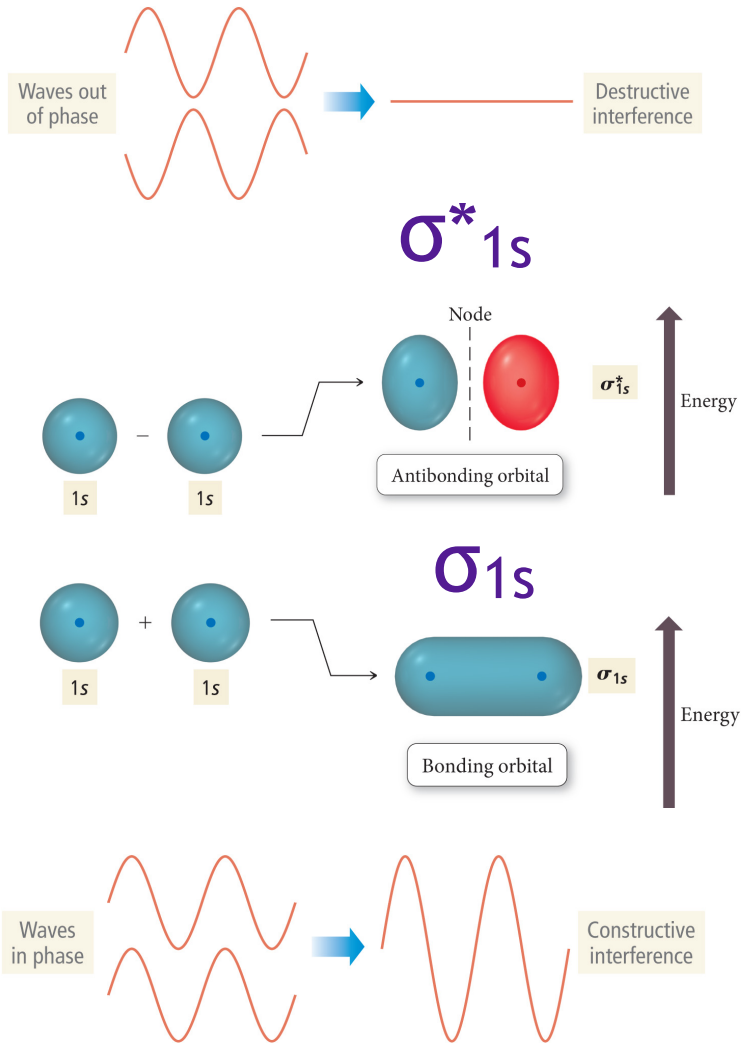




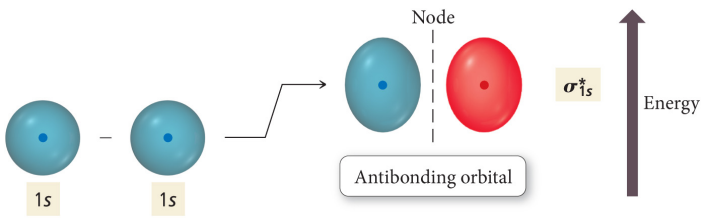
MO Theory, LCAO Strategy

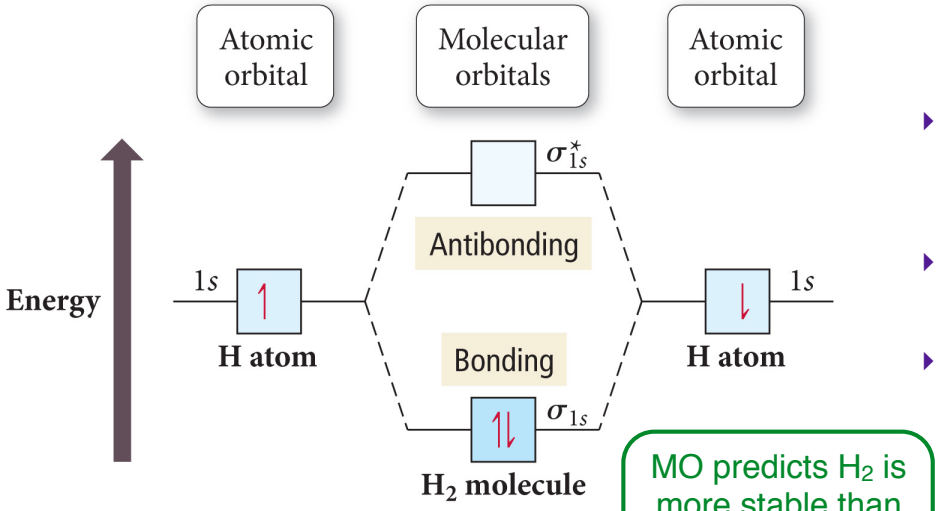
- When you combine orbitals, you always end up with the same number of orbitals and same net energy.
- But depending on the electron configuration within those orbitals, the atoms might end up in a lower energy state.
- When two s orbitals form a bonding orbital we get a sigma bond and we name that orbital after the AO's used to form it. Example σ_{1s}
- The complementary anti bonding orbital is named the same way, except we add an asterisk. Example σ^*_{1s}
- Even without optimization, LCAO strategy can predict the bond order that will likely form between atoms.
- For example, consider the H_2 molecule.



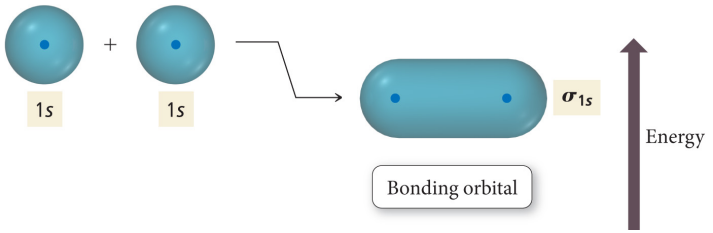


MO Theory, LCAO Strategy





MO predicts H_2 is more stable than two H atoms

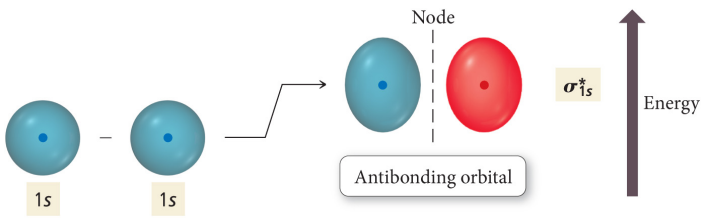


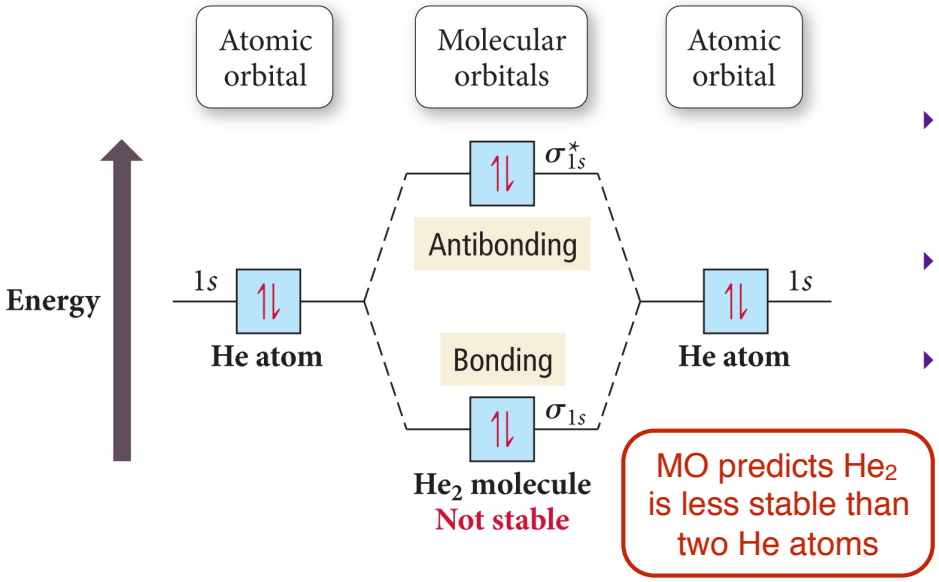
- When you combine orbitals, you always end up with the same number and same net energy.
- Constructive addition creates an orbital that allows electrons to flow between the two atoms — a bonding configuration.
  - Bonding configurations are more stable (lower energy).
- Destructive addition creates an orbital that isolates the electrons from each atom — an anti bonding configuration.
  - Anti-Bonding configurations are less stable (higher energy).
- You can use orbital diagrams to predict how many electrons can be shifted to lower energy, bonding orbitals, and how many get stuck in higher energy anti-bonding orbitals.
- If more electrons end up in bonding orbitals than end up in anti-bonding orbitals the atoms prefer to be bonded.
- You can predict the bond order of a molecule by subtracting the anti-bonding electrons from the bonding electrons and dividing the result by two.

$$\text{Bond Order} = \frac{\text{Bonding e's - Anti-Bonding e's}}{2}$$

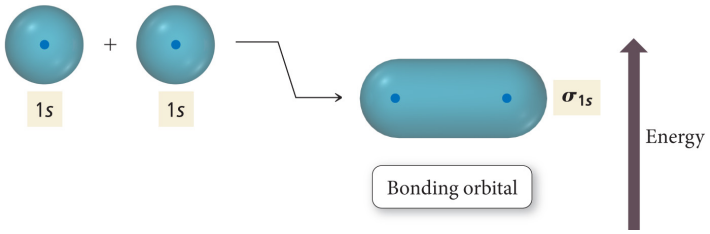
$$H_2 \text{ Bond Order} = \frac{2 - 0}{2} = 1 \text{ (single bond)}$$

MO Theory, LCAO Strategy





MO predicts He_2 is less stable than two He atoms



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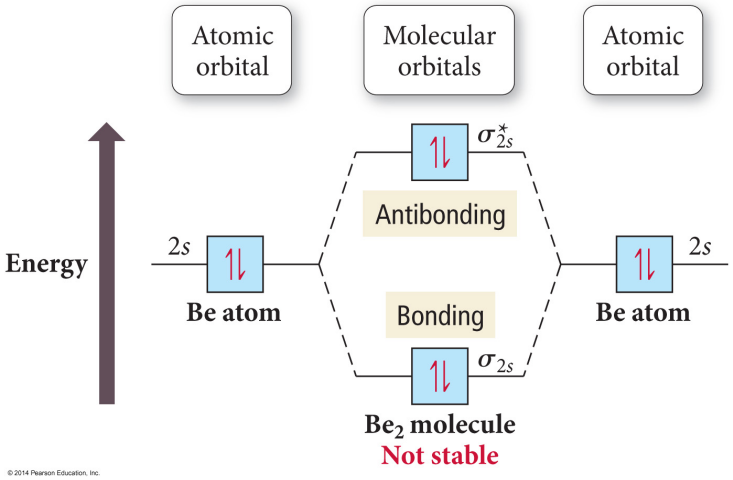
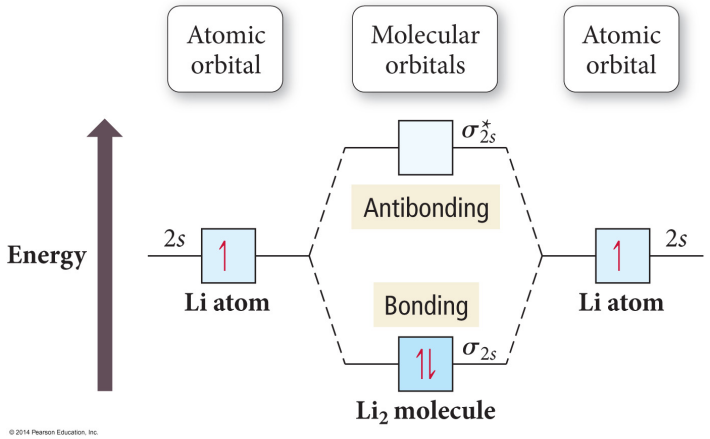
$$\text{He}_2\ \text{Bond Order} = \frac{2 - 2}{2} = 0\ \text{(no bond formed)}$$

MO Theory, LCAO Strategy

- Only valence electrons are used to form molecular orbitals.



$$Be_2 \text{ Bond Order} = \frac{2 - 2}{2} = 0 \text{ (no bond formed)}$$



$$Li_2 \text{ Bond Order} = \frac{2 - 0}{2} = 1 \text{ (single bond formed)}$$

Valence Bond & MO Theories

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  - Net Dipole Moment
  - Adding dipoles: vector addition
    - one dimension
    - two dimensions
    - three dimensions
    - common cases
- Valence Bond Theory: Orbital Overlap as a Covalent Bond
  - Valence Bond theory
    - interaction energy diagram
    - overlap of atomic orbitals
    - shape determined by geometry of overlapping orbitals
- Valence Bond Theory: Hybridization of Atomic Orbitals
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    - sp3
      - 4 equivalent orbitals
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    - sp2
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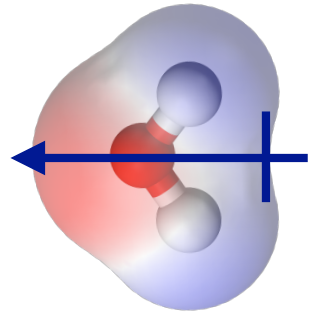
      - trigonal planar arrangement
      - sigma bonds and pi bonds
      - rotation restricted for pi bonds
    - sp hybridization
      - 2 equivalent orbitals + 2 p orbitals remaining
    - sp3d hybridization
      - 5 equivalent hybrid orbitals
    - sp3d2 hybridization
      - 6 equivalent hybrid orbitals
  - Determining hybridization and drawing valence bond models
    - Lewis structure
    - VSEPR geometry
    - hybridization
    - molecular sketch
      - hybrid orbitals
      - sigma and pi bonds



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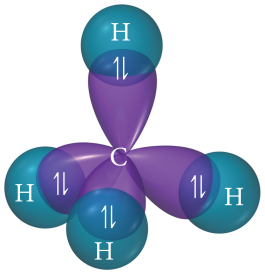

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    - Polyatomic molecules
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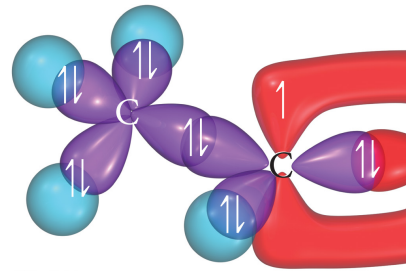

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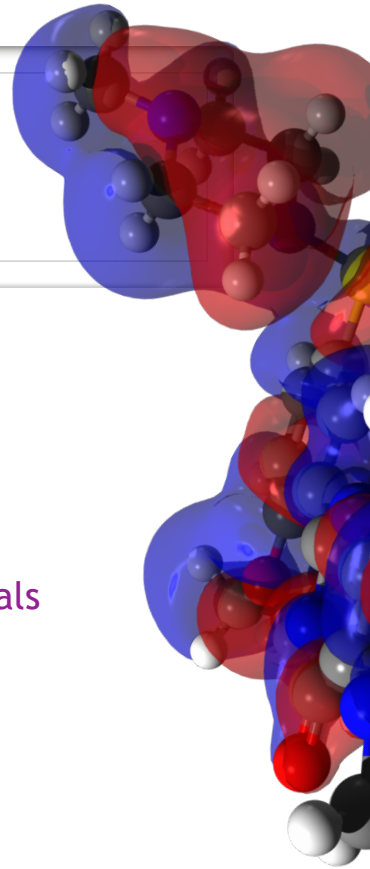

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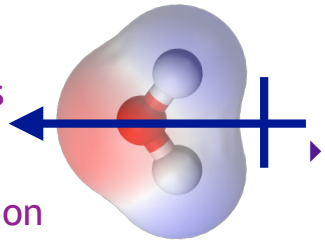

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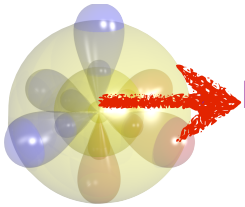

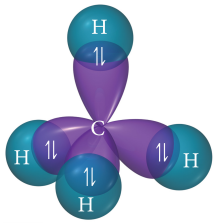

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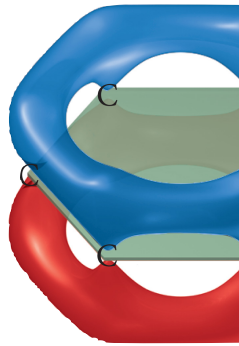

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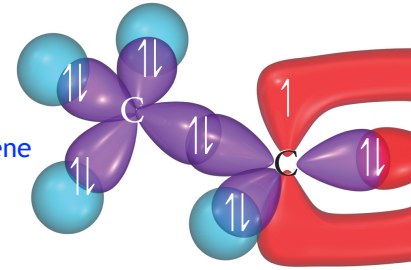
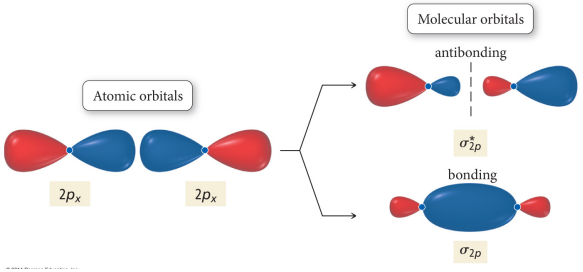
    - electron delocalization in ozone, benzene

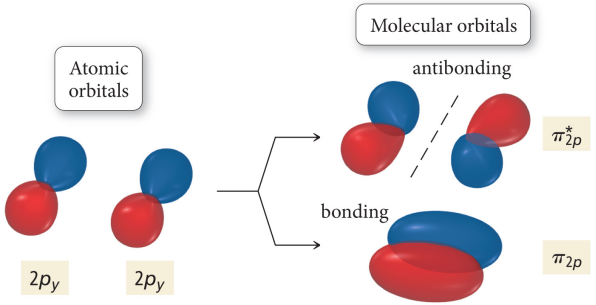


MO Theory π Bonding

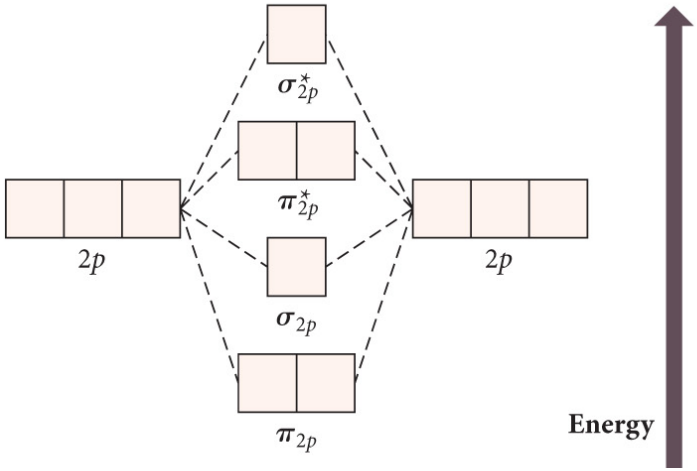
- p orbitals on adjacent atoms combine…
  - head on to form a σ bond
  - sideways to form a π bond

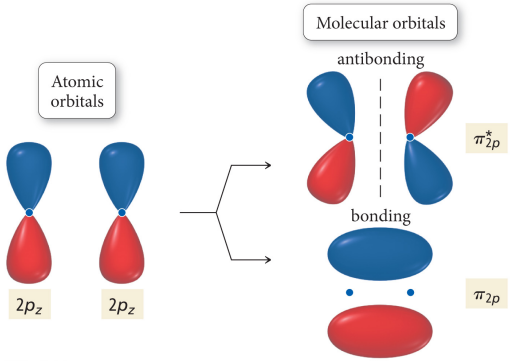


- Each set of p orbitals combine to make a pair of molecular orbitals.
- The molecular orbitals are named according to the atomic orbitals that make them and the bond that results.



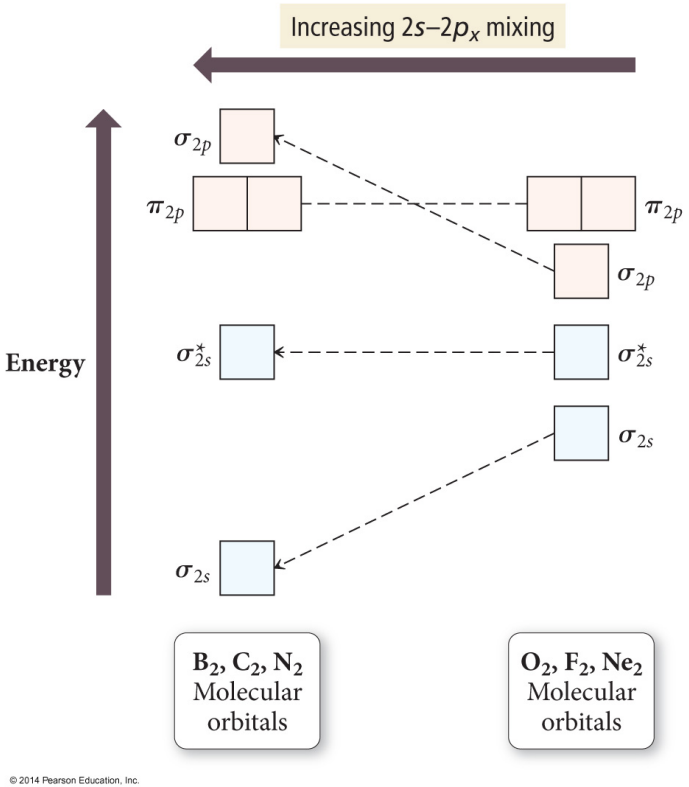
- Two $2p_x$ orbitals combine to form: σ_{2p} and σ^*_{2p} orbitals
- Two 2py and two 2pz orbitals combine to form: two π_{2p} and two π^*_{2p} orbitals

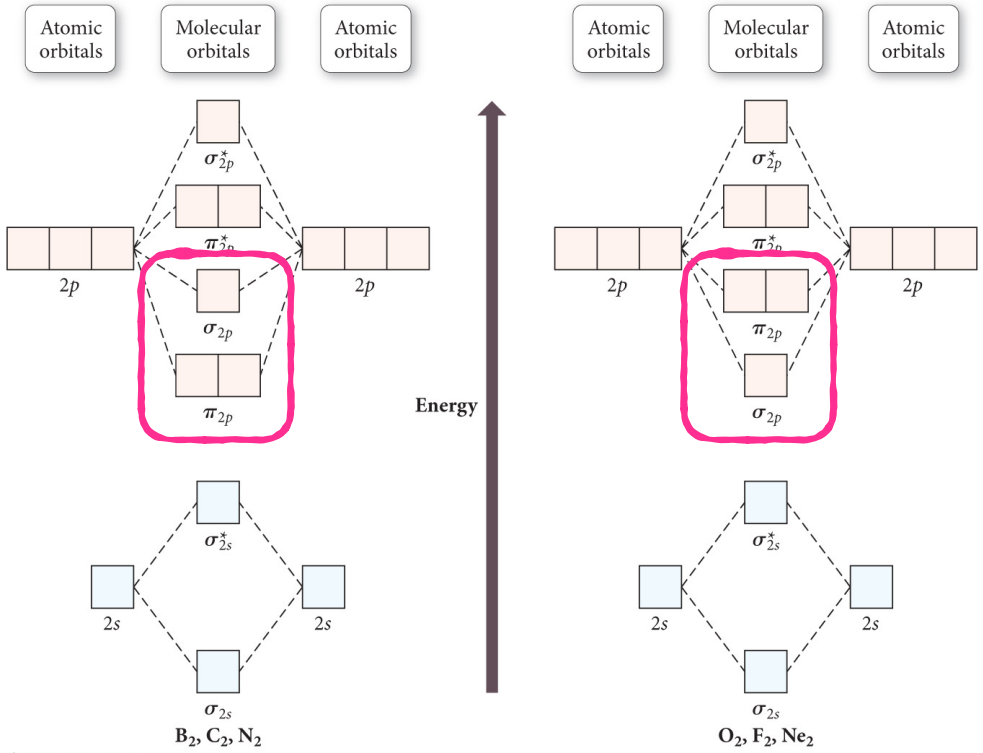




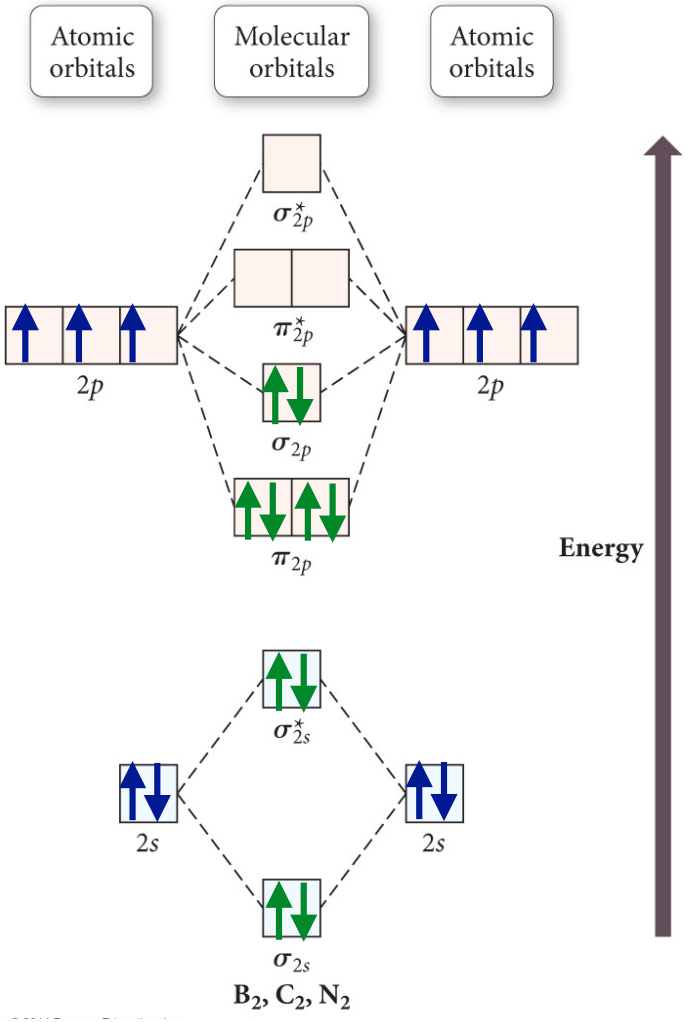
Energy Levels of n=2 Orbitals

- The relative energy of molecular orbitals is not easy to predict.
- For n=2 diatomic molecules there is a switch between N and O.
- N and below π is lower than σ bonding orbitals.
- O and above σ is lower than π bonding orbitals.

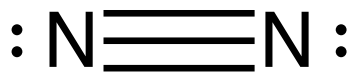




Nitrogen Gas (N_2)



- Nitrogen gas forms a triple bond.
- Nitrogen gas is diamagnetic.

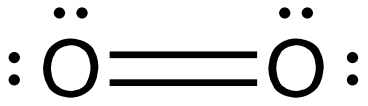


$$N_2 \text{ Bond Order} = \frac{8 - 2}{2} = 3 \text{ (triple bond)}$$

No unpaired electrons

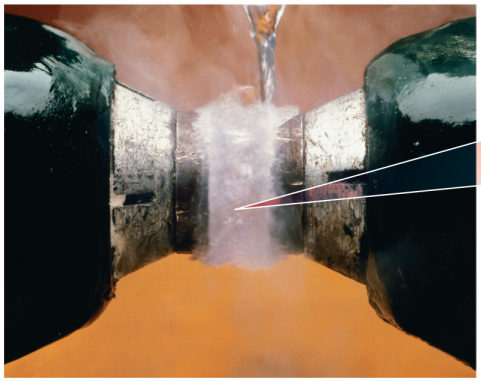
Oxygen Gas (O_2)

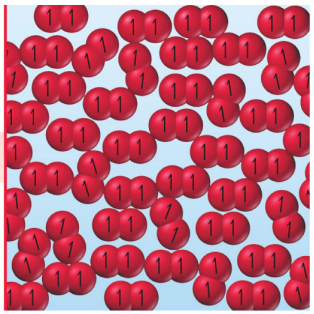
- Oxygen Gas form a double bond.
- Oxygen Gas is paramagnetic.

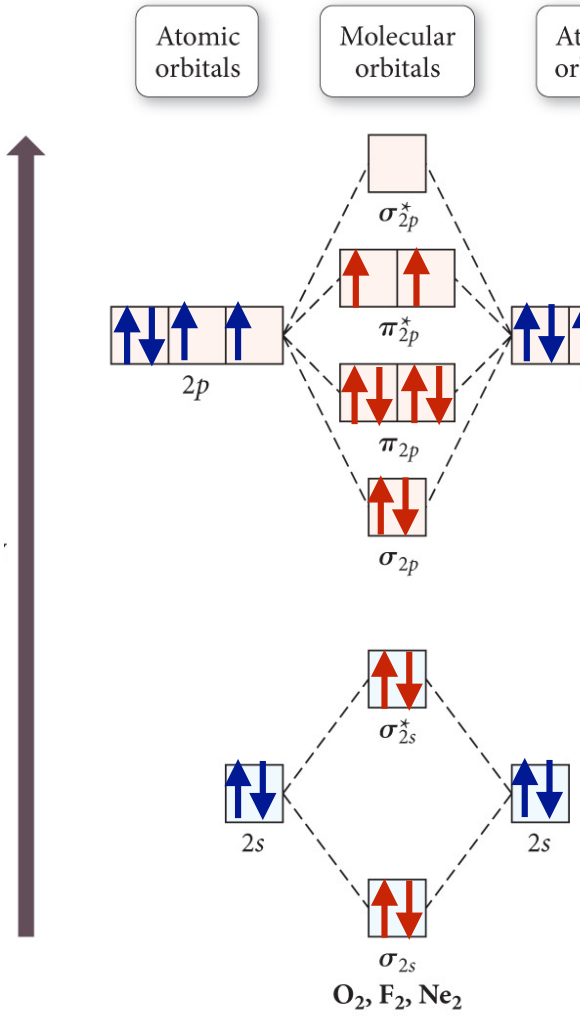


$$O_2 \text{ Bond Order} = \frac{8 - 4}{2} = 2 \text{ (double bond)}$$

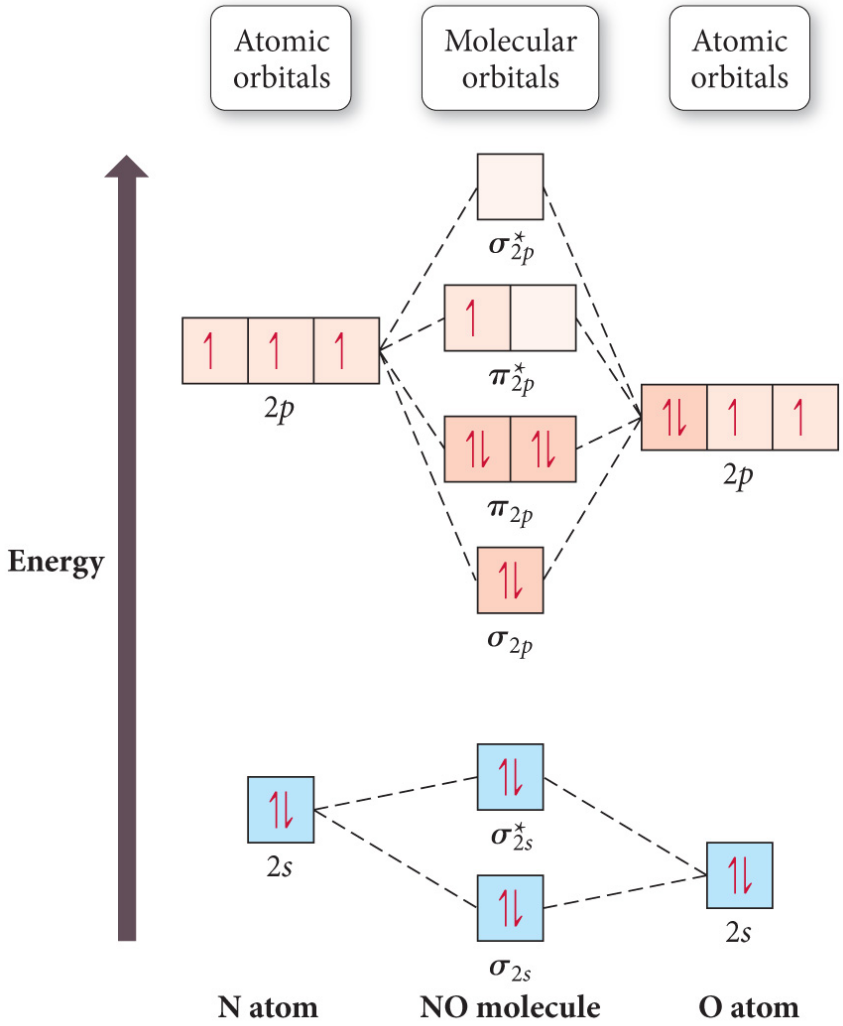
Two unpaired electrons



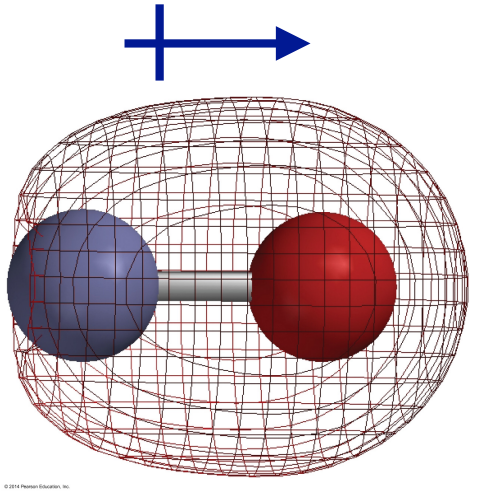




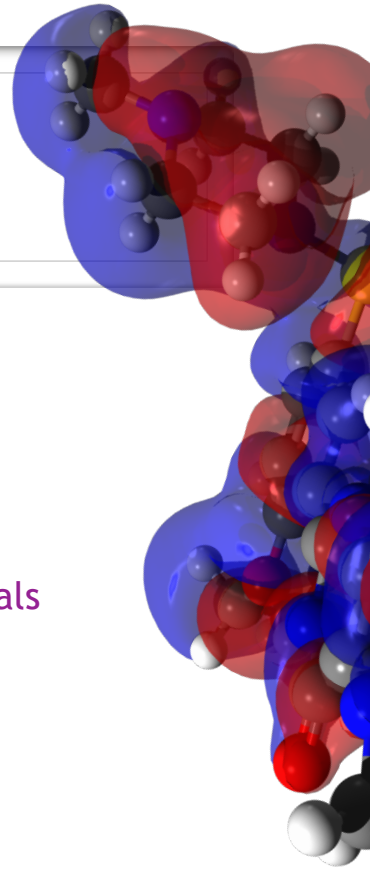
Nitrogen Monoxide (NO)



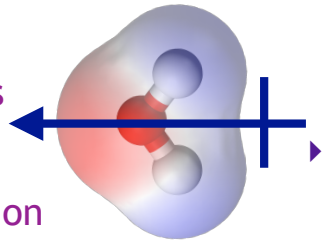
- For molecules composed of different elements, electronegativity affects orbital stability.
- More electronegative elements better stabilize electrons.
- More electronegative elements contributed orbitals are lower in energy.
- Molecules favor those orbitals when blending.
- Bonding orbitals are composed more of the more electronegative elements orbital.
- So more electron density ends up on the more electronegative atom.
- Producing a dipole.



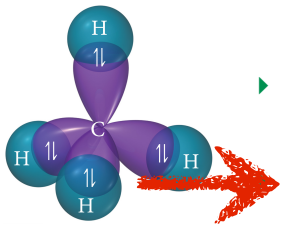
Valence Bond & MO Theories



- Molecular Shape and Polarity
  - Polar Bond & Polar Molecules
  - Net Dipole Moment
  - Adding dipoles: vector addition
    - in one dimension
    - two & three dimensions
    - try some examples



- Valence Bond Theory
  - Quantum View of Covalent Bonds
    - Bonding with Schrödinger's Quantum Atom
    - Orbital Overlap is a Covalent Bond
  - Forming Molecules w/ Quantum Atoms
    - H_2S & H_2C
  - Hybridization of Atomic Orbitals
    - Atomic Orbitals inside a molecule are not the same as the atom by itself.
    - sp3 orbitals
    - Sigma & Pi bonding: sp2 & sp orbitals
    - d-Orbital Hybridization: sp3d & sp3d2



- Determining Hybridization
  - Look at electronic shape of the atom
- Molecular Orbital Theory
  - Electron Delocalization
  - Linear combinations of atomic s orbitals
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    - destructive: antibonding
    - Molecular orbital diagrams
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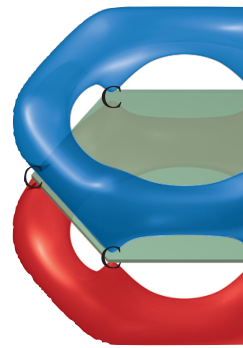
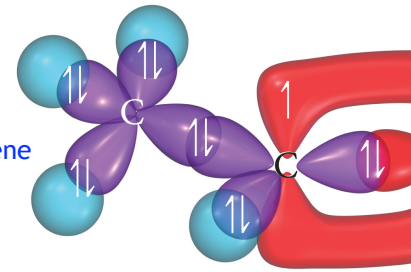
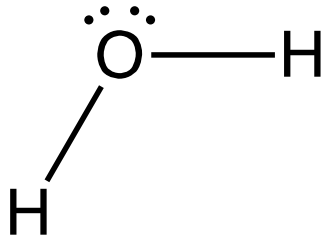


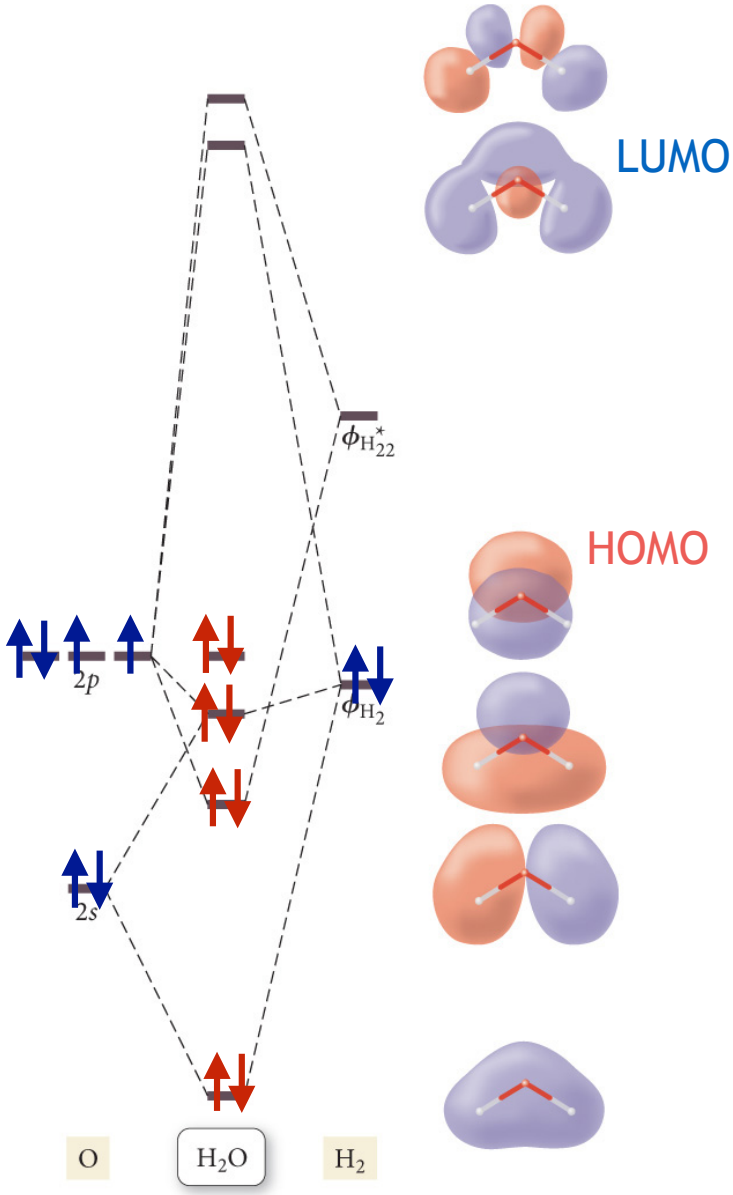


Water (H_2O)

- Larger molecules, even those as simple as water or ammonia require a huge number of calculations to identify their molecular orbitals.
- We won't be able to do these with pen and paper, a super computer is required to process all the calculations.
- Like a Mac.
- But analyzing the results helps us understand the behavior of molecules.
- We can predict the number of bonds in a molecule and see how it will interact with other molecules.
- HOMO (highest occupied molecular orbital) is where the atom is most likely to loose electron density, or donate it to another molecule.
- LUMO (lowest unoccupied molecular orbital) is where the atom is most likely to receive electron density from another molecule.

This is just for illustration, you aren't expected to be able to reproduce these calculations.





Ammonia (NH_3)

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- Like a Mac.
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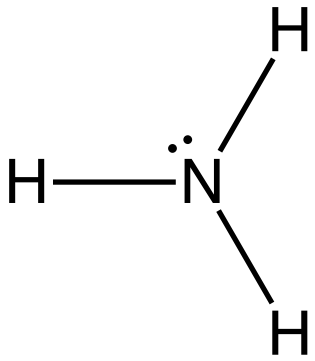
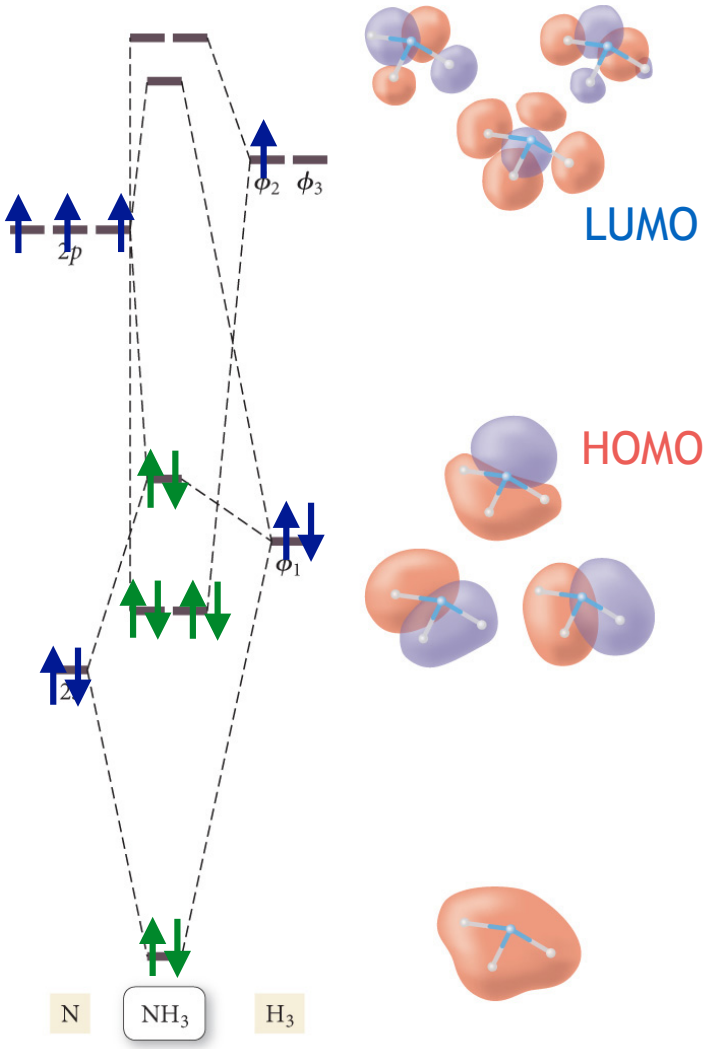
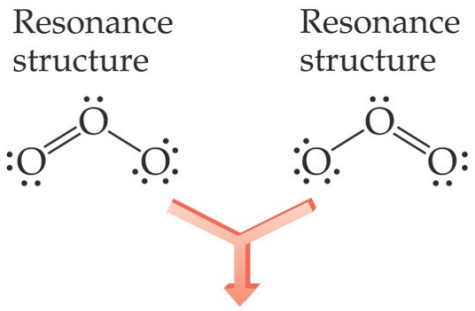
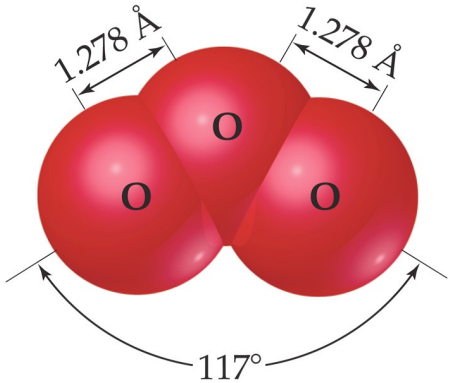


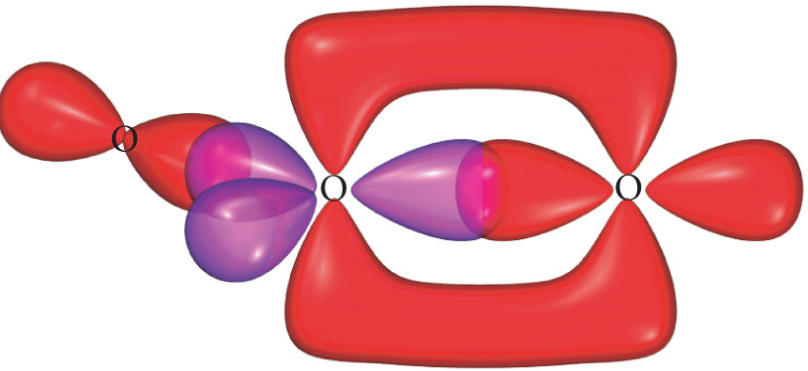


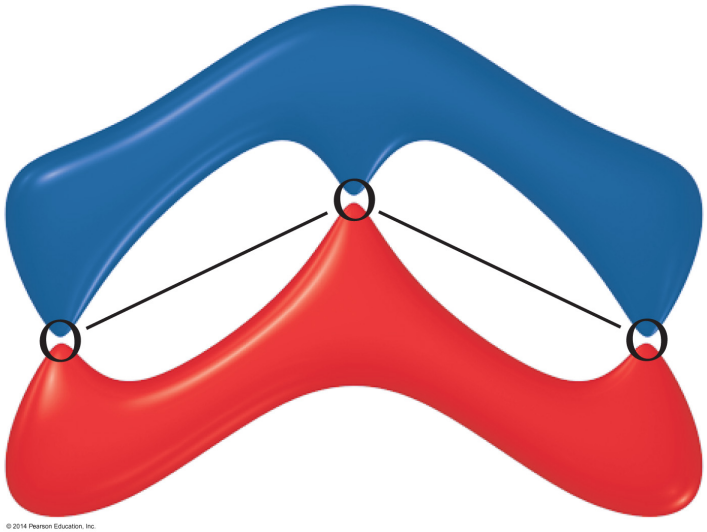
Ozone

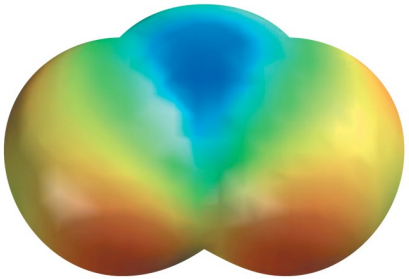
- Lewis models require two structures to show the experimental shape of ozone.
- Valence Bond Theory predicts a single and a double bond.
- MO Theory shows us that each oxygen has an equal 1.5 bond order bond and that electron density is found mostly above and below the plane of the three oxygens.





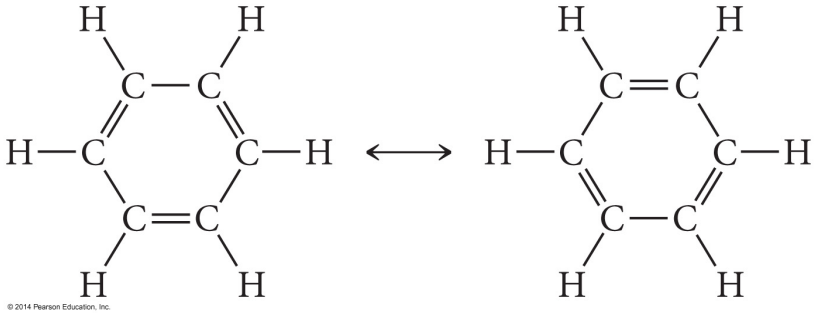


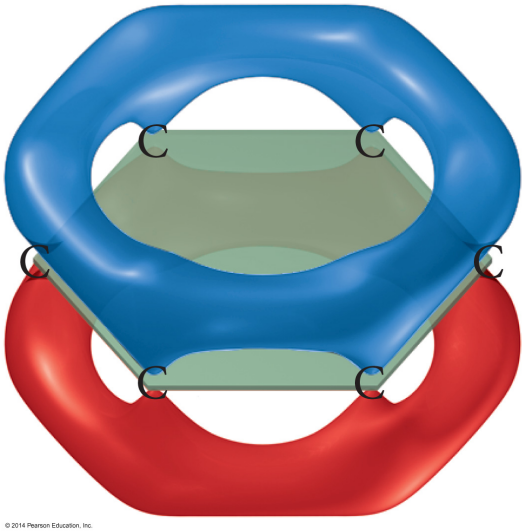




Benzene

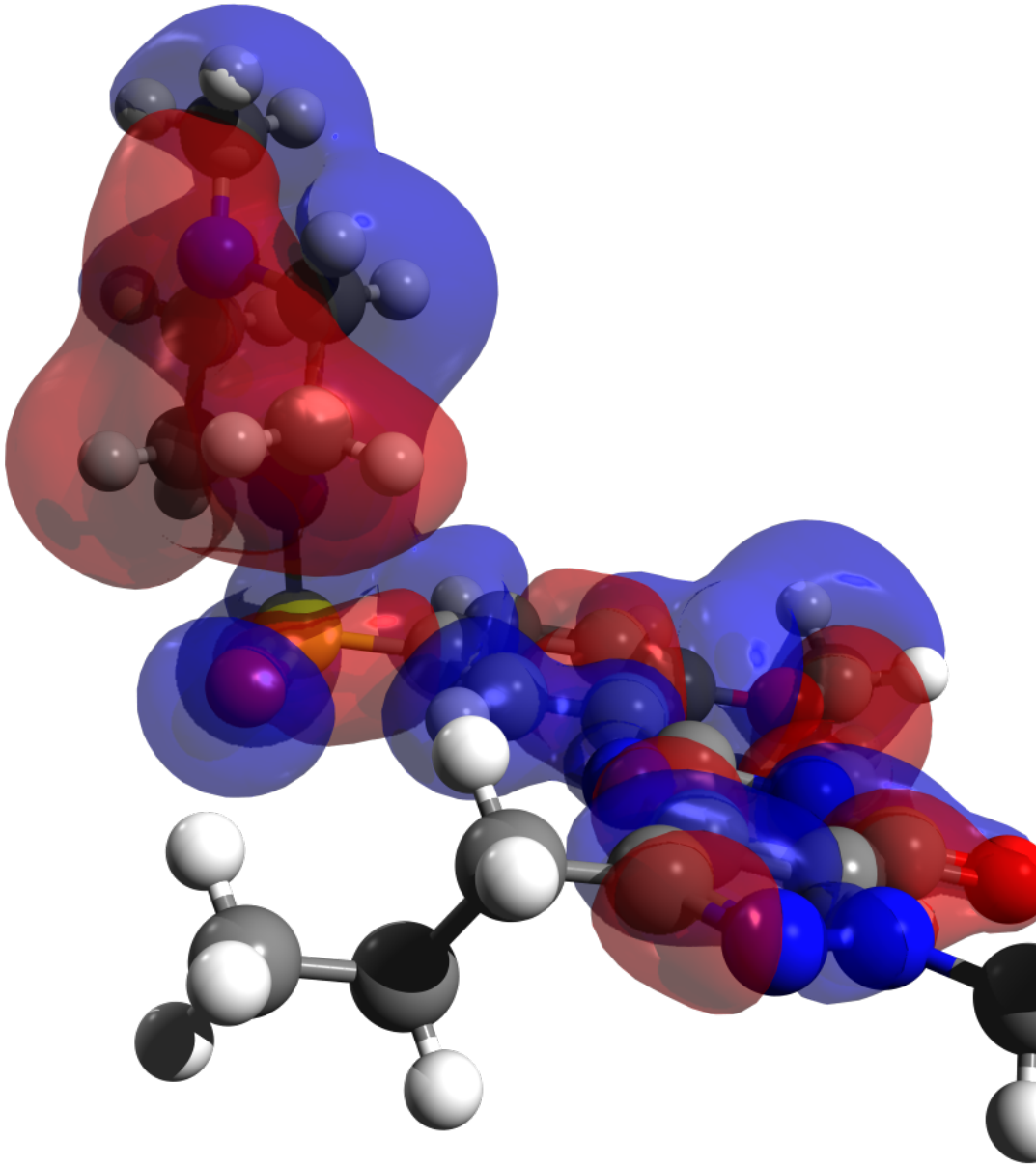
- MO Theory shows us multiple double bonds act as a conduit for electron flow between atoms.
- In Benzene we see a circular pattern of orbitals above and below plane of the carbons.
- In experiment we find each bond has a bond distance corresponding to a 1.5 bond order and we can even detect e-m fields generated by a circular flow of electrons.





Value of MO Theory

- It can provide an exact 3D structure of very complicated structures.
  - Although this requires powerful computation resources, the results are much more accurate than any other theory.
- Even simple MO calculations can show us bond order and magnetic tendencies.
- HOMO-LUMO
  - Identifying the highest occupied and lowest unoccupied orbitals help us understand points of reactivity or vulnerability in molecules.
- The complete MO picture helps us understand how molecules can bend, twist, and allow electrons to flow over their surface.



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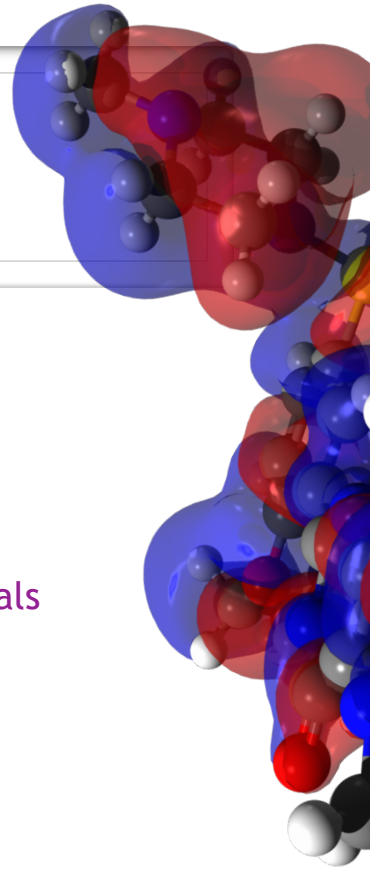

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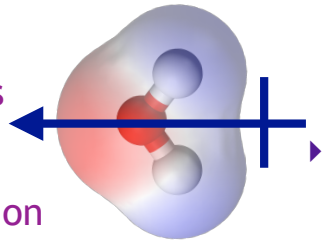

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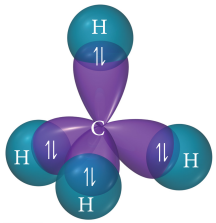

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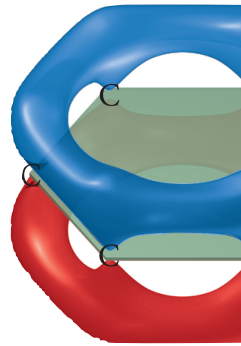

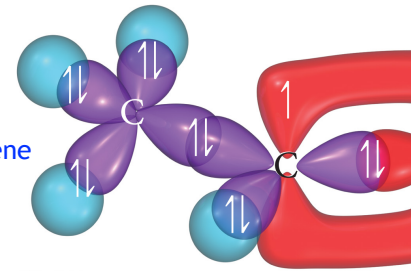

Questions?