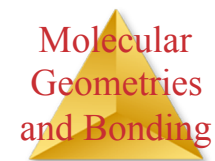


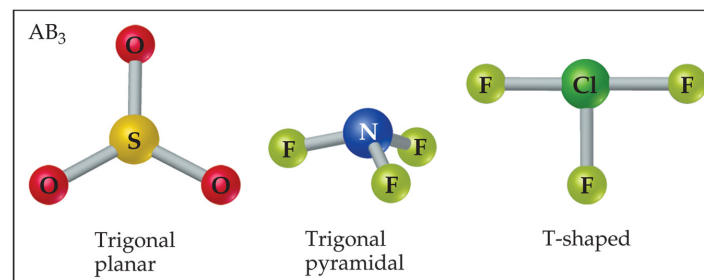
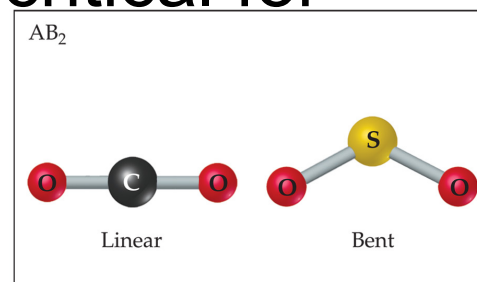
Lecture 22-24

Molecular Geometries and Covalent Bonding Theories

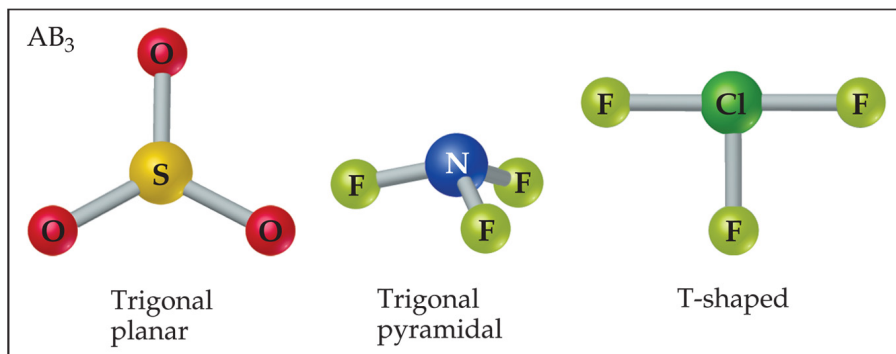
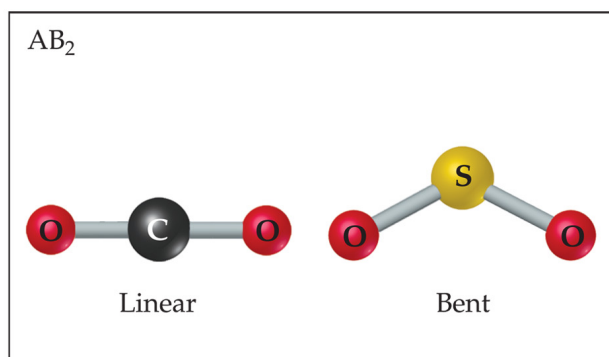


Molecular Shapes

- we've learned to draw Lewis structures and account for all the valence electrons in a molecule.
- But: Lewis structures are two dimensional and molecules are 3 dimensional objects.
- The 3D structure is absolutely critical for understanding molecules.



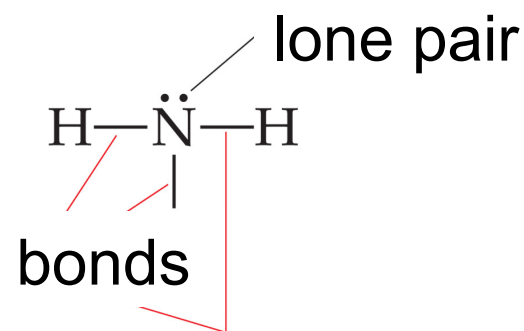
Molecular Shapes



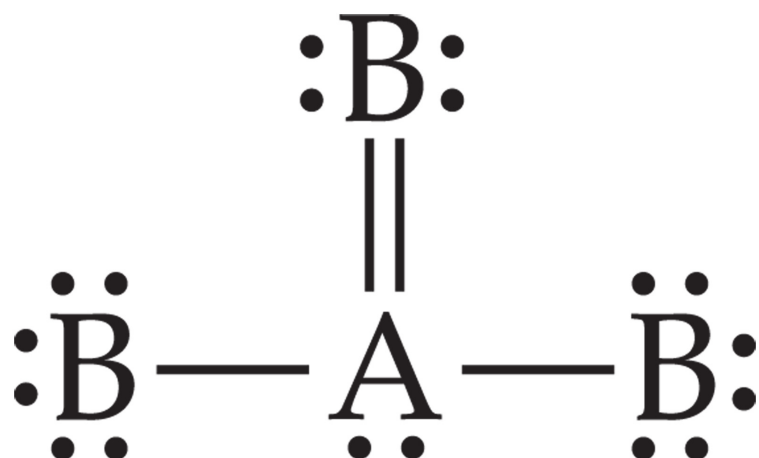
- geometry & shape of molecule critical
- we can easily predict the 3D structure of a molecule just by **adding up:**
 - **bound atoms + lone pairs**

What Determines the Shape of a Molecule?

- atoms and lone pairs take up space and prefer to be as far from each other as possible
- shape can be predicted from simple geometry



“Things”



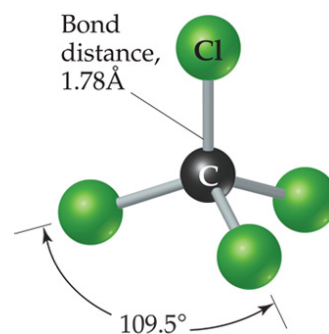
- The central atom has four “things” around it. A “thing” is an atom or a lone pair of electrons.
- # things = atoms plus lone pairs
- ***Equivalent to bonding pairs and nonbonding pairs***

Valence Shell Electron Pair Repulsion Theory (VSEPR)

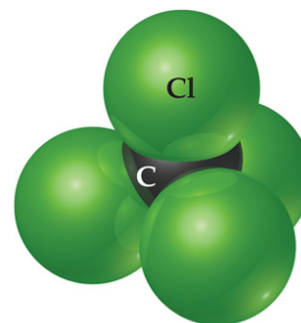
“The best arrangement of a given number of things is the one that minimizes the repulsions among them.”



(a)



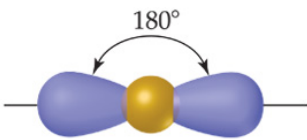
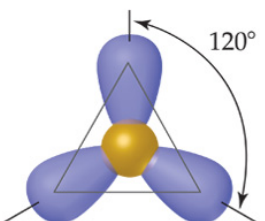
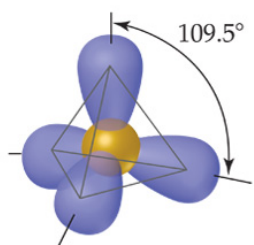
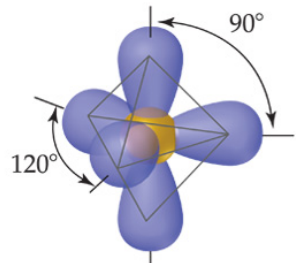
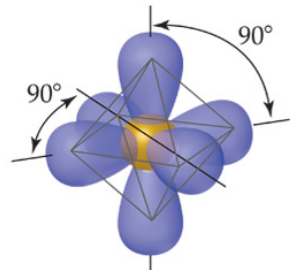
(b)



(c)

number of
things

arrangement bond angles

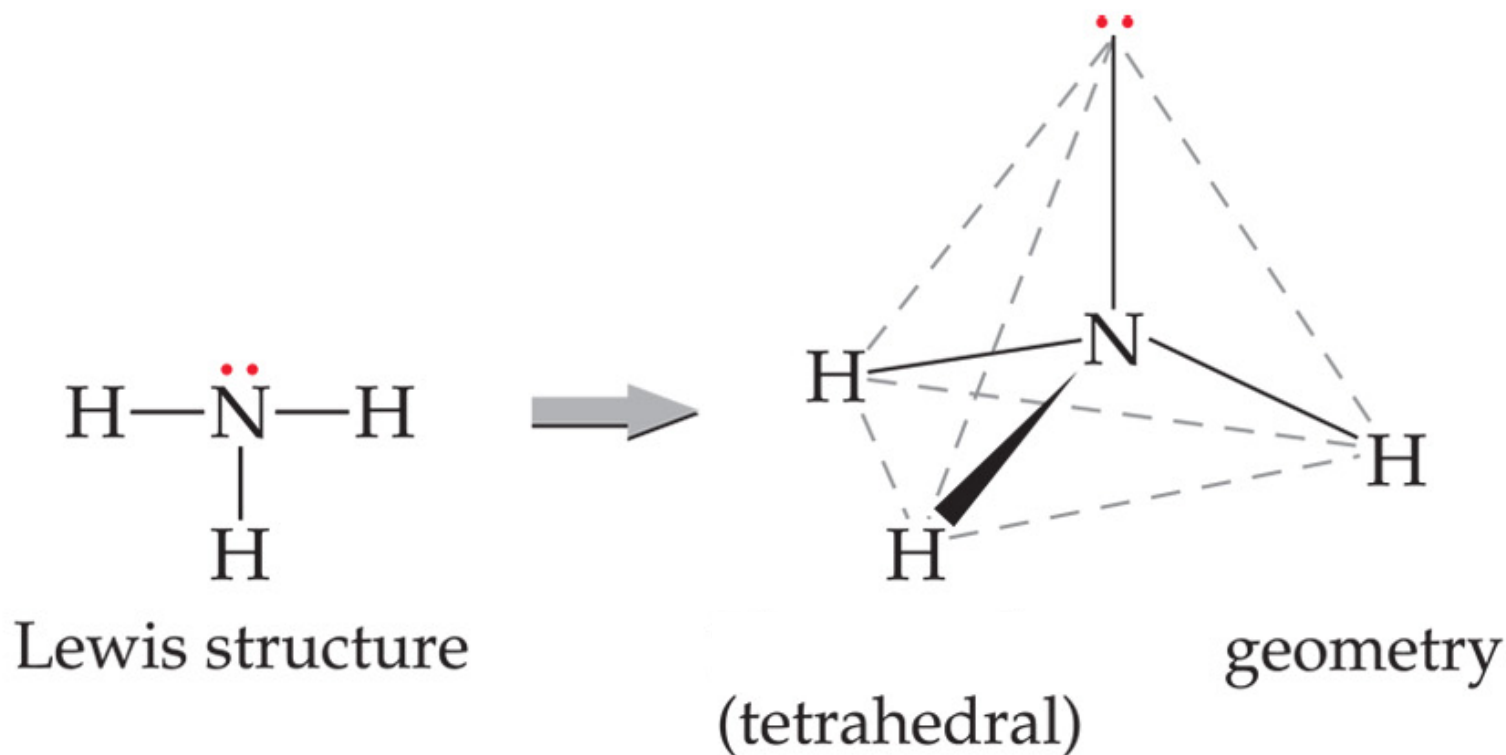
2		Linear	180°
3		Trigonal planar	120°
4		Tetrahedral	109.5°
5		Trigonal bipyramidal	120° 90°
6		Octahedral	90°

Arrangement

These are the
arrangement for two
through six things
around a central atom.

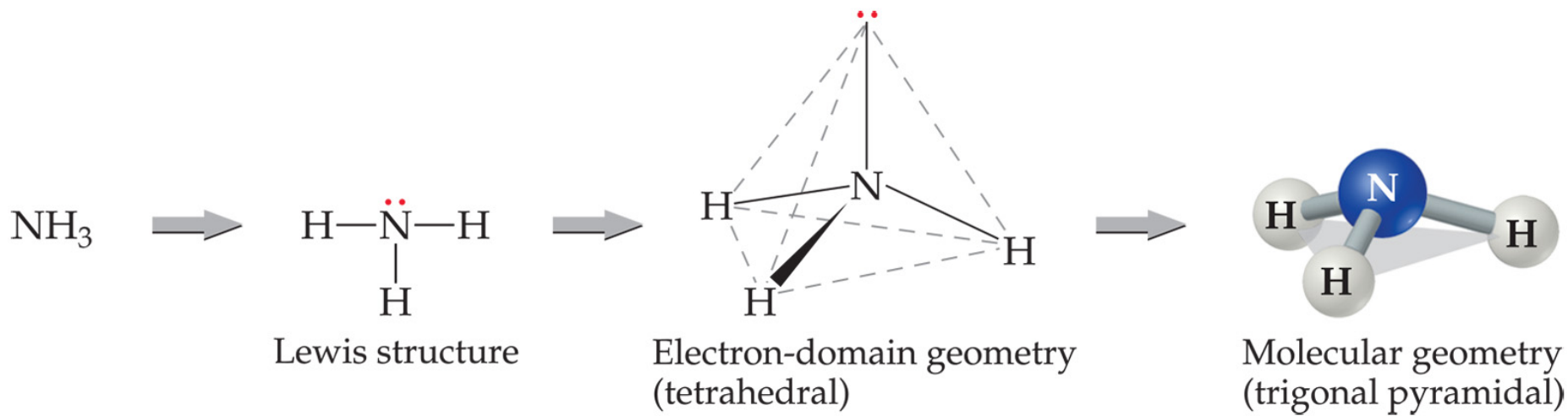
You must learn these!

ARRANGMENTS



- All one must do is count the number of “things” in the Lewis structure.
- The geometry will be that which corresponds to that number of “things.”

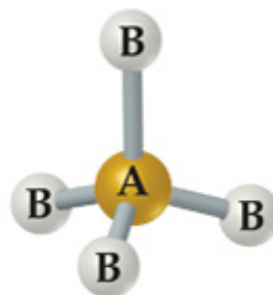
Molecular Arrangements



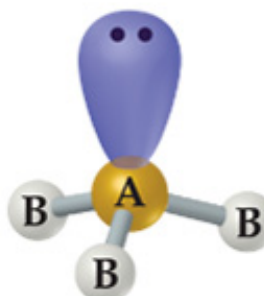
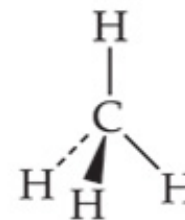
- The geometry is often *not* the shape of the molecule, however.
- The “**shape**” is defined by the positions of **only the atoms in the molecules, not the lone pairs.**

Arrangement vs. shape

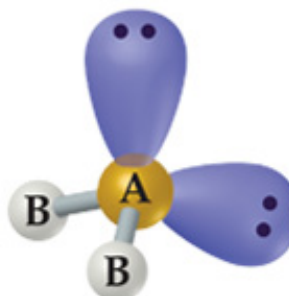
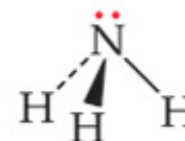
Within each
geometry, there
might be more than
one shape.



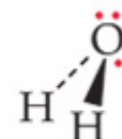
Tetrahedral



Trigonal
pyramidal



Bent



Linear arrangement two things

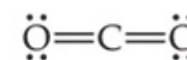
things	geometry	atoms	lone pairs	shape	example
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2



2

0

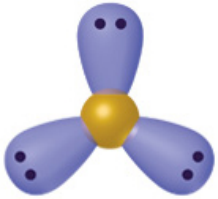
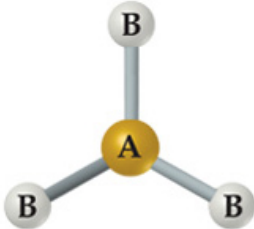
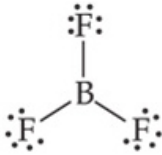
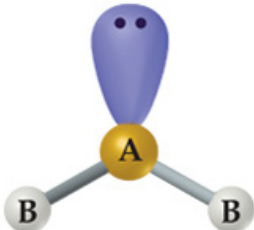
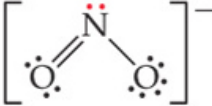


- In this geometry, there is only one molecular geometry: linear.
- NOTE: If there are only two atoms in the molecule, the molecule will be linear no matter what the geometry is.

Trigonal Planar arrangement

3 things

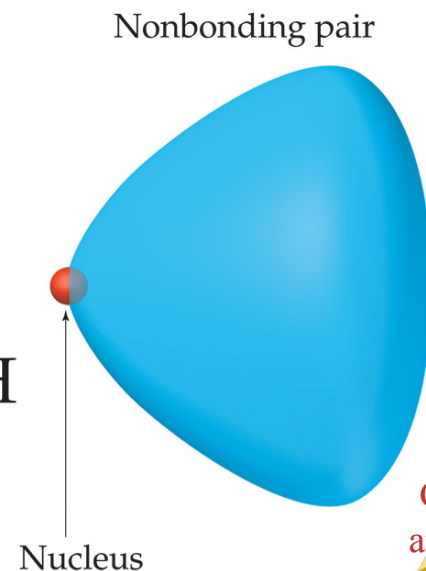
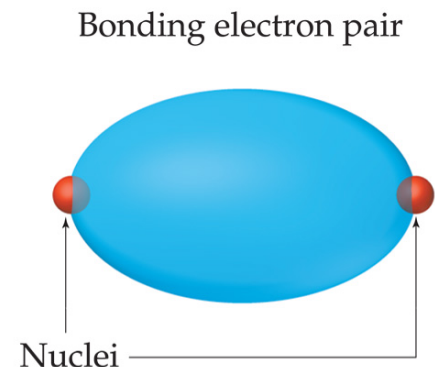
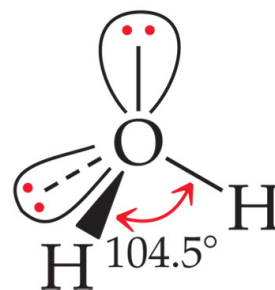
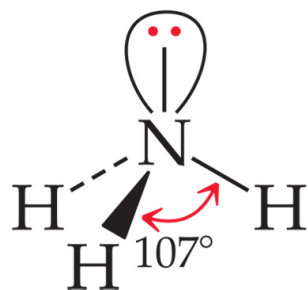
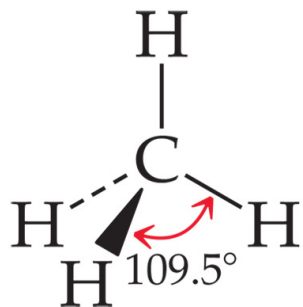
things	geometry	atoms	lone pairs	shape	example
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3		3	0		
	Trigonal planar			Trigonal planar	
		2	1		
				Bent	

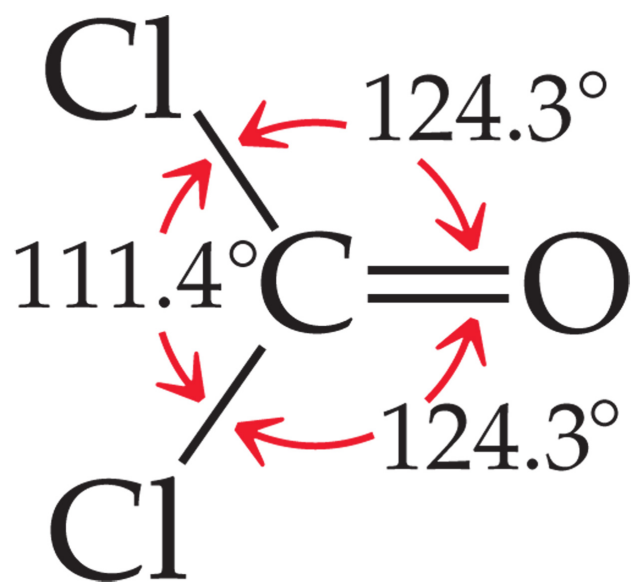
- There are two molecular geometries:
 - Trigonal planar, if there are no lone pairs
 - Bent, if there is a lone pair.

Lone pairs and Bond Angle

- Lone pairs are physically larger than atoms.
- Therefore, their repulsions are greater; this tends to decrease bond angles in a molecule.



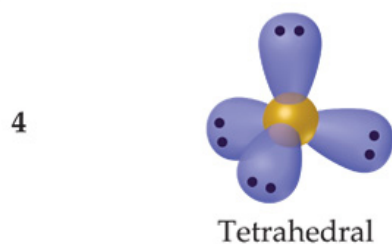
Multiple Bonds and Bond Angles



- Double and triple bonds place greater electron density on one side of the central atom than do single bonds.
- Therefore, they also affect bond angles.

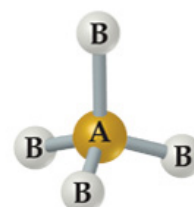
Tetrahedral arrangement 4 things

Things geometry atoms lone pairs shape example

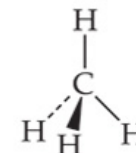


4

0

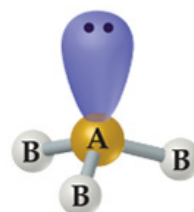


Tetrahedral

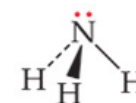


3

1

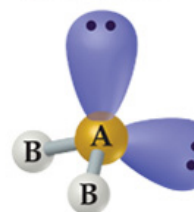


Trigonal
pyramidal

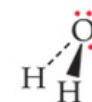


2

2



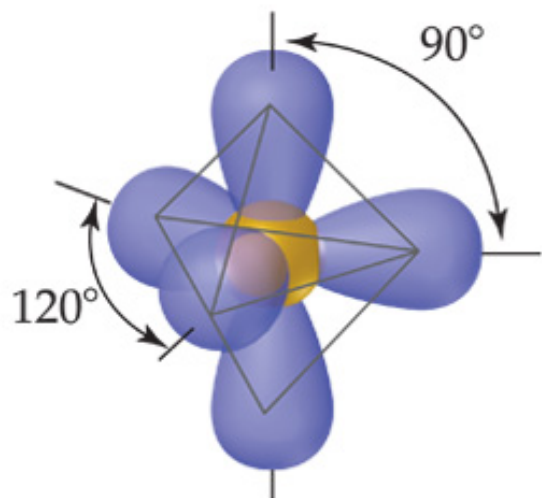
Bent



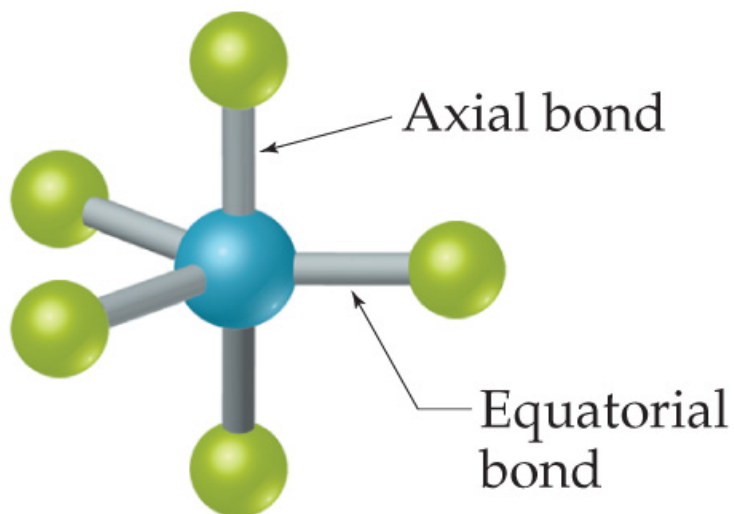
- There are three molecular geometries:
 - Tetrahedral, if no lone pairs
 - Trigonal pyramidal if one is a lone pair
 - Bent if there are two lone pairs

Trigonal Bipyramidal arrangement

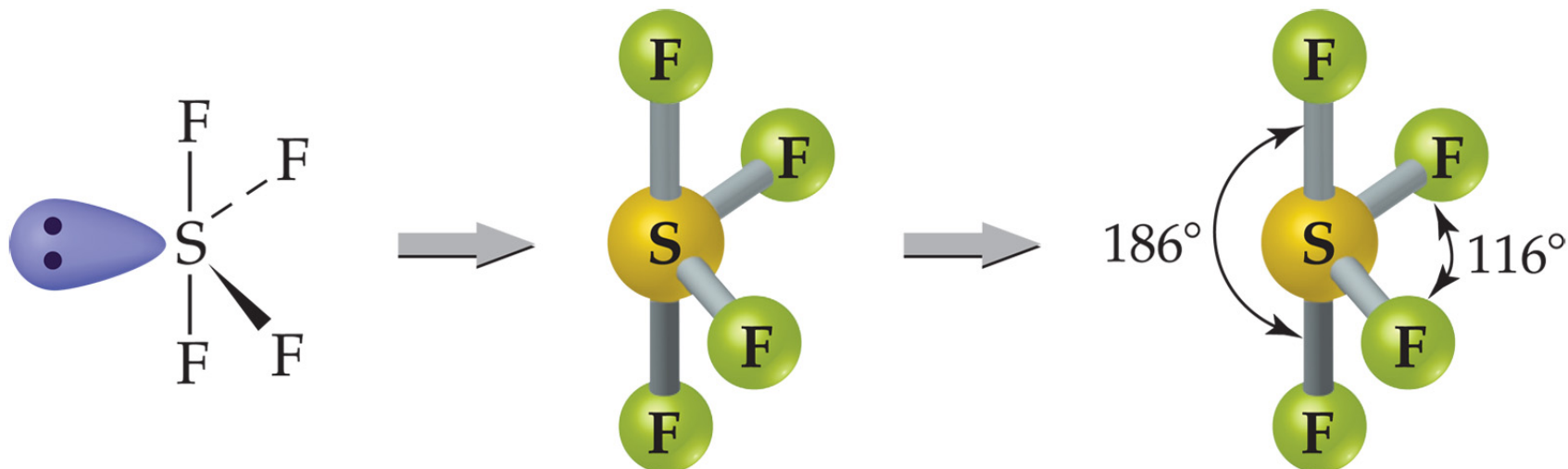
5 things



- There are two distinct positions in this geometry:
 - Axial
 - Equatorial



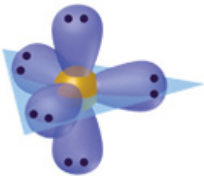
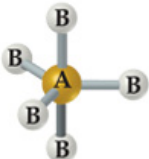
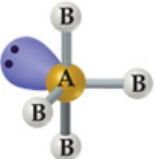
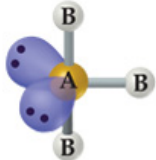
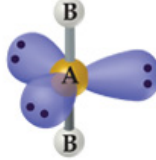
Trigonal Bipyramidal arrangement



Lower-energy conformations result from having lone pairs in equatorial, rather than axial, positions in this geometry.

Trigonal Bipyramidal arrangement

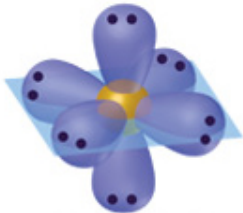

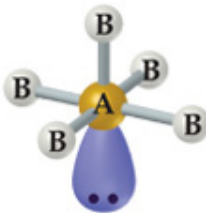
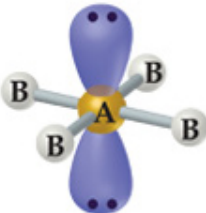
Things geometry atoms lone pairs shape example

5		5	0		PCl ₅
	Trigonal bipyramidal			Trigonal bipyramidal	
		4	1		SF ₄
				Seesaw	
		3	2		ClF ₃
				T-shaped	
		2	3		XeF ₂
				Linear	

- There are four distinct molecular geometries in this domain:

- Trigonal bipyramidal
- Seesaw
- T-shaped
- Linear

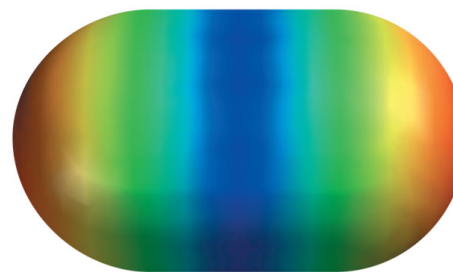
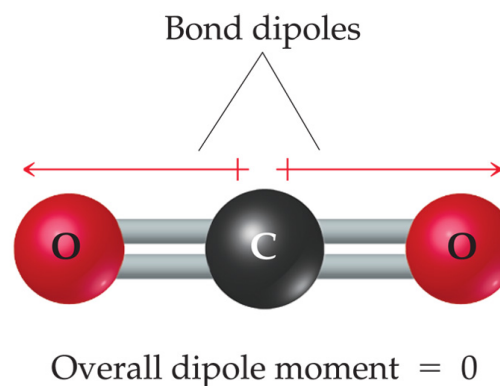
Octahedral arrangement 6 things

Things	geometry	atoms	lone pairs	shape	example
6	 Octahedral	6	0	 Octahedral	SF_6
		5	1	 Square pyramidal	BrF_5
		4	2	 Square planar	XeF_4

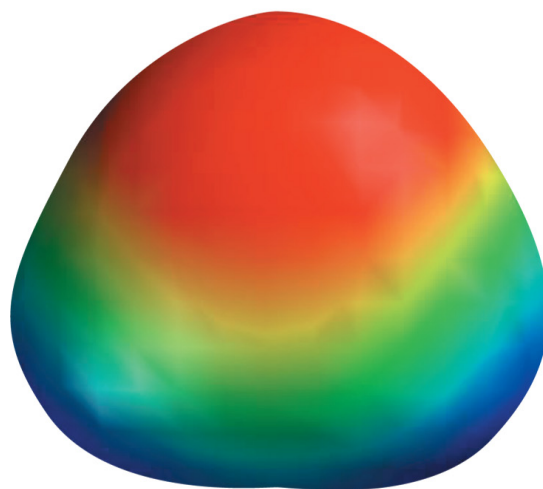
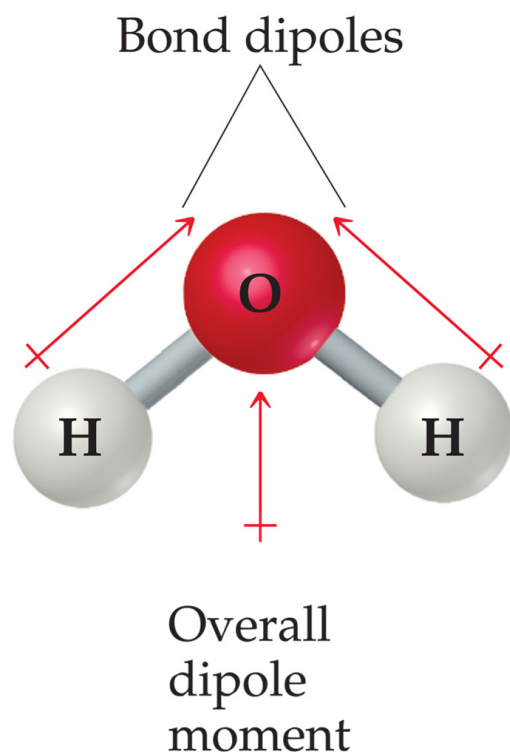
- All positions are equivalent in the octahedral domain.
- There are three molecular geometries:

Polarity

- In Chapter 8 we discussed bond dipoles.
- polar bonds versus polar molecules. We must think about the molecule as a whole.



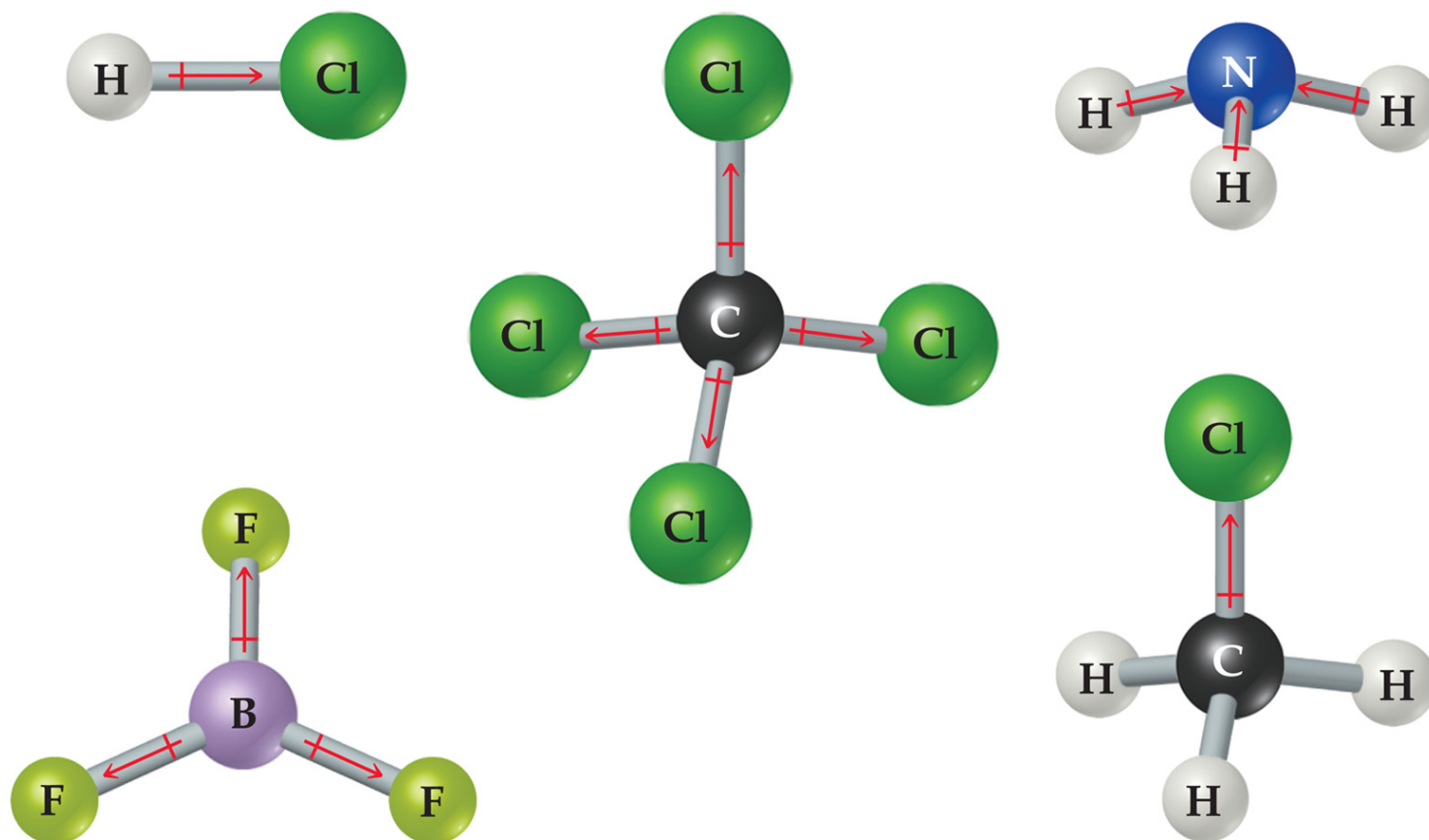
Polarity



By adding the individual bond dipoles, one can determine the overall dipole moment for the molecule.

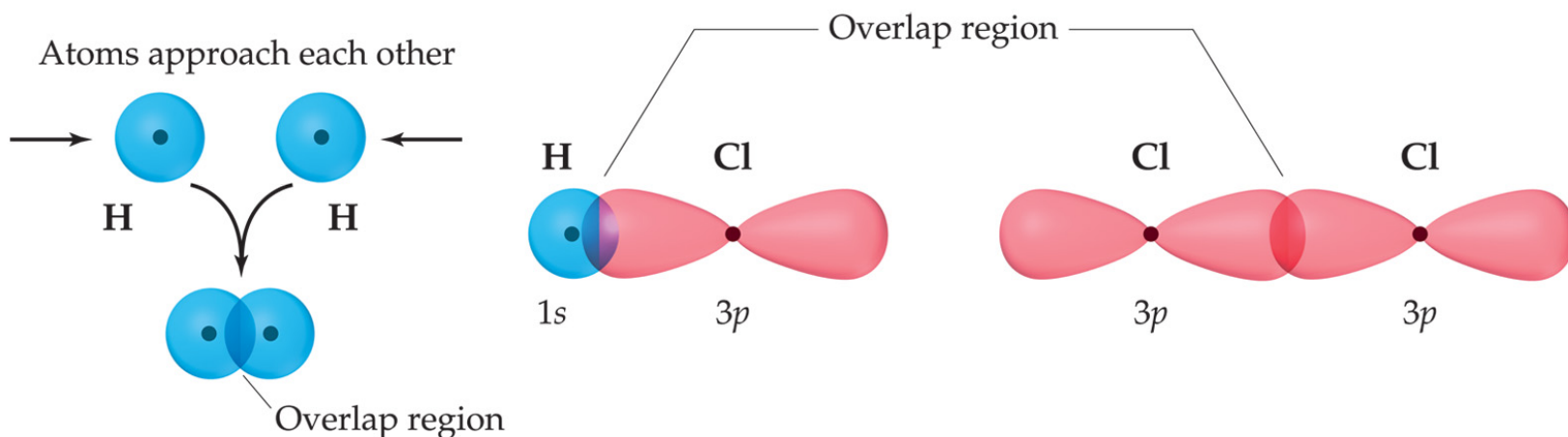
Polarity

“The tractor pull”



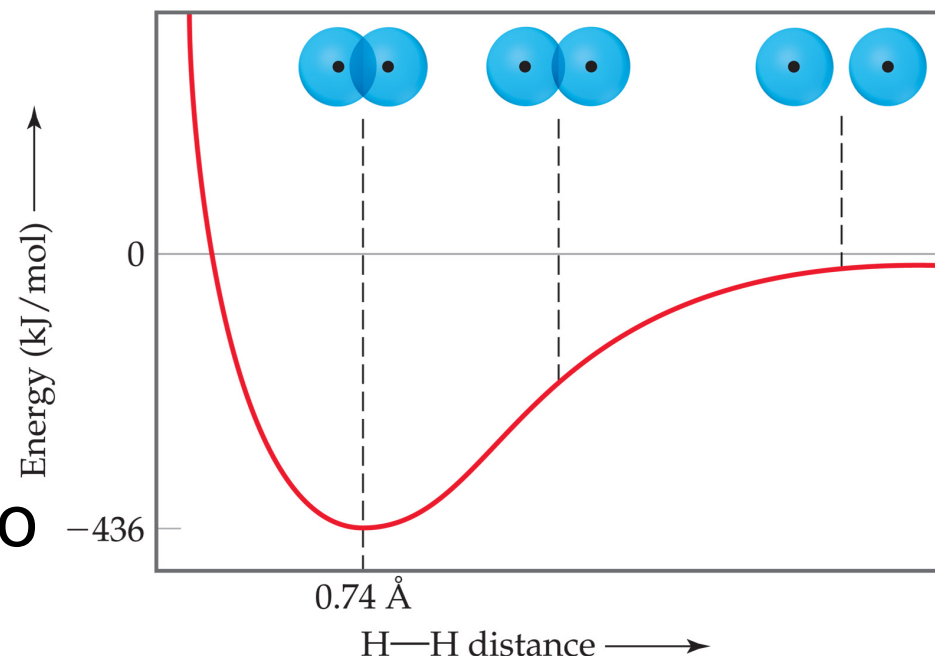
Overlap and Bonding

- covalent bonds form when electrons are “shared.”
- But how, when the electrons are in these atomic orbitals? Do atomic orbitals overlap?
- Yes.

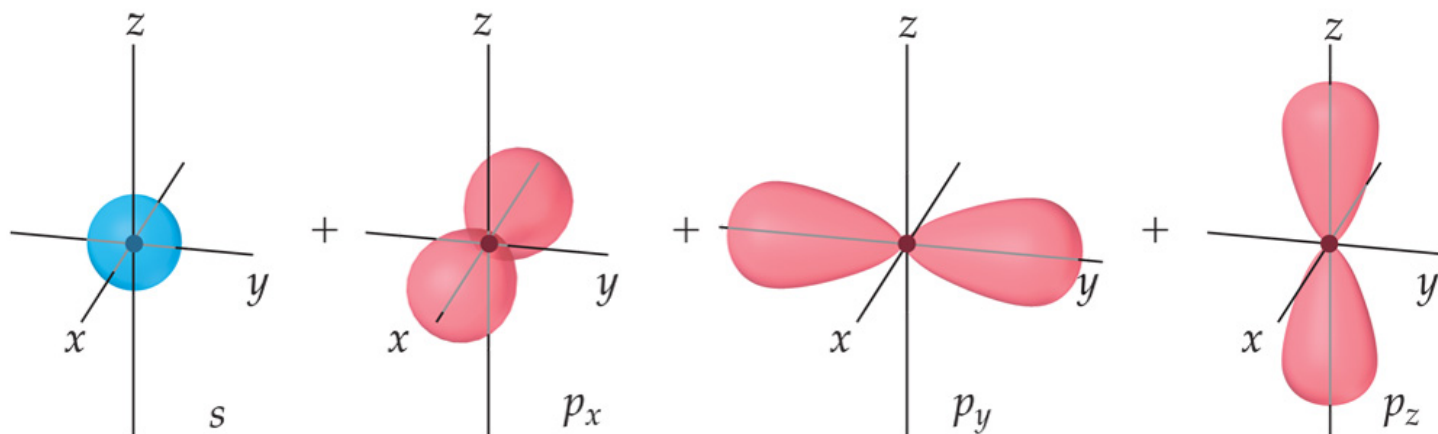


Overlap and Bonding

- Increased overlap brings the electrons and nuclei closer together while simultaneously decreasing electron-electron repulsion.
- However, if atoms get too close, the internuclear repulsion greatly raises the energy.



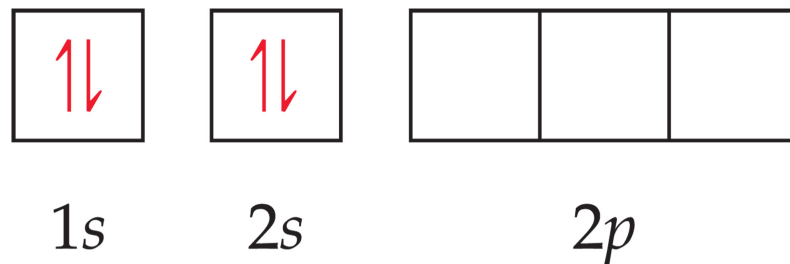
Hybrid Orbitals



But how do you get tetrahedral, trigonal bipyramidal, and other geometries when the atomic orbitals seem to be at right angles from each other all the time?

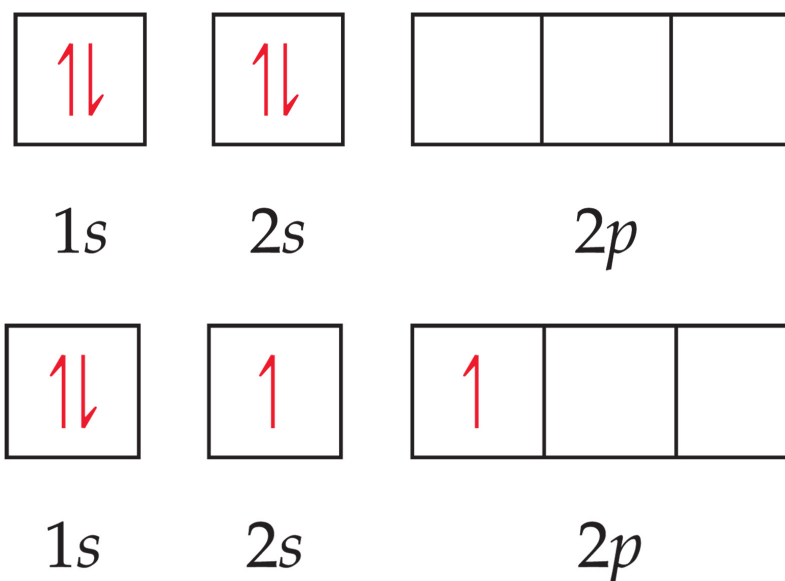
Hybrid Orbitals

- Consider beryllium:
 - In its ground electronic state, it would not be able to form bonds because it has no singly-occupied orbitals.



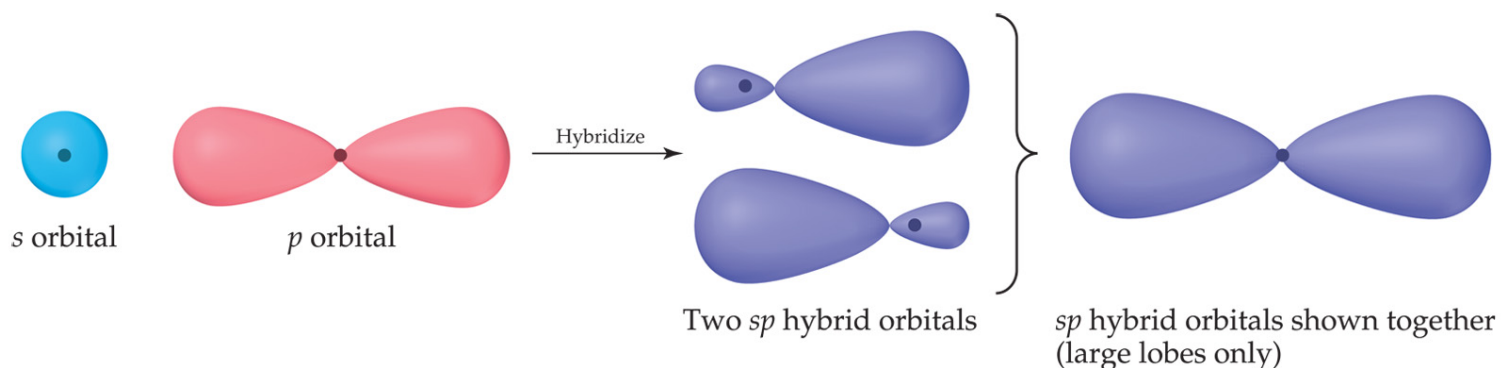
Hybrid Orbitals

But if it absorbs the small amount of energy needed to promote an electron from the $2s$ to the $2p$ orbital, it can form two bonds.



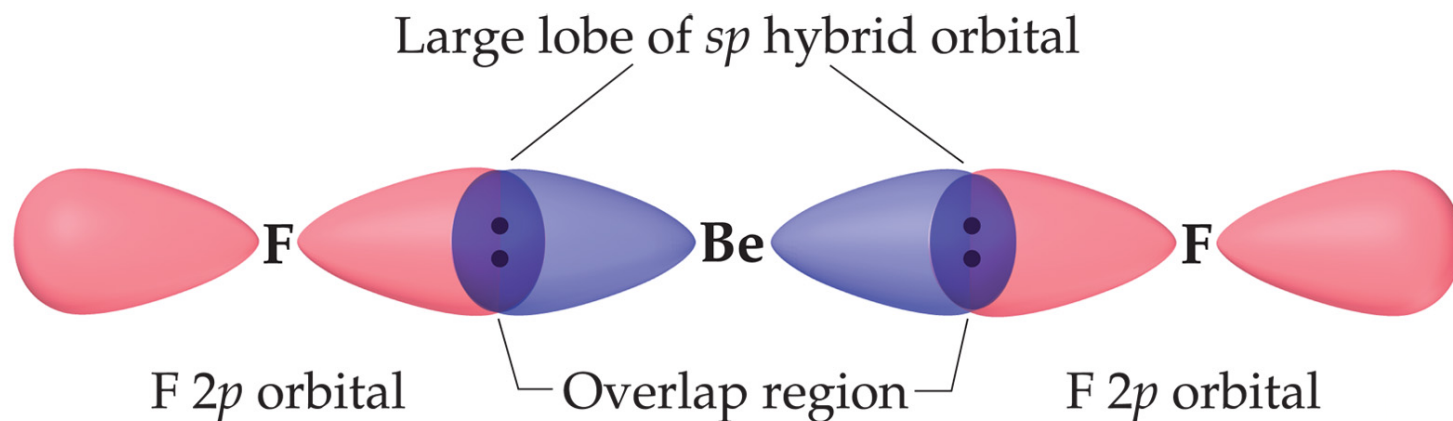
Hybrid Orbitals

- Mixing the s and p orbitals yields two degenerate orbitals that are hybrids of the two orbitals.
 - These sp hybrid orbitals have two lobes like a p orbital.
 - One of the lobes is larger and more rounded as is the s orbital.

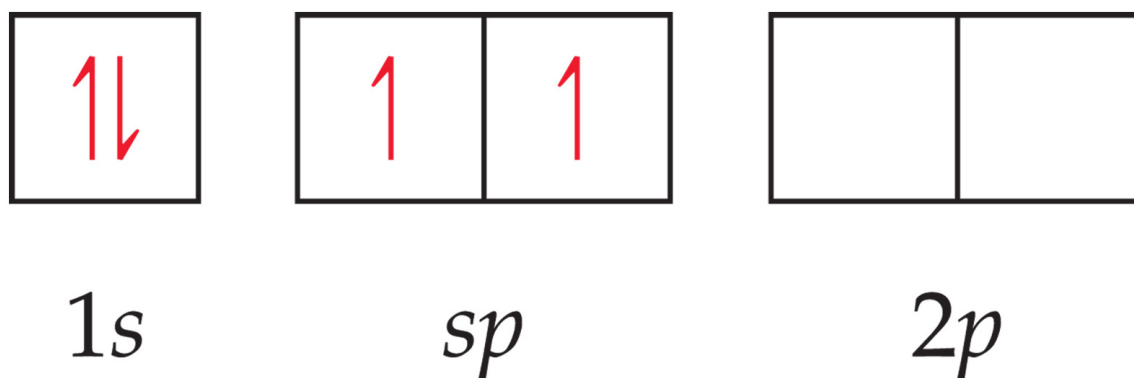


Hybrid Orbitals

- These two degenerate orbitals would align themselves 180° from each other.
- This is consistent with the observed geometry of beryllium compounds: linear.



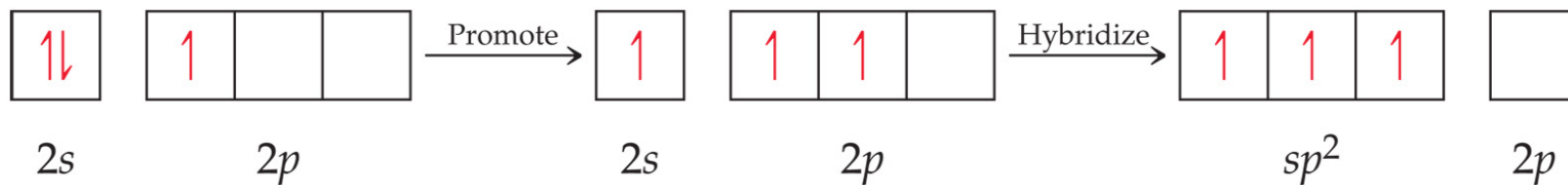
Hybrid Orbitals



- With hybrid orbitals the orbital diagram for beryllium would look like this.
- The sp orbitals are higher in energy than the $1s$ orbital but lower than the $2p$.

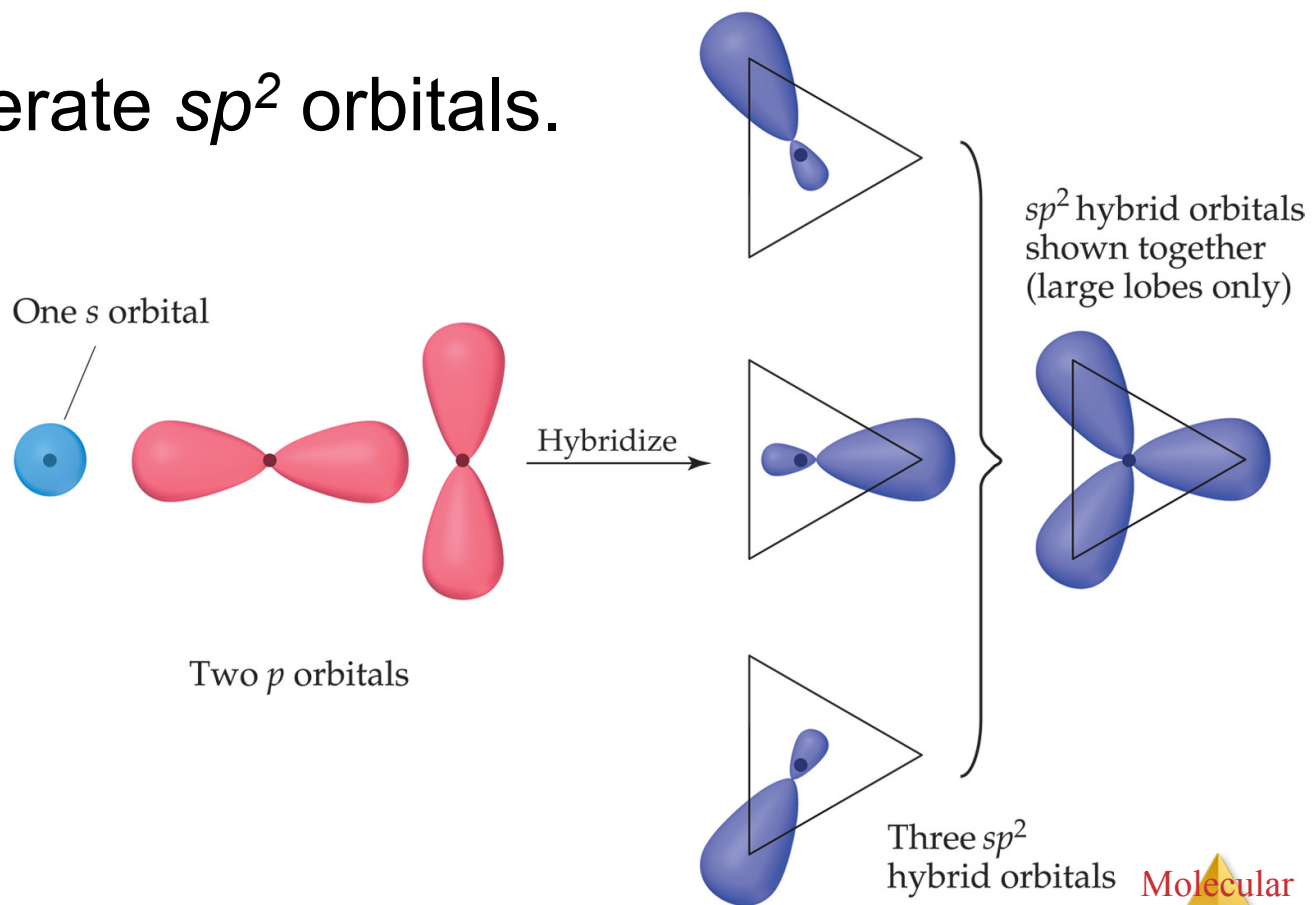
Hybrid Orbitals

Using a similar model for boron leads to...



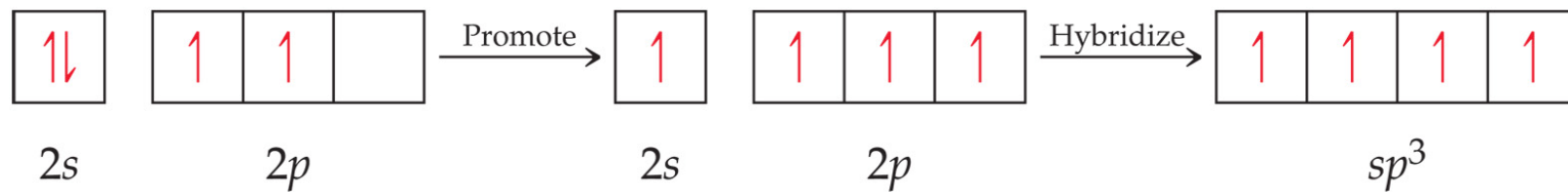
Hybrid Orbitals

...three degenerate sp^2 orbitals.



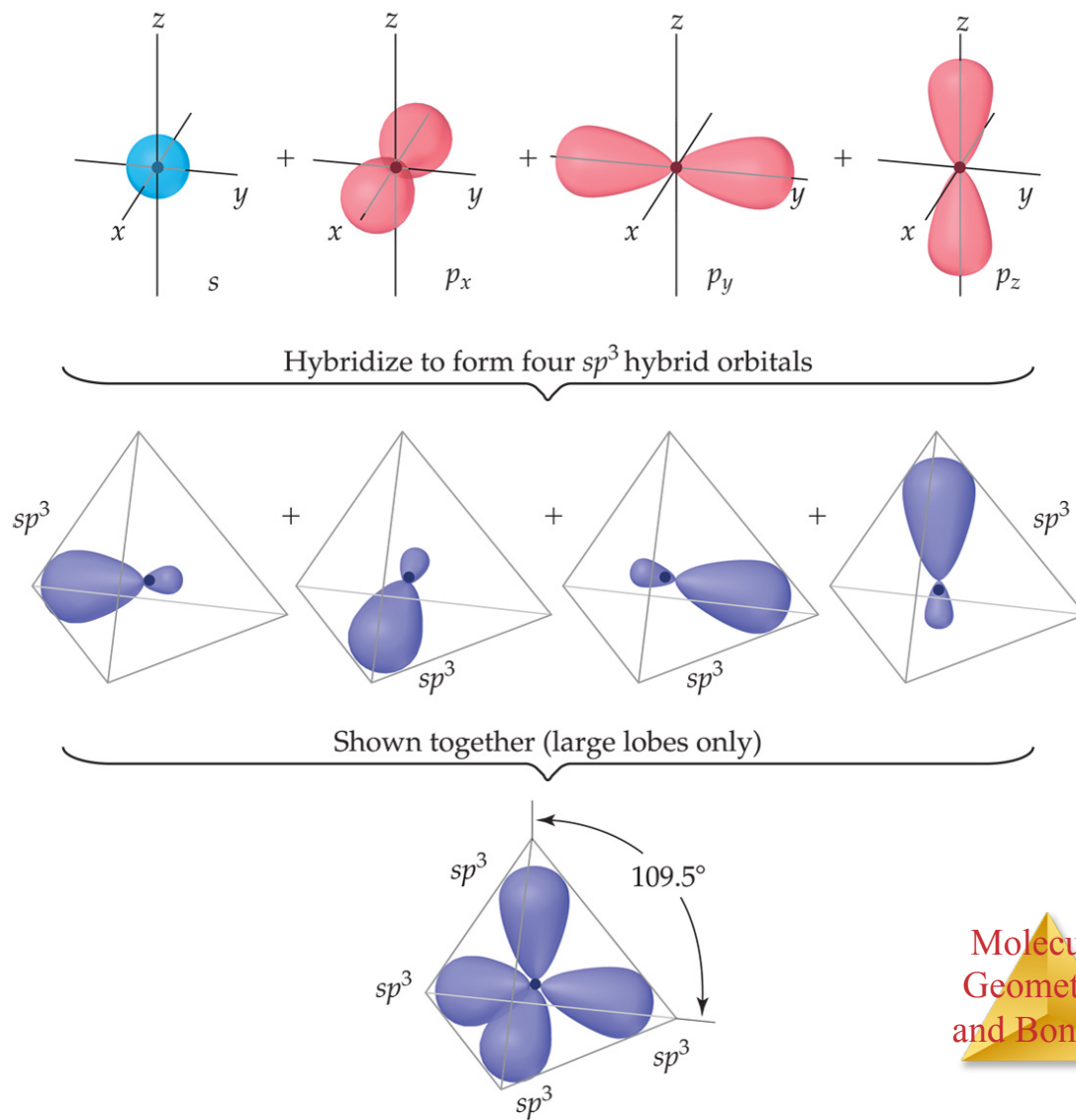
Hybrid Orbitals

With carbon we get...



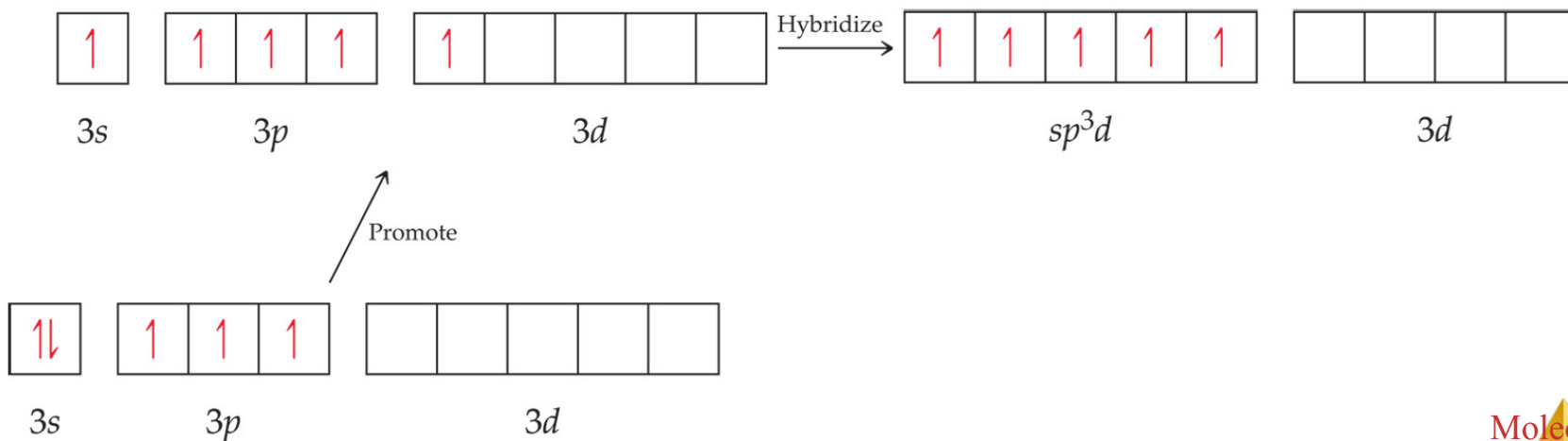
Hybrid Orbitals

...four degenerate sp^3 orbitals.

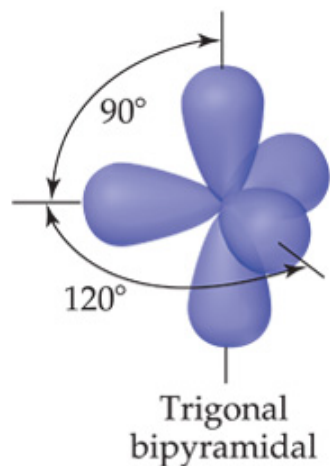


Hybrid Orbitals

For geometries involving expanded octets on the central atom, we must use *d* orbitals in our hybrids.



Hybrid Orbitals

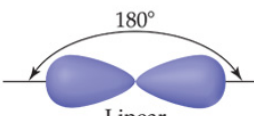
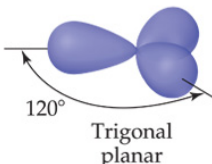
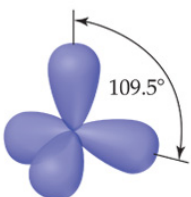
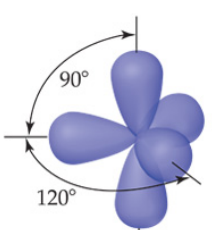
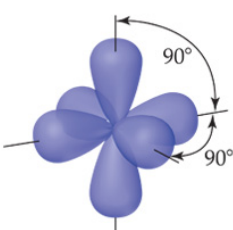


This leads to five degenerate sp^3d orbitals...

...or six degenerate sp^3d^2 orbitals.

Hybrid Orbitals

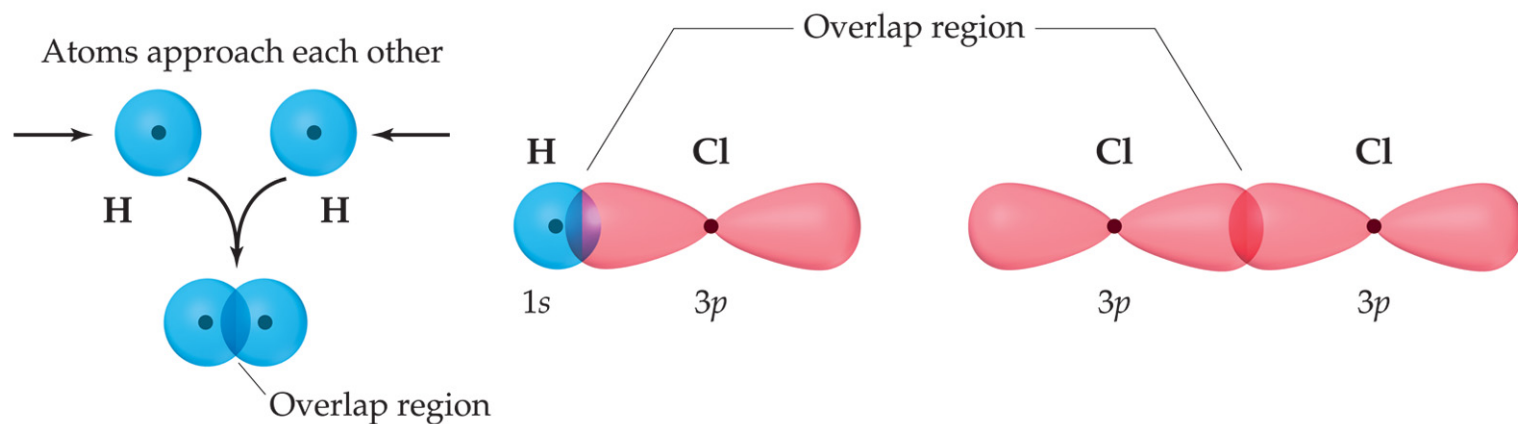
Once you know the number of things around an atom, you know the hybridization state of the atom if you can count letters up to six.

Atomic Orbital Set	Hybrid Orbital Set	Geometry	Examples
s, p	Two sp	 Linear	$\text{BeF}_2, \text{HgCl}_2$
s, p, p	Three sp^2	 Trigonal planar	BF_3, SO_3
s, p, p, p	Four sp^3	 Tetrahedral	$\text{CH}_4, \text{NH}_3, \text{H}_2\text{O}, \text{NH}_4^+$
s, p, p, p, d	Five sp^3d	 Trigonal bipyramidal	$\text{PF}_5, \text{SF}_4, \text{BrF}_3$
s, p, p, p, d, d	Six sp^3d^2	 Octahedral	$\text{SF}_6, \text{ClF}_5, \text{XeF}_4, \text{PF}_6^-$

Valence Bond Theory

- Hybridization is a major player in this approach to bonding.
- There are two ways orbitals can overlap to form bonds between atoms.

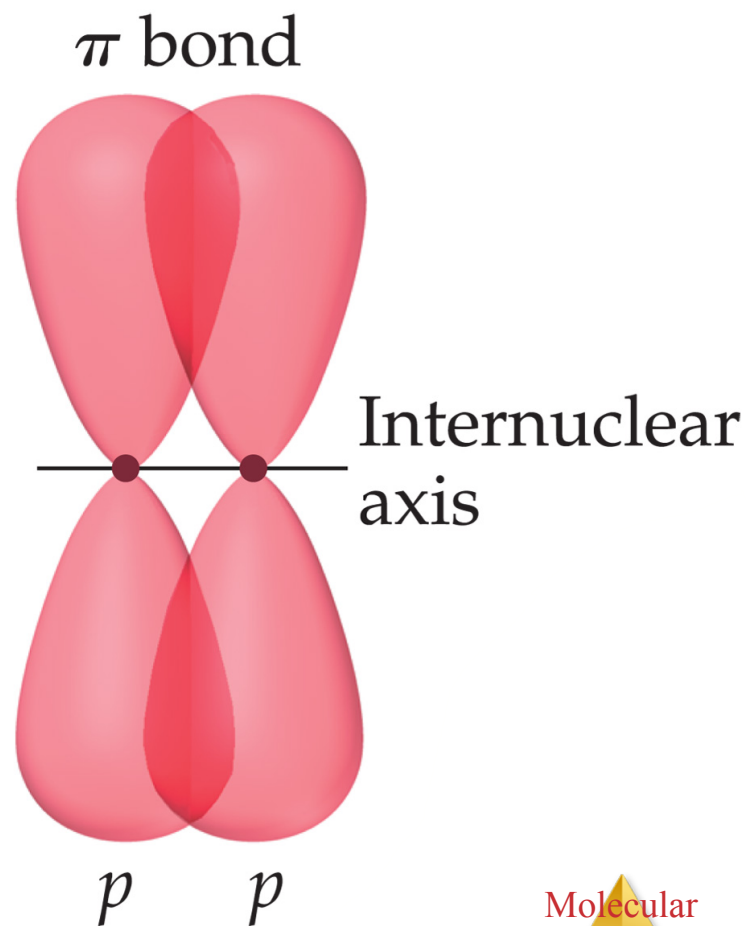
Sigma (σ) Bonds



- Sigma bonds are characterized by
 - Head-to-head overlap.
 - Cylindrical symmetry of electron density about the internuclear axis.

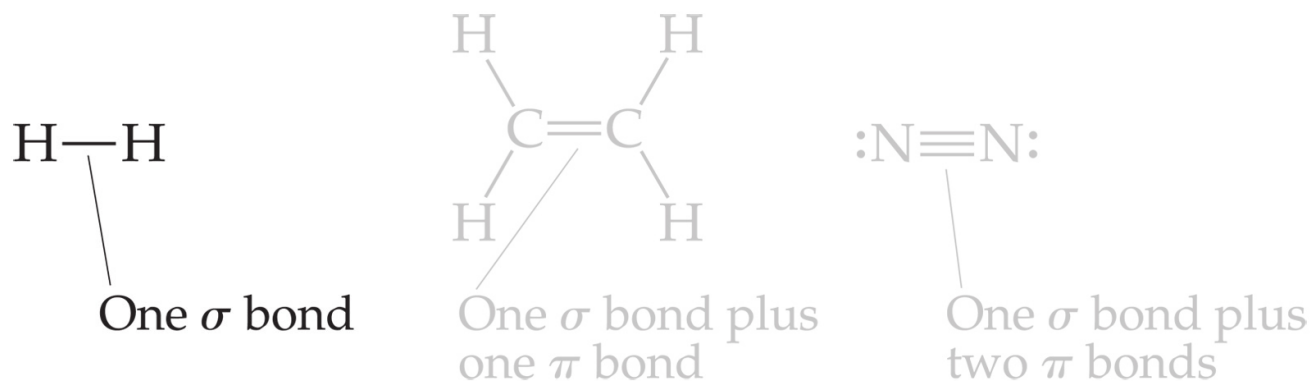
Pi (π) Bonds

- Pi bonds are characterized by
 - Side-to-side overlap.
 - Electron density above and below the internuclear axis.



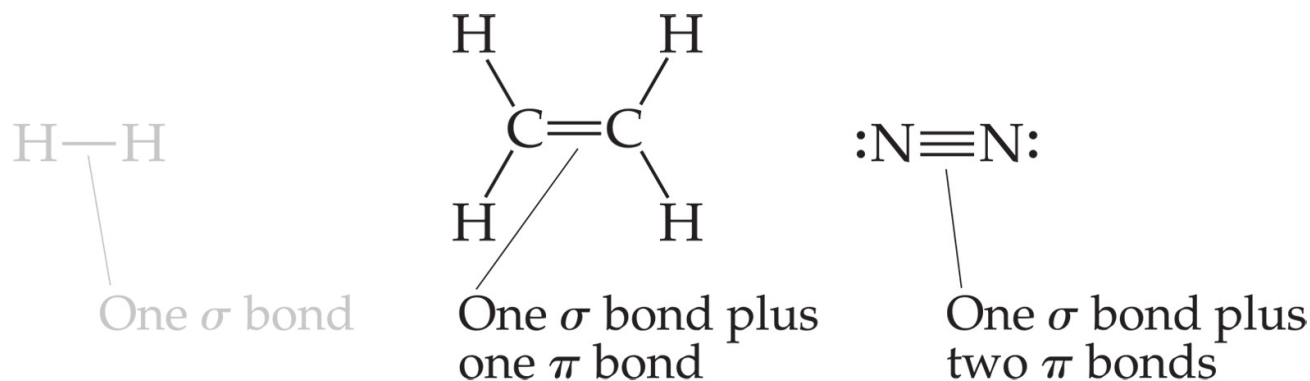
Single Bonds

Single bonds are always σ bonds, because σ overlap is greater, resulting in a stronger bond and more energy lowering.

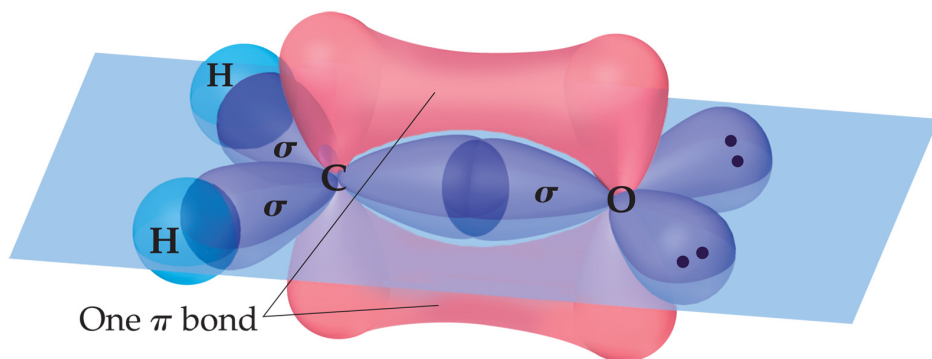
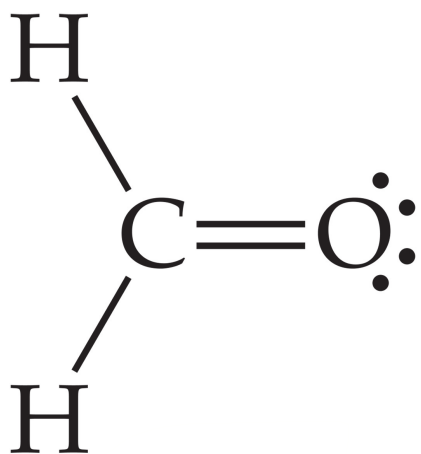


Multiple Bonds

In a multiple bond one of the bonds is a σ bond and the rest are π bonds.



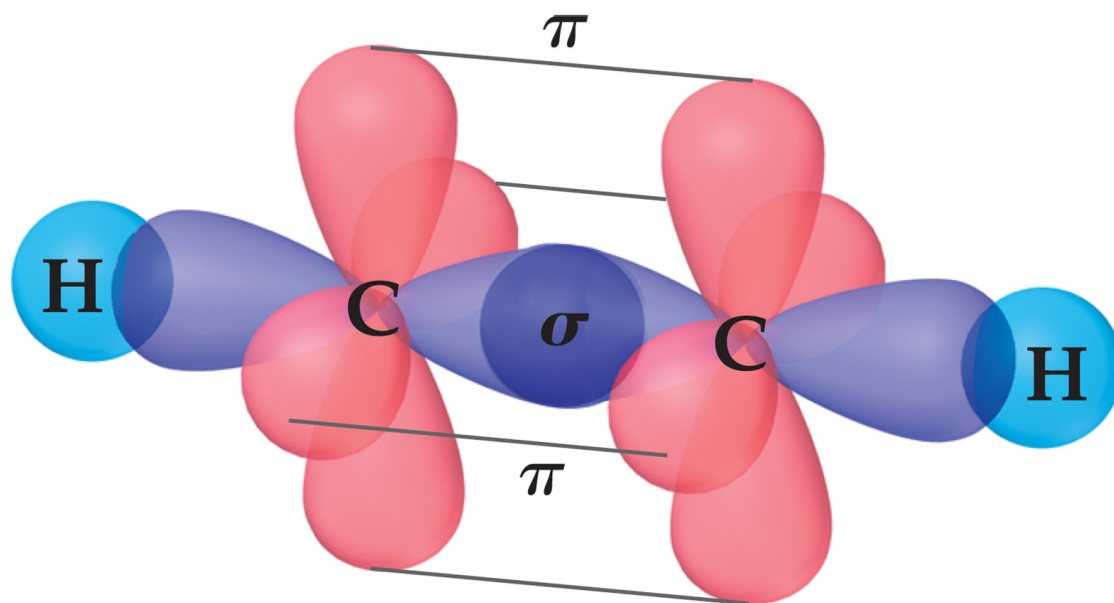
Multiple Bonds



- Example:
formaldehyde an sp^2 orbital on carbon overlaps in σ fashion with the corresponding orbital on the oxygen.
- The unhybridized p orbitals overlap in π fashion.

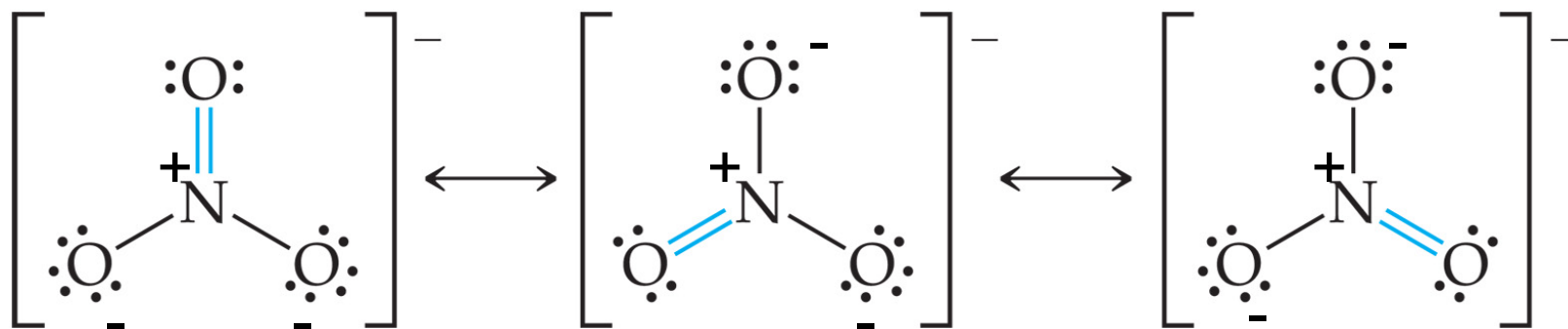
Multiple Bonds

In triple bonds, as in acetylene, two sp orbitals form a σ bond between the carbons, and two pairs of p orbitals overlap in π fashion to form the two π bonds.

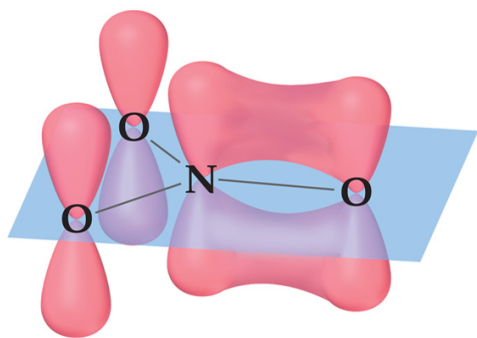


Delocalized Electrons: Resonance

When writing Lewis structures for species like the nitrate ion, we draw resonance structures to more accurately reflect the structure of the molecule or ion.

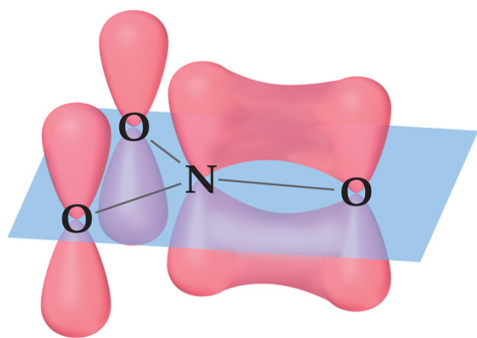


Delocalized Electrons: Resonance

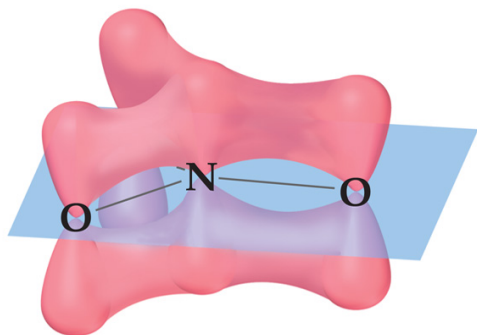


- each of the four atoms in the nitrate ion has a p orbital.
- The p orbitals on all three oxygens overlap with the p orbital on the central nitrogen.

Delocalized Electrons: Resonance

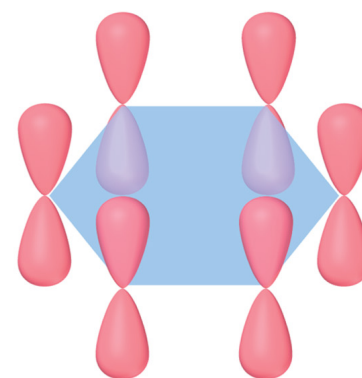
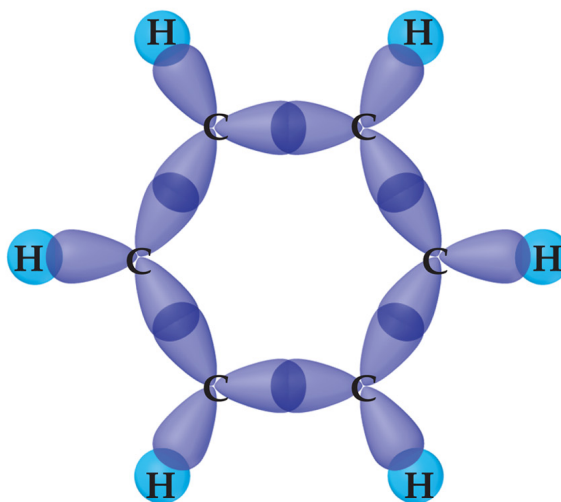
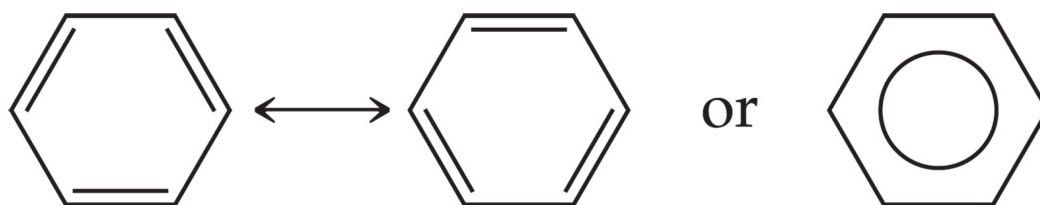


This means the π electrons are not localized between the nitrogen and one of the oxygens, but rather are **delocalized** throughout the ion.



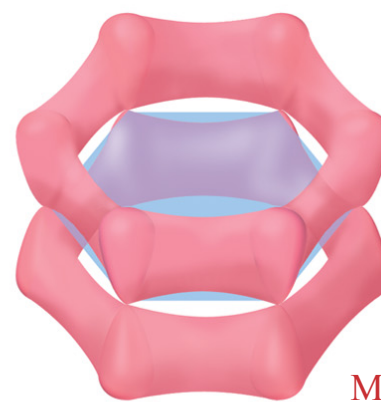
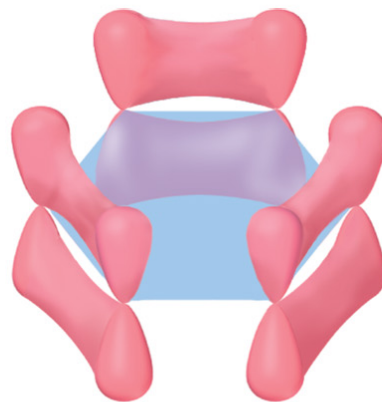
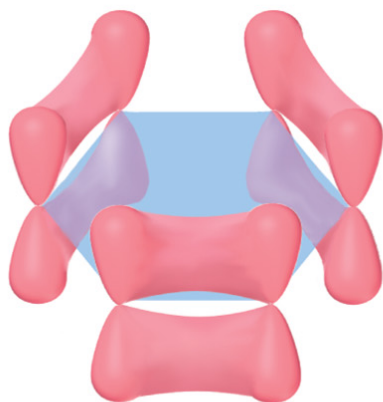
Resonance

The organic molecule benzene has six σ bonds and a p orbital on each carbon atom.



Resonance

- In reality the π electrons in benzene are not localized, but delocalized.
- The even distribution of the π electrons in benzene makes the molecule unusually stable.



Valence bond theory

- Hybridization to explain geometry.
- What orbitals are involved in multiple bonds?
- Delocalization and resonance.

Orbitals in Molecules

- **Molecular orbital theory**, another way to look at bonding.
- We will only, briefly look at diatomic molecules:

Orbitals in Molecules

- In MO theory, you combine atomic orbitals from each atom. For orbitals to combine:
 - Energy must be similar
 - Orbitals must overlap.
 - Orbitals must have the same symmetry

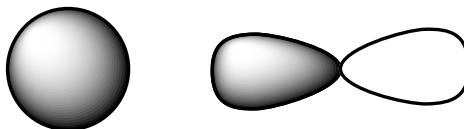
Orbitals in Molecules

- What atomic orbitals can combine to form sigma (σ) bonds?

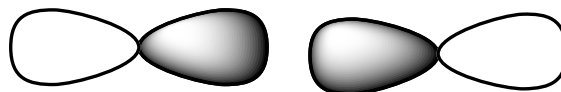
s + s



s + p



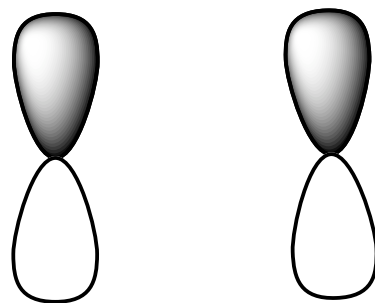
p + p



Orbitals in Molecules

- What atomic orbitals can combine to form pi (π) bonds?

p + p



p + d

