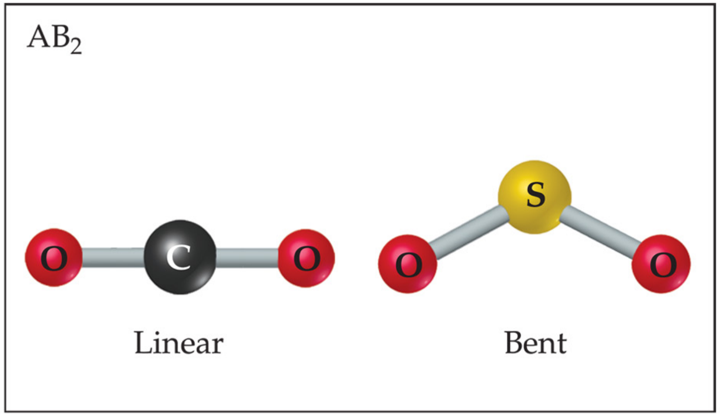
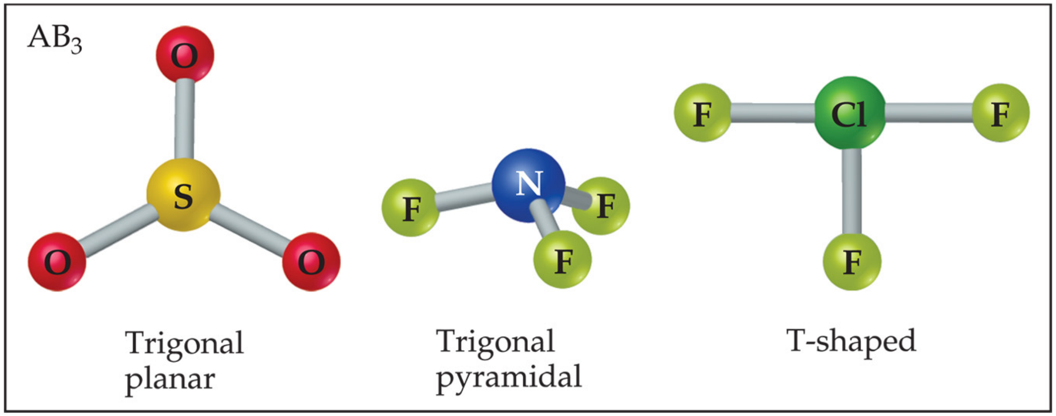
Chapter 9
Molecular Geometries and Bonding Theories

Molecular Shapes

- Lewis structures 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

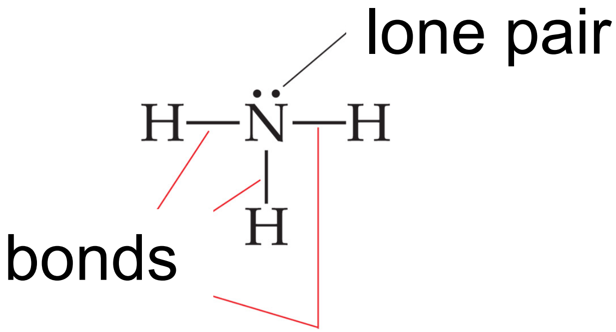




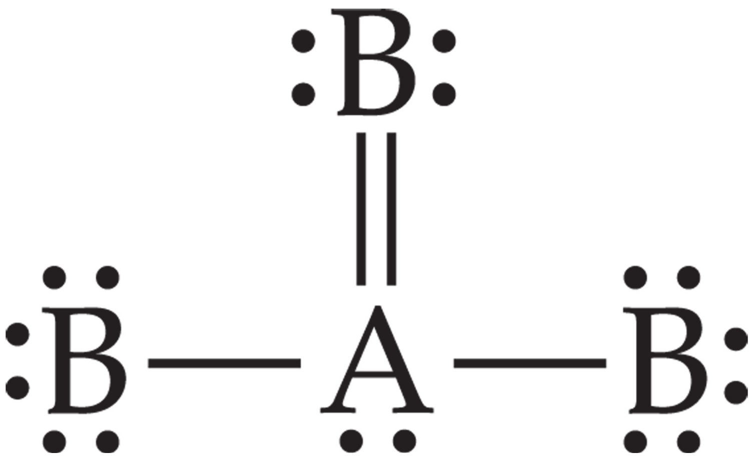
- geometry & shape of molecule critical
- we can easily predict the 3D structure of a molecule just by **adding up:**
- **bound atoms + lone pairs**

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



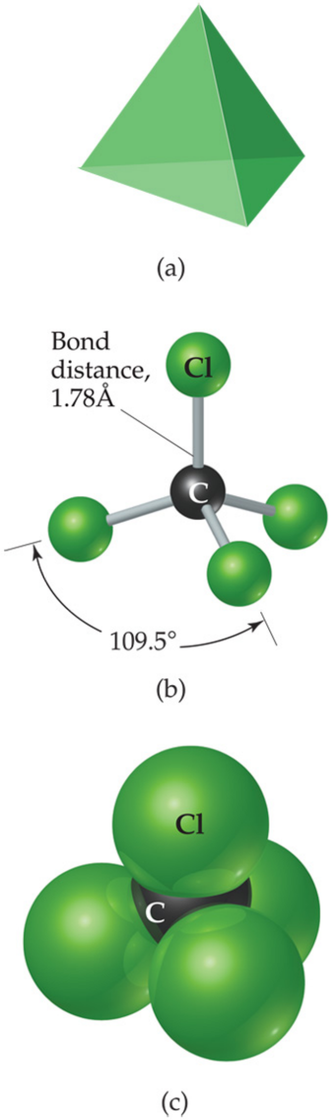
"Things"



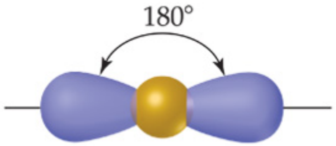
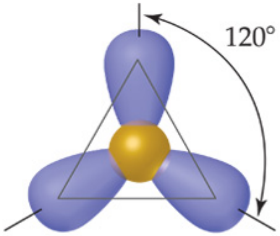
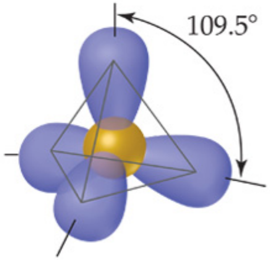
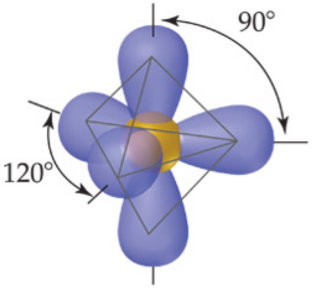
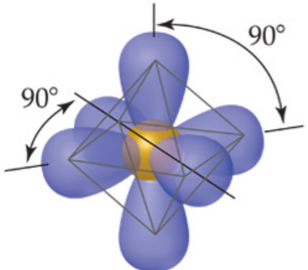
- The central atom has four "things" around it. A "thing" is an atom or a lone pair of electrons.
- # things = atoms plus lone pairs

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.”



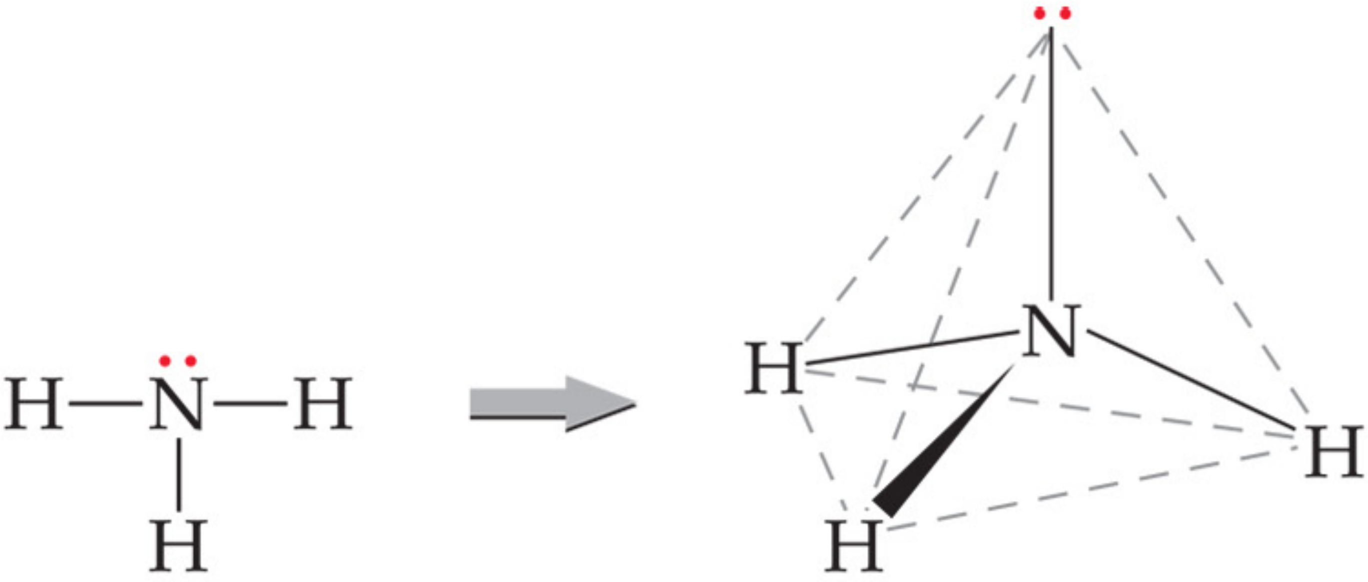
Geometries

number of things	arrangement	geometry	bond angles
2		Linear	180°
3		Trigonal planar	120°
4		Tetrahedral	109.5°
5		Trigonal bipyramidal	120° 90°
6		Octahedral	90°

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

You must learn these!

GEOMETRIES

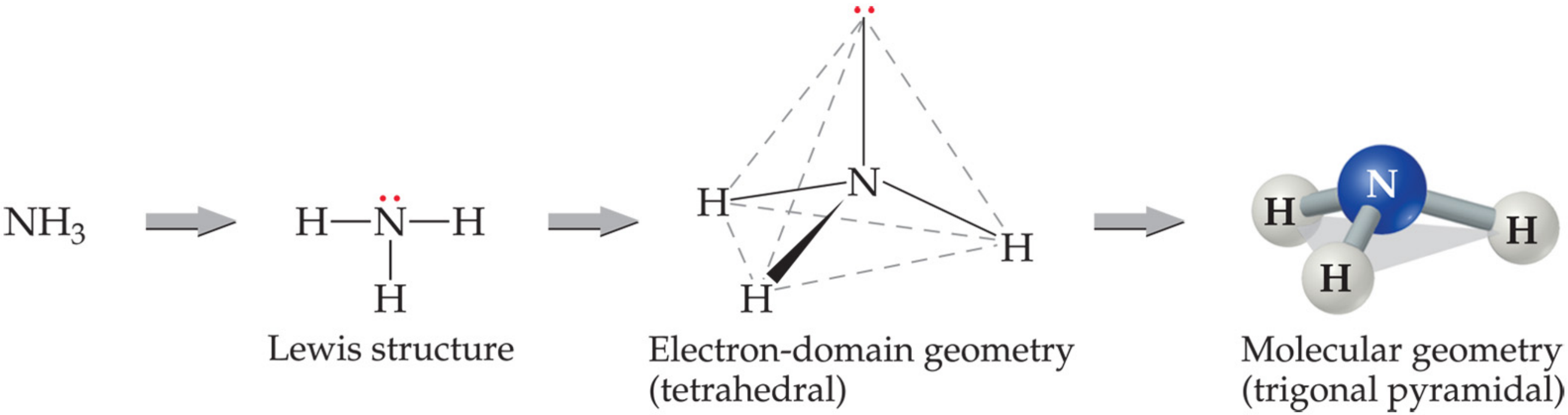


Lewis structure

(tetrahedral)

- All one must do is count the number of "things" in the Lewis structure.
- The **geometry** is determined by the number of "things."

Molecular Geometries



Lewis structure

Electron-domain geometry (tetrahedral)

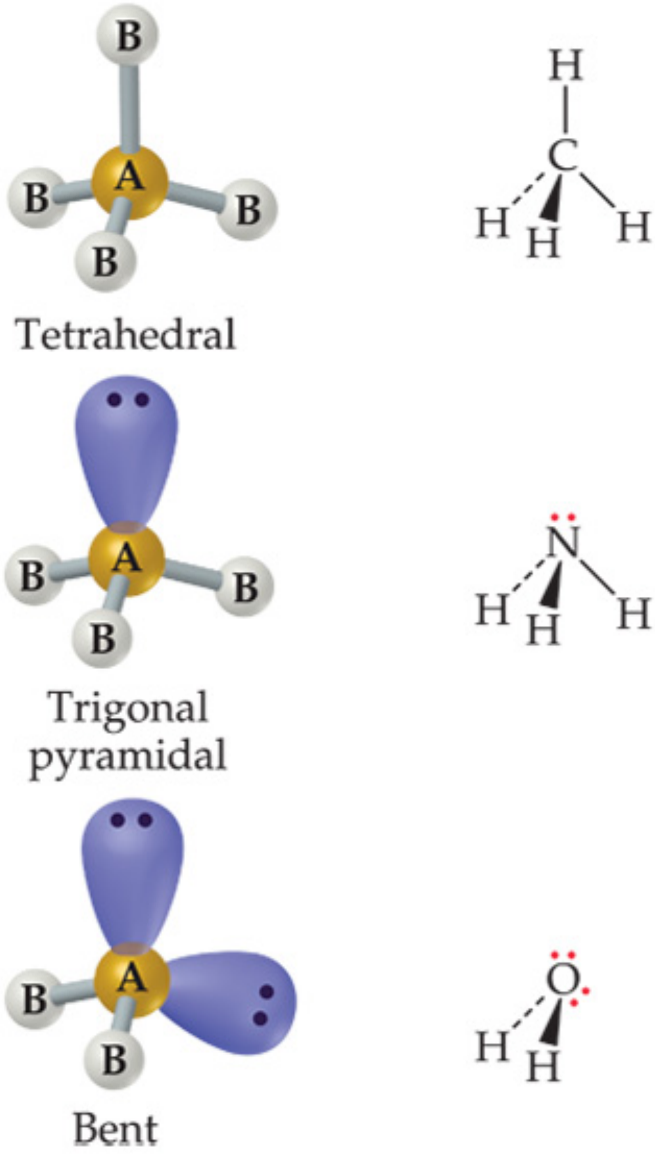
Molecular geometry (trigonal pyramidal)

- 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.**

Geometries vs. shape

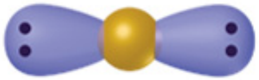
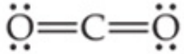
Within each geometry, there might be more than one shape.


Tetrahedral

Trigonal pyramidal

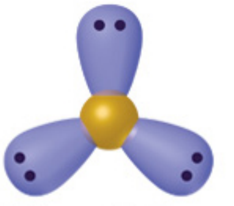
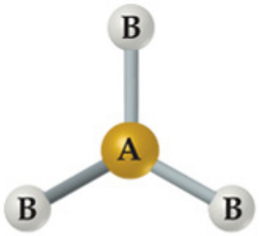
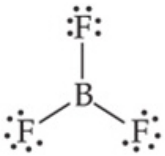
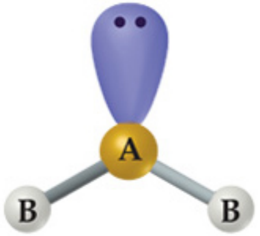
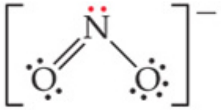
Bent

Linear geometry two things

things	geometry	atoms	lone pairs	shape	example
2	 Linear	2	0	 Linear	

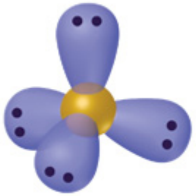
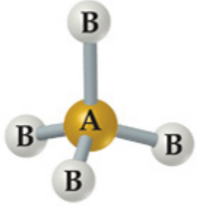
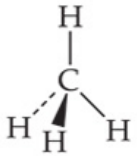
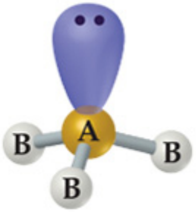
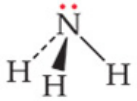
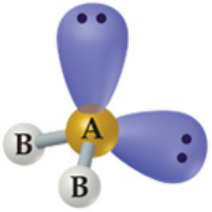
- In this geometry, there is only one molecular geometry: linear.
- NOTE: If there are only two atoms in the molecule, the molecule will be linear no matter what the geometry is.

Trigonal Planar geometry
3 things

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

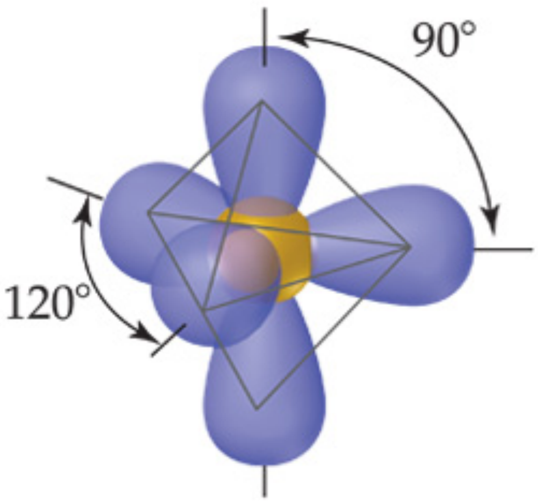
- There are two molecular geometries:
  - Trigonal planar, if there are no lone pairs
  - Bent, if there is a lone pair.

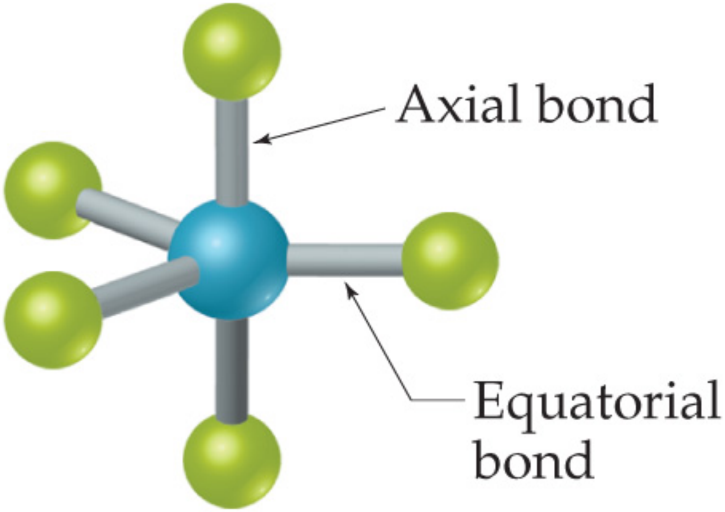
Tetrahedral geometry 4 things

Things	geometry	atoms	lone pairs	shape	example
4	 Tetrahedral	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

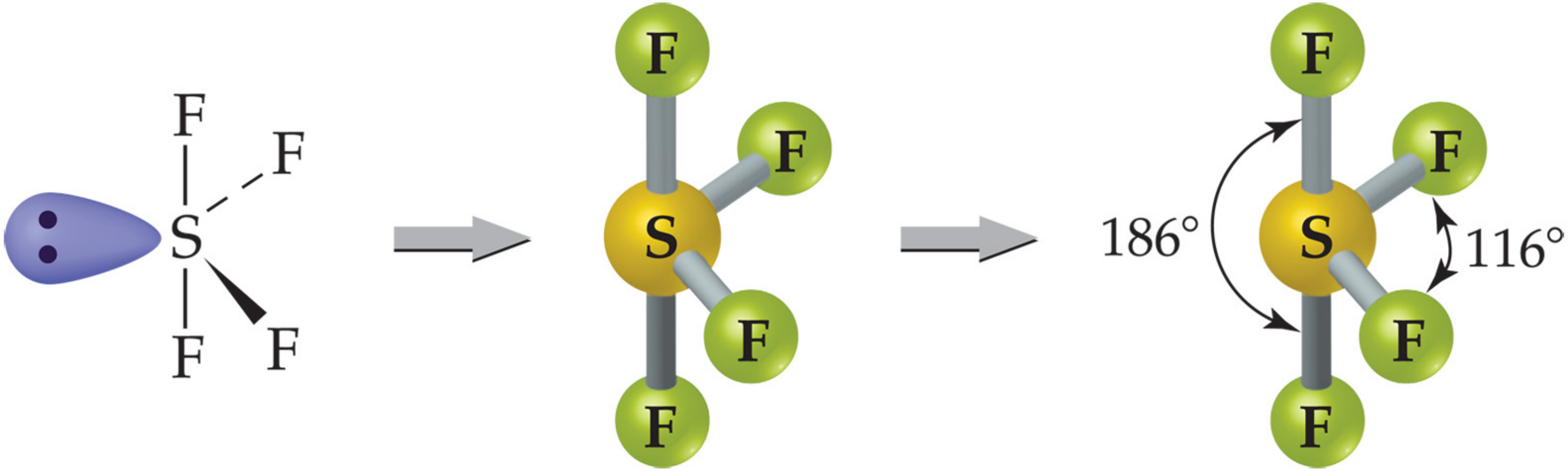
Trigonal Bipyramidal geometry
5 things





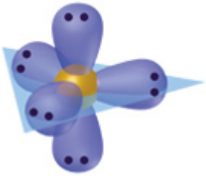
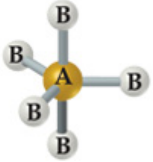
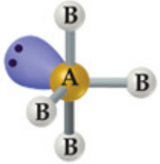
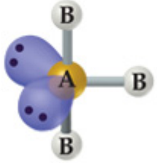
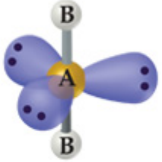
- There are two distinct positions in this geometry:
  - Axial
  - Equatorial

Trigonal Bipyramidal geometry



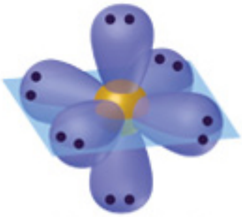
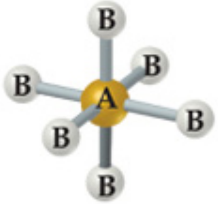
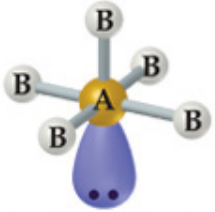
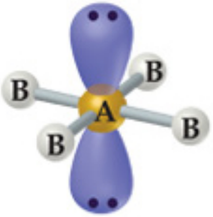
Lower-energy conformations result from having lone pairs in equatorial, rather than axial, positions in this geometry.

Trigonal Bipyramidal geometry

Things	geometry	atoms	lone pairs	shape	example
5	 Trigonal bipyramidal	5	0	 Trigonal bipyramidal	PCl_5
		4	1	 Seesaw	SF_4
		3	2	 T-shaped	ClF_3
		2	3	 Linear	XeF_2

- There are four distinct molecular geometries in this domain:
  - Trigonal bipyramidal
  - Seesaw
  - T-shaped
  - Linear

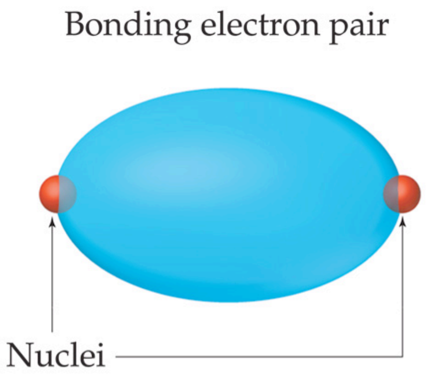
Octahedral geometry 6 things

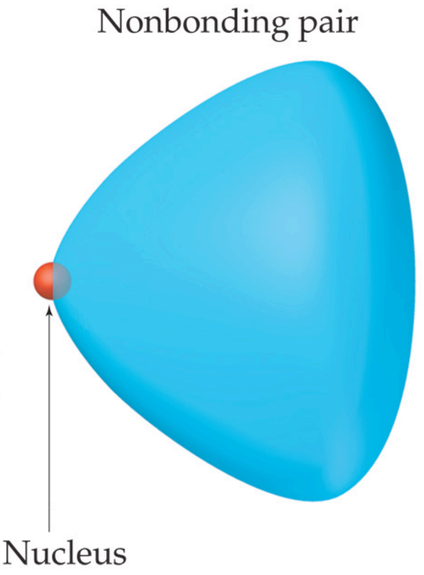
Things	geometry	atoms	lone pairs	shape	example
6	 Octahedral	6	0	 Octahedral	SF_6
		5	1	 Square pyramidal	BrF_5
		4	2	 Square planar	XeF_4

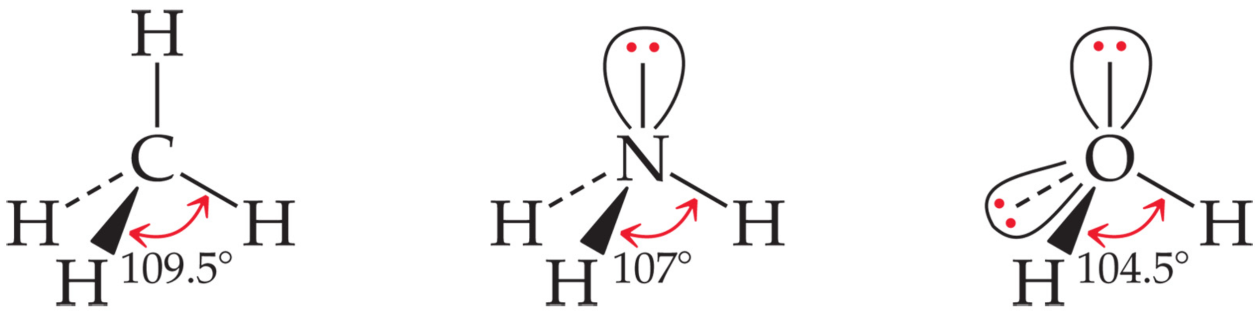
- All positions are equivalent in the octahedral domain.
- There are three molecular geometries:

Lone pairs and Bond Angle

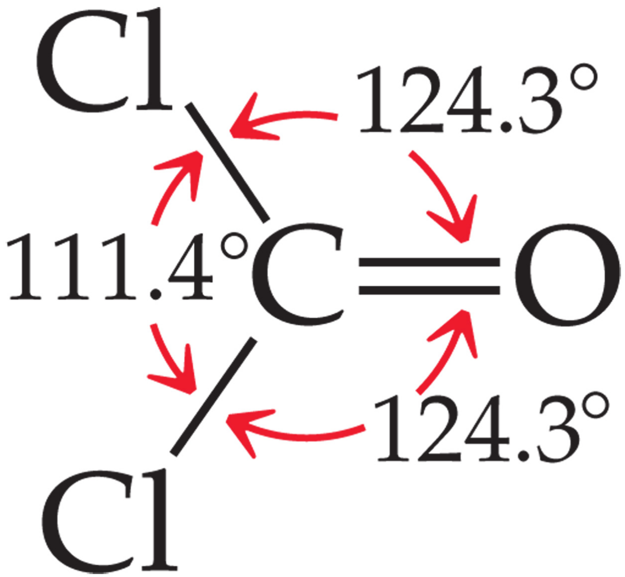
- Lone pairs are physically larger than atoms.
- Therefore, their repulsions are greater; this tends to decrease bond angles in a molecule.







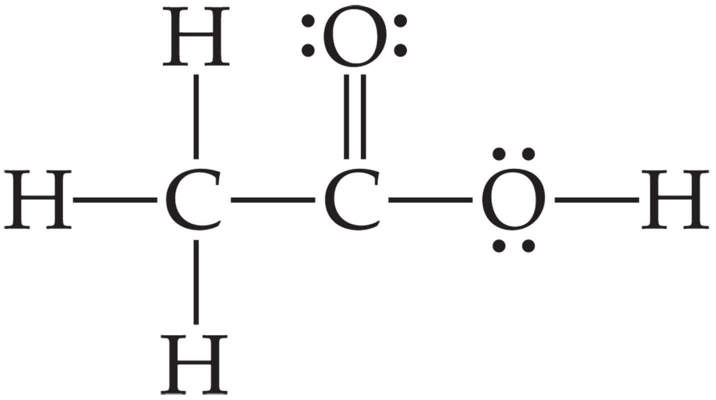
Multiple Bonds and Bond Angles

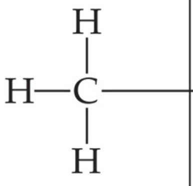
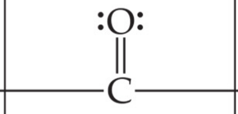


- Double and triple bonds place greater electron density on one side of the central atom than do single bonds.
- Therefore, they also affect bond angles.

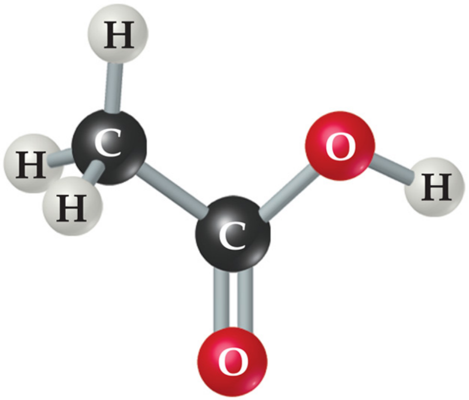
Larger Molecules

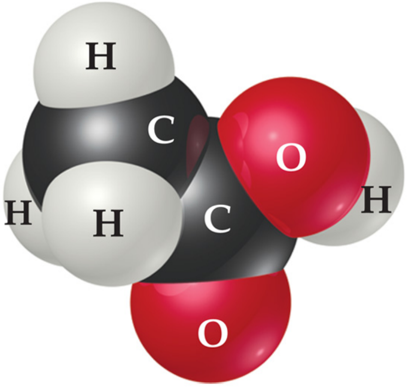
In larger molecules, we talk about the geometry about a particular atom rather than the geometry of the molecule as a whole.



			
Number of electron domains	4	3	4
Electron-domain geometry	Tetrahedral	Trigonal planar	Tetrahedral
Predicted bond angles	109.5°	120°	109.5°

Larger Molecules



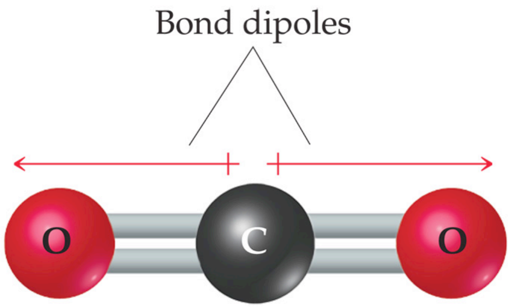


The geometry about each atom follows the same rules!

The molecular structure is the result.

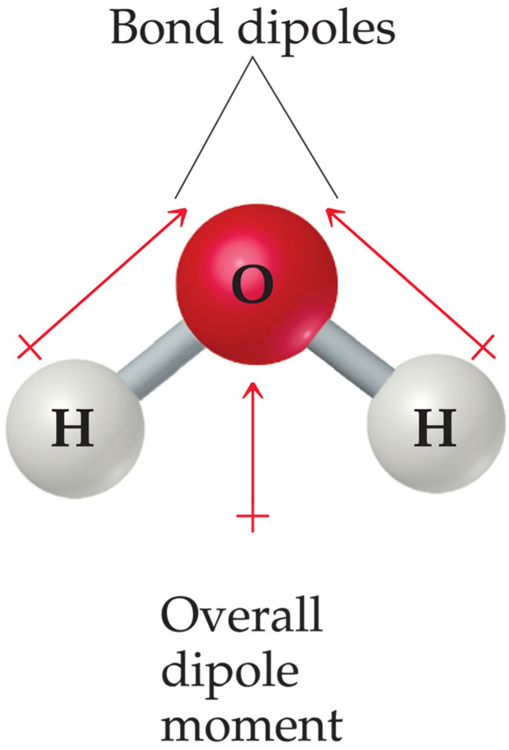
Polarity

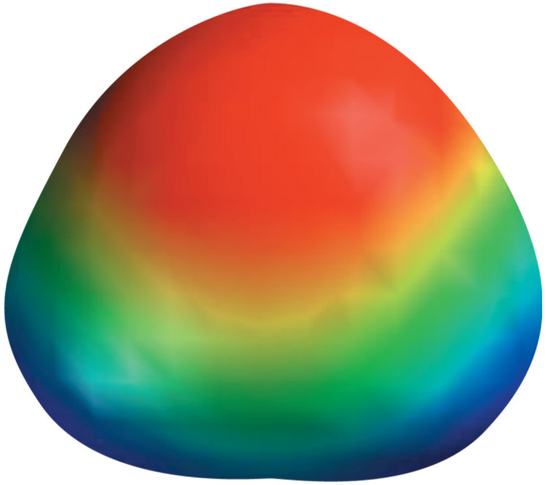
- In Chapter 8 we discussed bond dipoles.
- Now we must think about the molecule **as a whole.**



Overall dipole moment = 0

Polarity

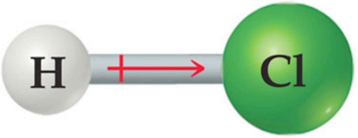


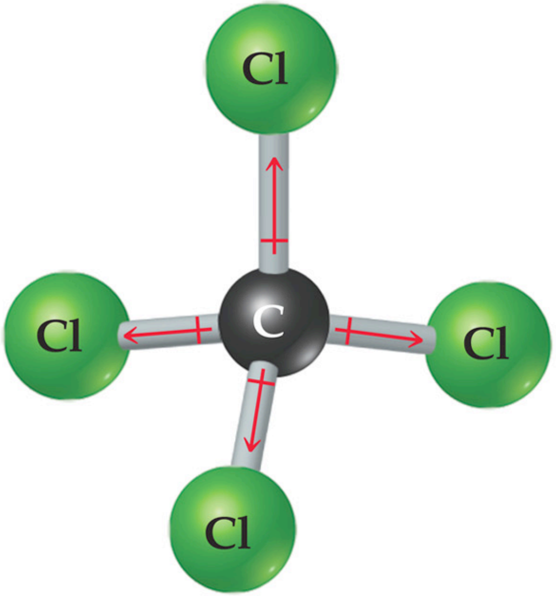


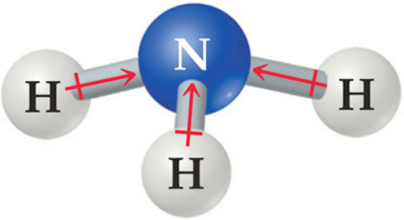
By adding the individual bond dipoles, one can determine the overall dipole moment for the molecule.

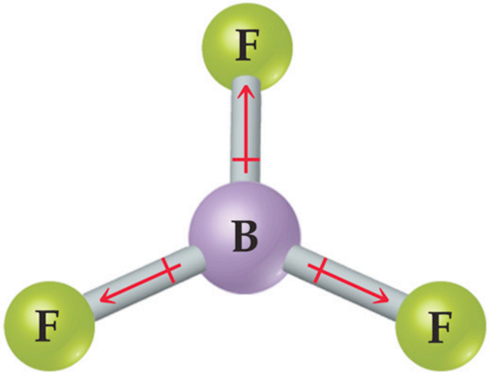
It's the overall polarity that determines the molecules properties.

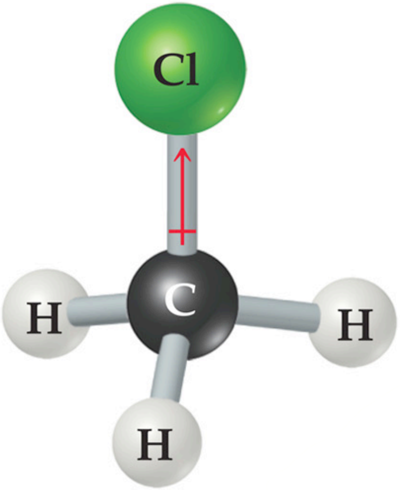
Polarity
"The tractor pull"





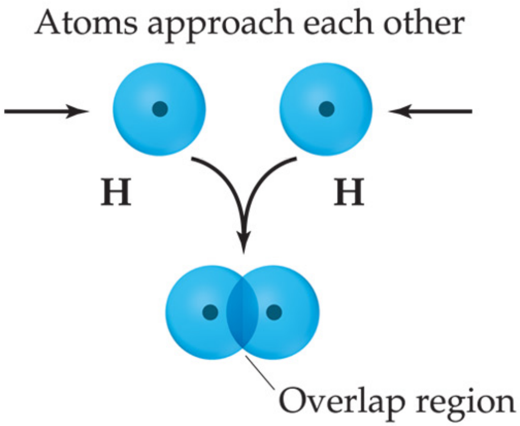


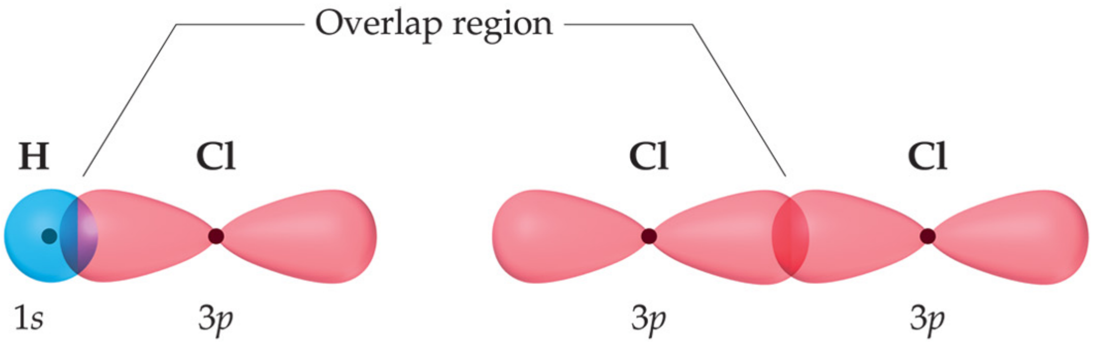




Overlap and Bonding

- covalent bonds form when electrons are "shared."
- But what does that mean? What's the relationship between an atom's atomic orbitals and bonding?
- 1. 2 Atomic orbitals
  - one from each atom
  - each occupied with one electron,
  - overlap, electrons go in these overlapped orbitals

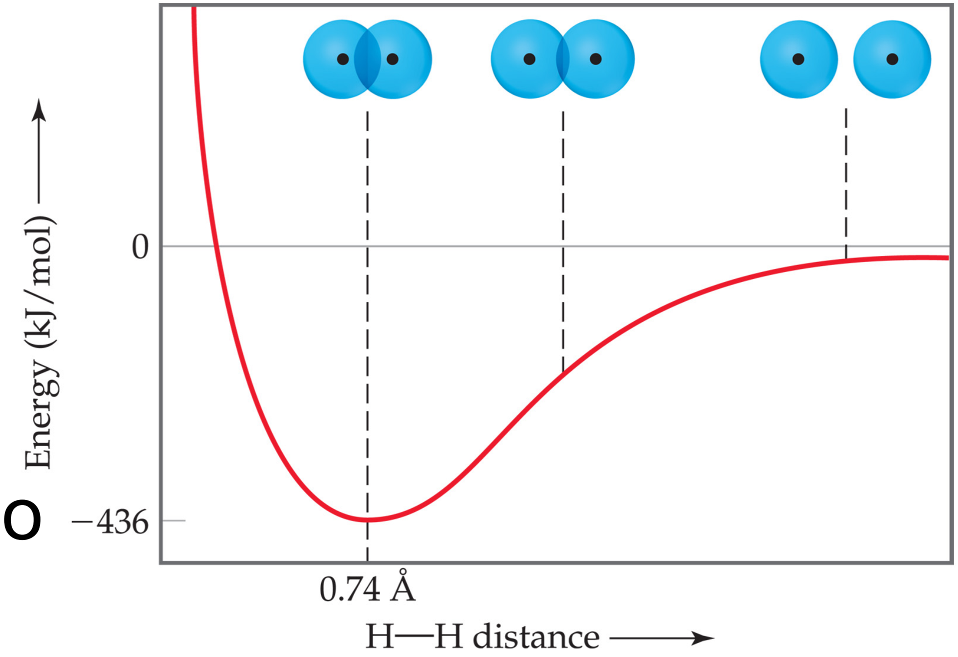




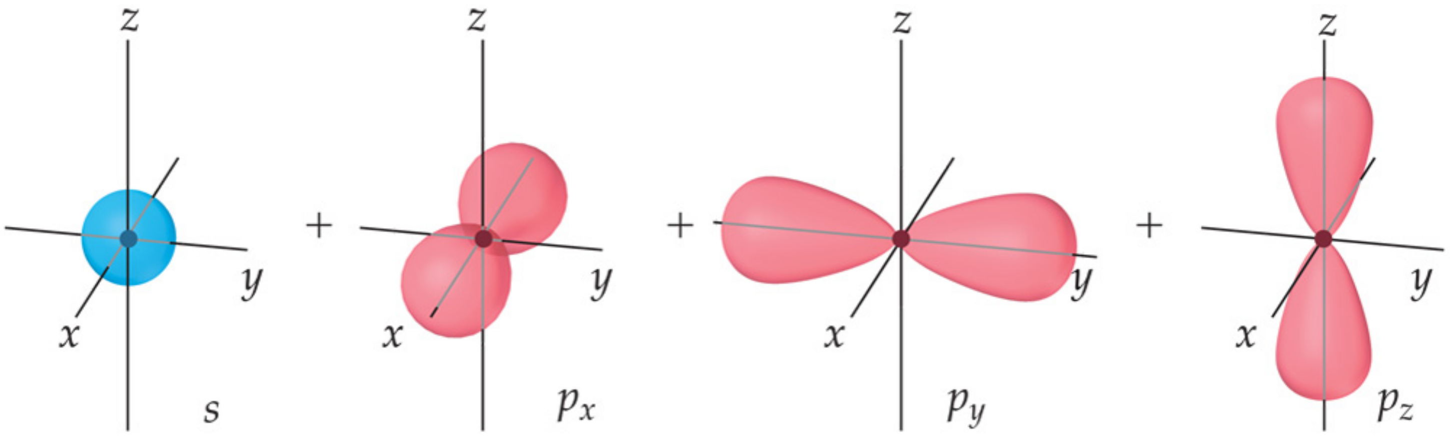
- 2. Atomic orbitals from each atom combine to make new orbitals called "molecular orbitals" and valence electrons go in those orbitals.

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.



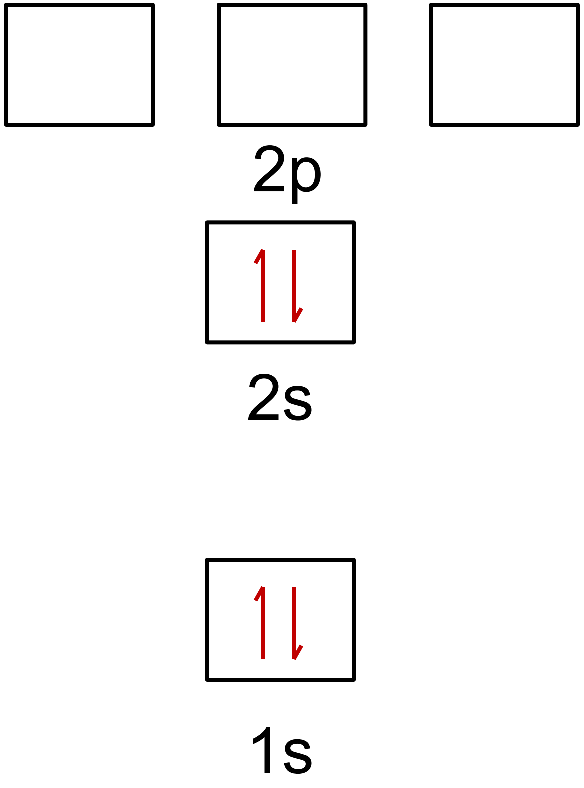
Hybrid Orbitals



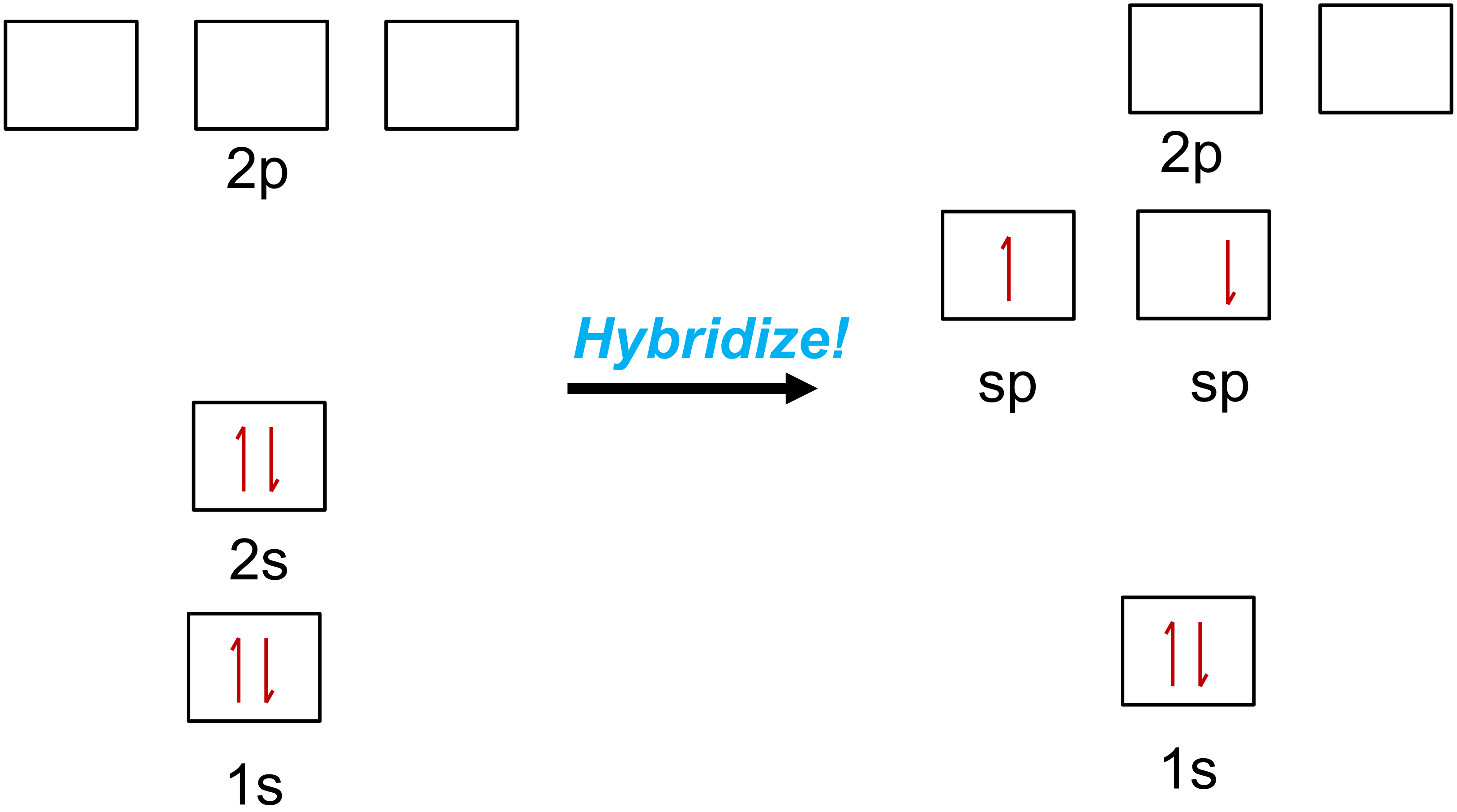
But how do you get tetrahedral, trigonal bipyramidal, and other geometries when the atomic orbitals seem to be at right angles from each other?

Hybrid Orbitals

- Consider beryllium in BeH_2 (a molecule):
  - It’s a linear molecule (2 things around the Be)
  - It has two **covalent** Be-H bonds.
- But which orbitals overlap with the 1s H orbitals?
  - The p orbitals are 90°
  - The s orbital is a ball.
- Hybrid orbitals!



Hybrid Orbitals



2p

2s

1s

Hybridize!

2p

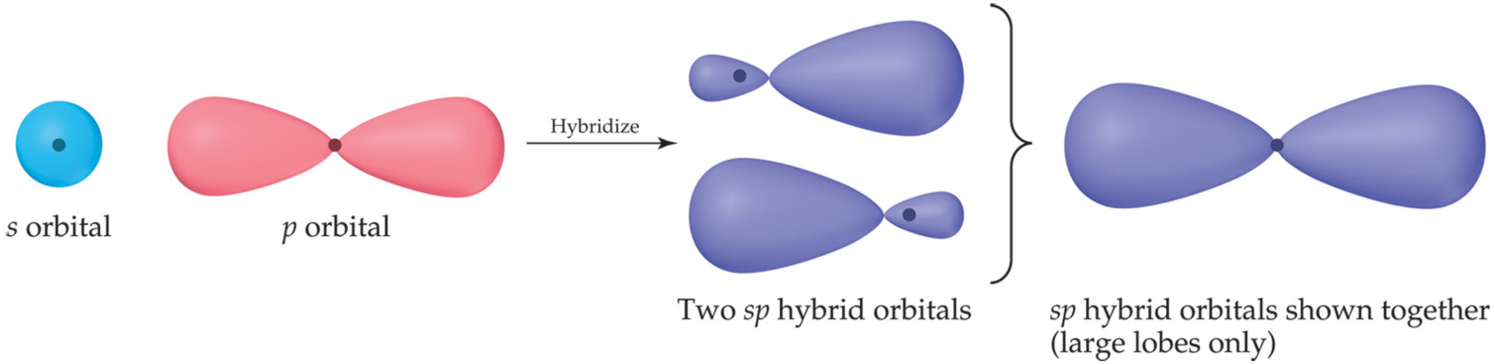
sp

sp

1s

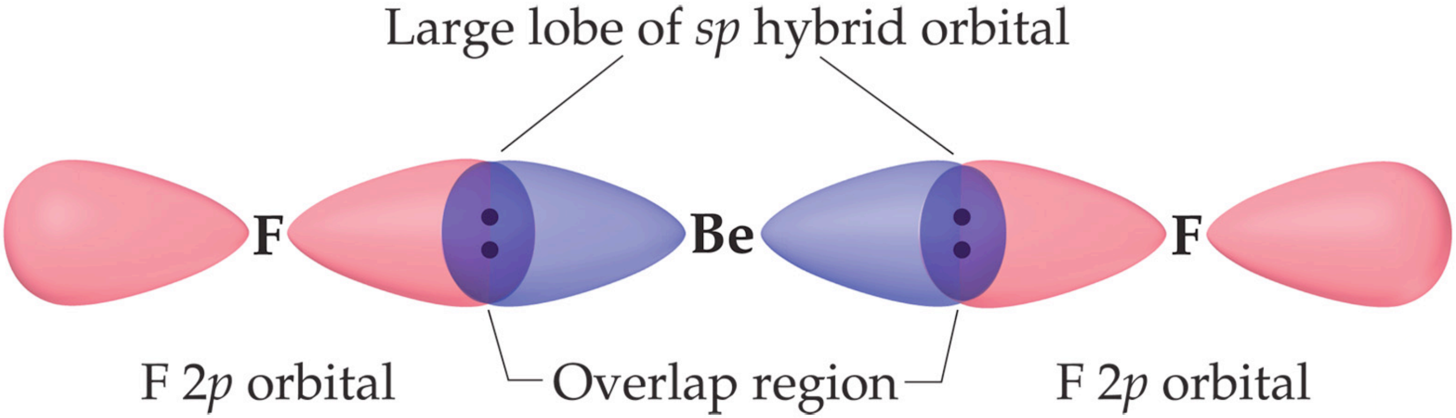
Hybrid Orbitals
What do they look like?

- Mixing the *s* and one *p* orbital 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.



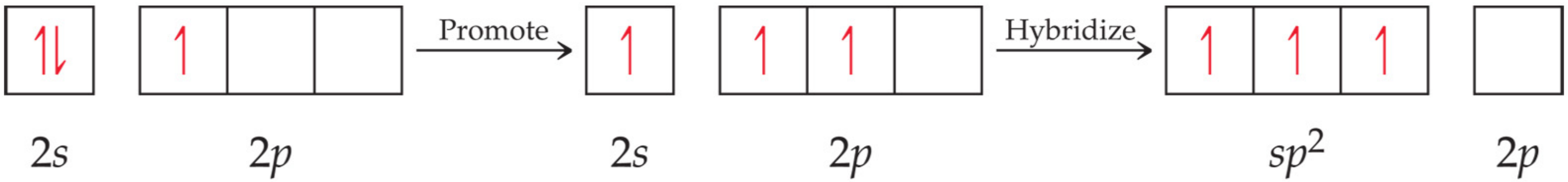
Hybrid Orbitals

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



Hybrid Orbitals

Using a similar model for boron in BH_3 leads to…

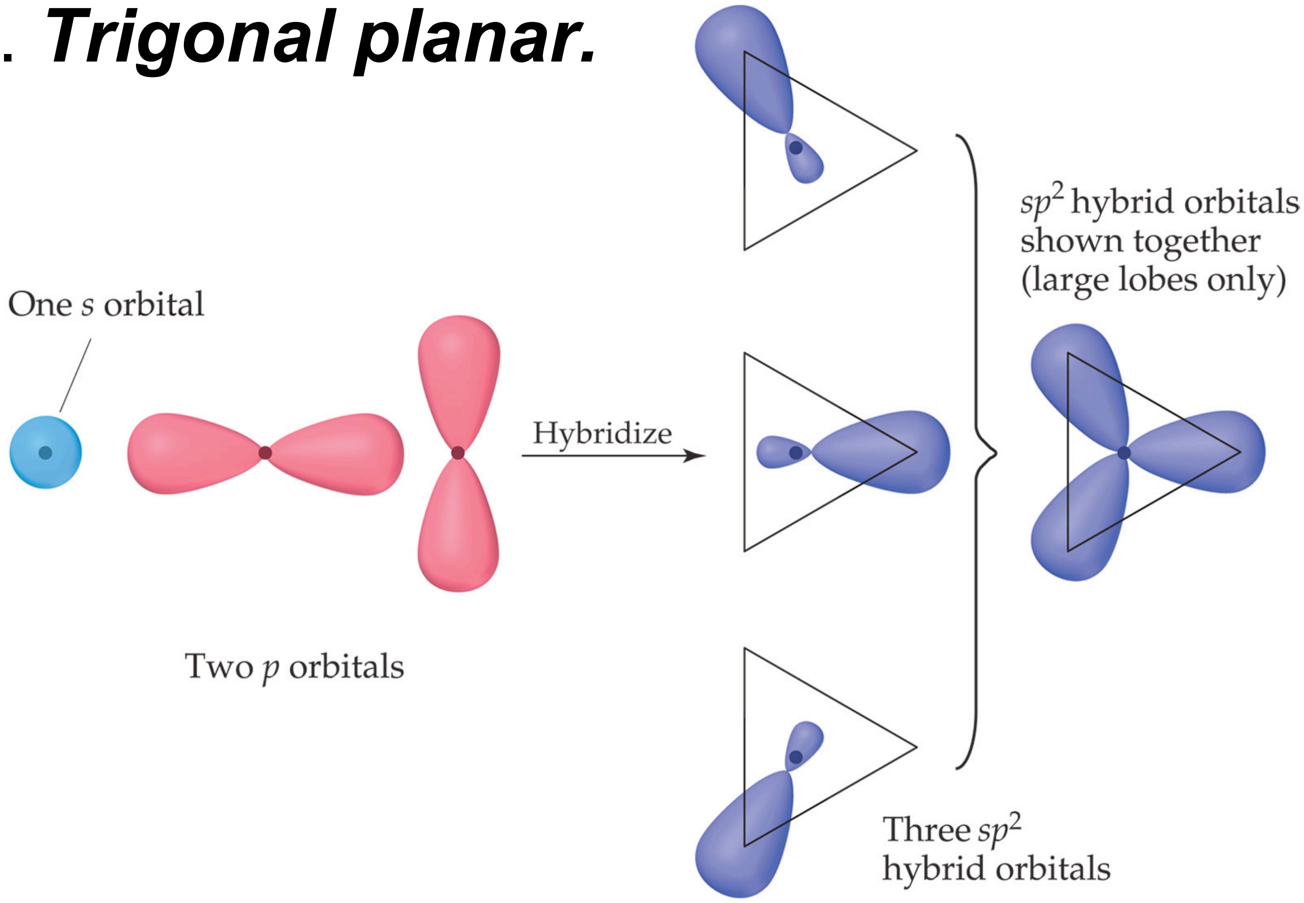


Three hybrid orbitals, one for each H bound to the central Boron atom

Hybrid Orbitals

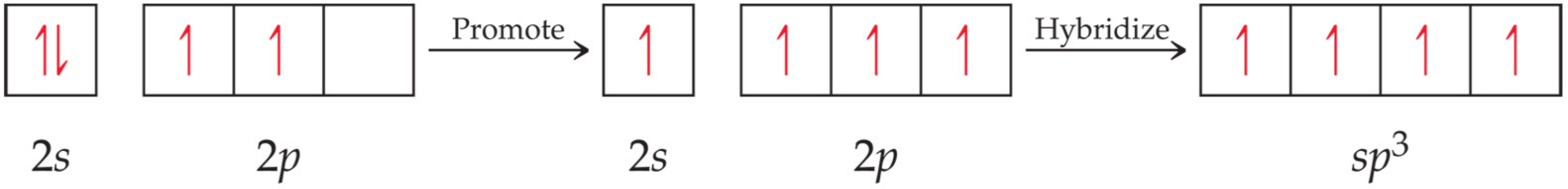
…three degenerate *sp*^{2} orbitals.

Make a triangle of orbitals. Pointing at 120° angles. ***Trigonal planar.***



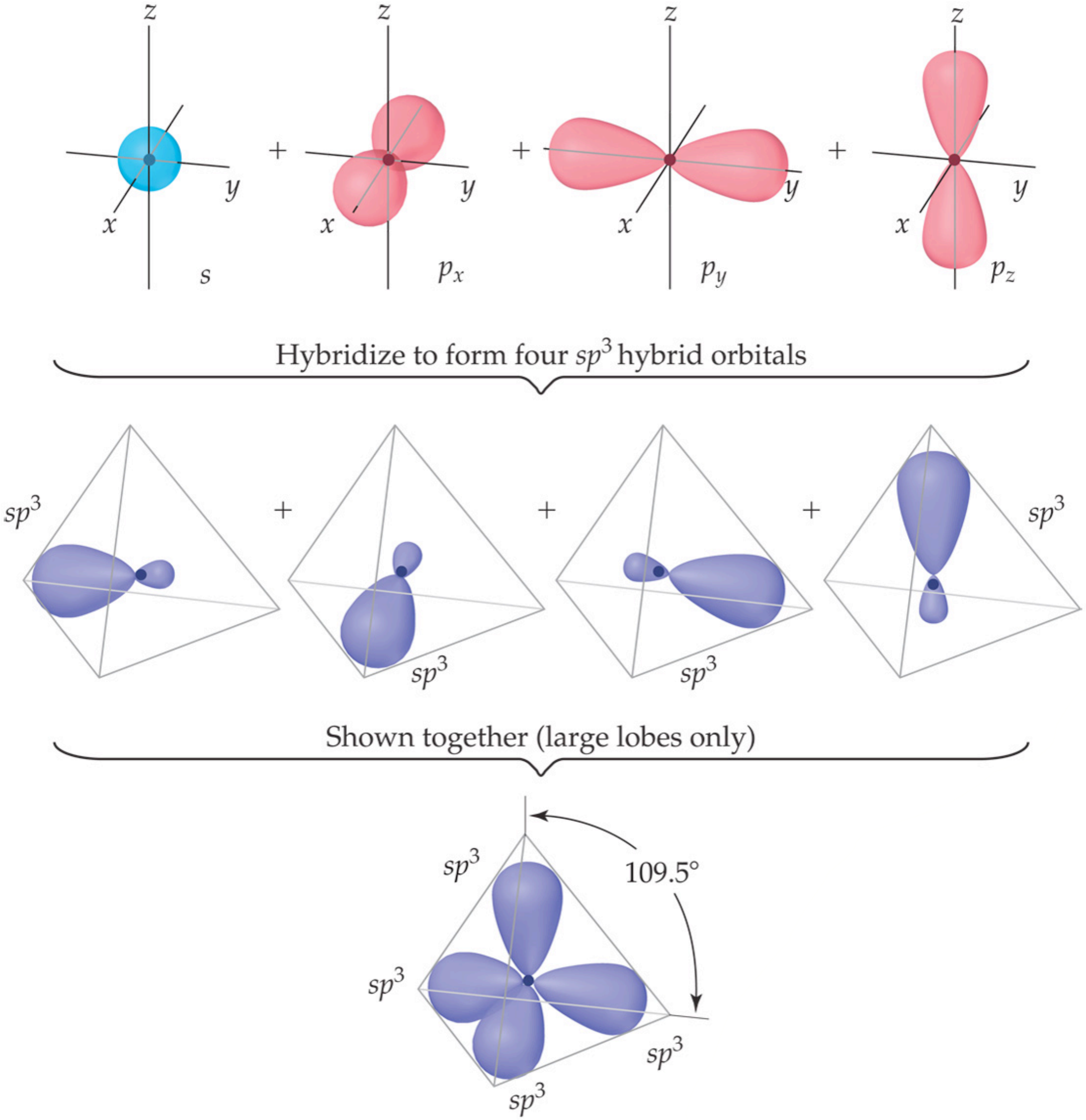
Hybrid Orbitals

With carbon in methane CH_4 we get…



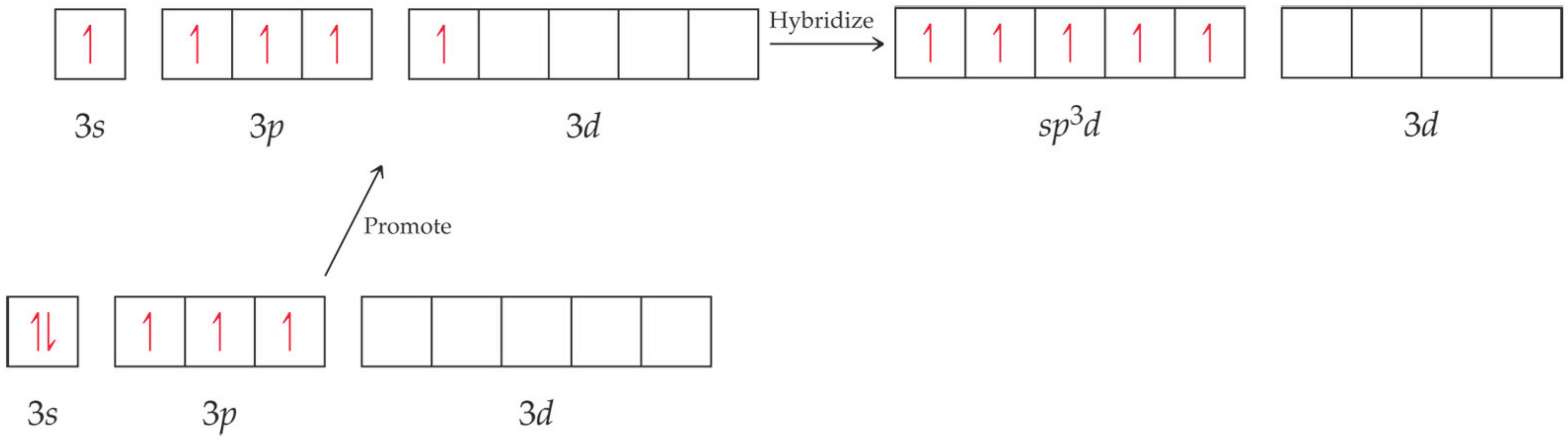
Hybrid Orbitals

…four degenerate
sp^3 orbitals.

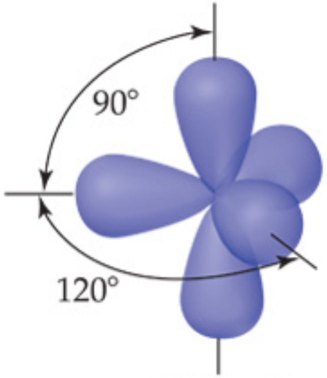


Hybrid Orbitals

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



Hybrid Orbitals



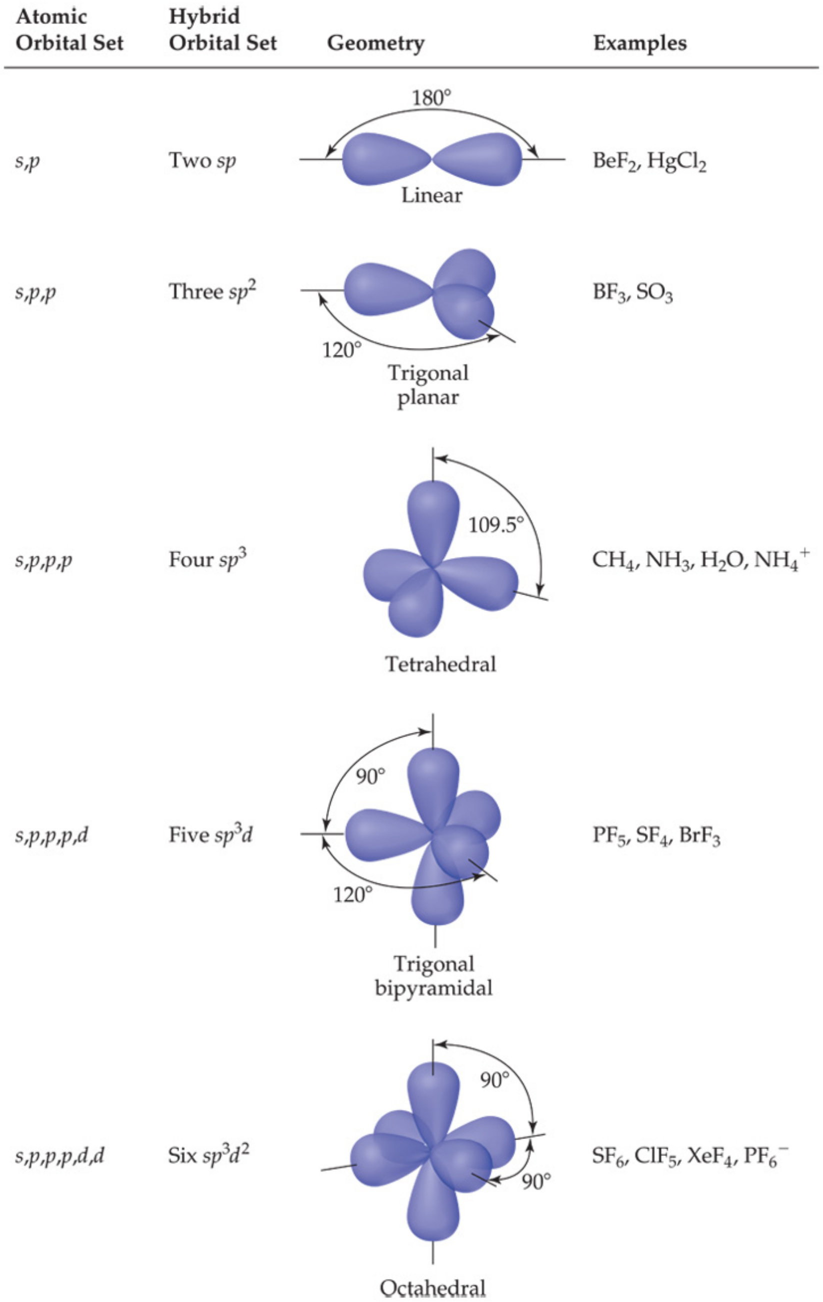
Trigonal bipyramidal

This leads to five degenerate *sp*^{3}*d* orbitals…

…or six degenerate *sp*^{3}*d*^{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*	180° Linear	BeF_2, $HgCl_2$
s,p,p	Three sp^2	120° Trigonal planar	BF_3, SO_3
s,p,p,p	Four sp^3	109.5° Tetrahedral	CH_4, NH_3, H_2O, NH_4^+
s,p,p,p,d	Five sp^3d	90° 120° Trigonal bipyramidal	PF_5, SF_4, BrF_3
s,p,p,p,d,d	Six sp^3d^2	90° 90° Octahedral	SF_6, ClF_5, XeF_4, PF_6^-

The exam

- Chapters 7-9
  - Periodic trends
    - Size
    - Ionization E
    - Electron affinity
    - Electroneg

The exam

- Start time: 12:10 P.M.
- End Time: 2:00 P.M.
- Effective nuclear charge
- Sizes of atoms
- Sizes of ions
- Trends in ionization energy
- Electronegativity
- Electron affinity

The exam

- Lewis structures
- Resonance
- Bond enthalpies

The exam

Molecular geometry

Molecular shape

Hybridization

The exam

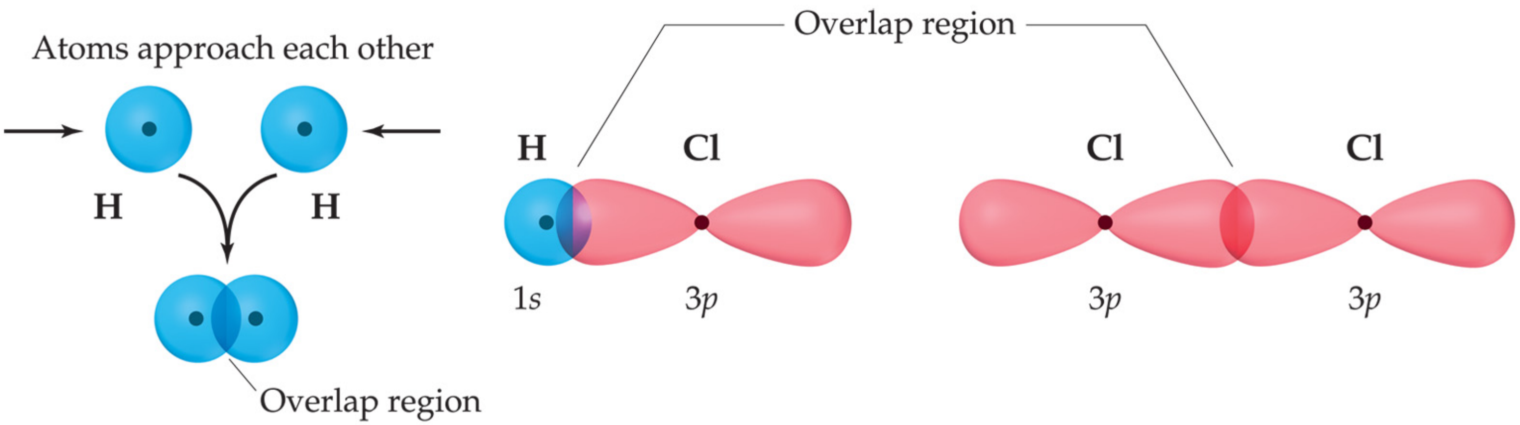
- 1 size trend
- 2 Effective nuclear charge
- 2 electron affinity
- 2 Ion. energy trend
- 1 ions/electron configuration
- 6 Lewis structures
- 1 Bond polarity
- 2 VSEPR
- 1 Molecular polarity
- 2 hybridization

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.

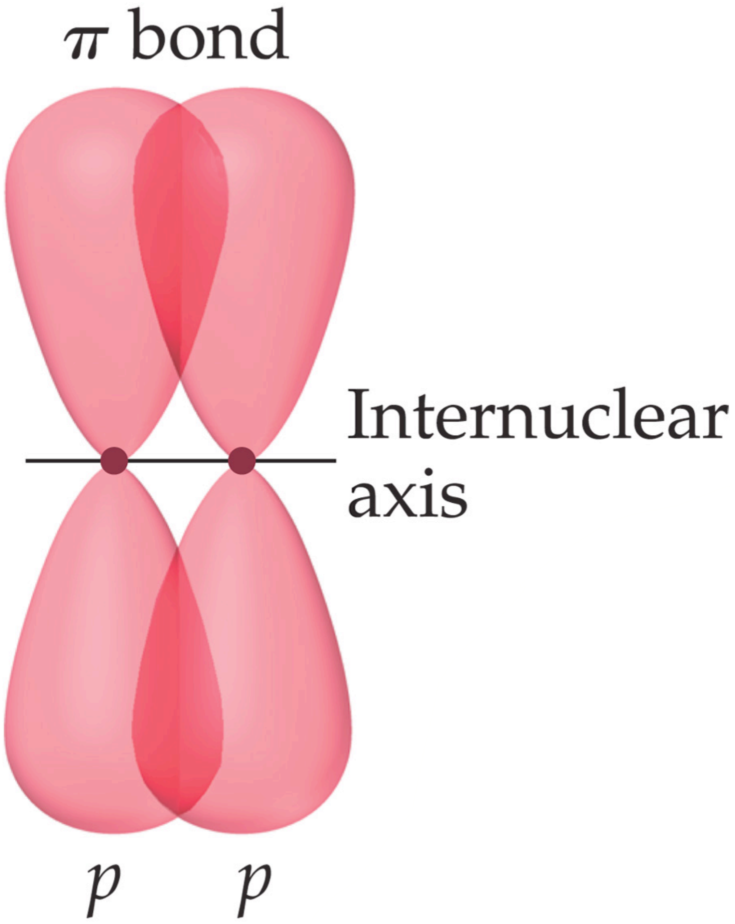
Sigma (σ) Bonds



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

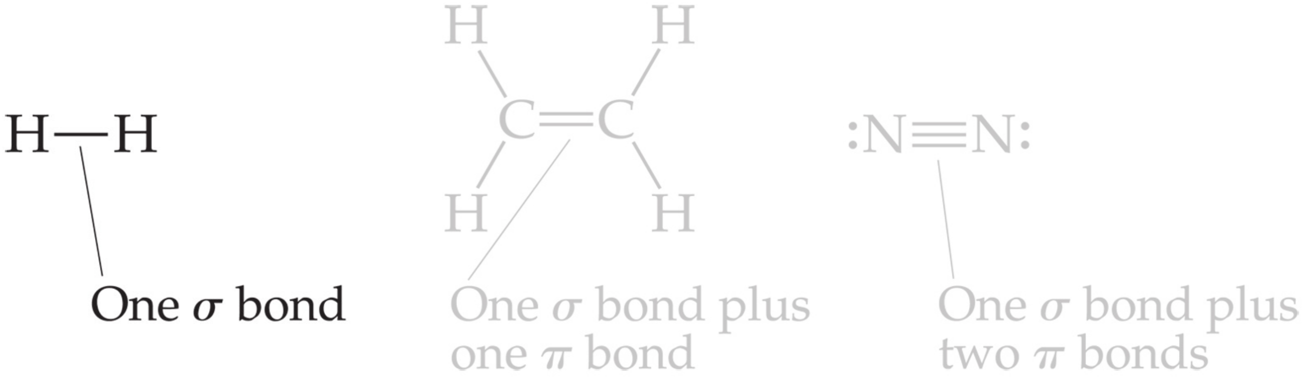
Pi (π) Bonds

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



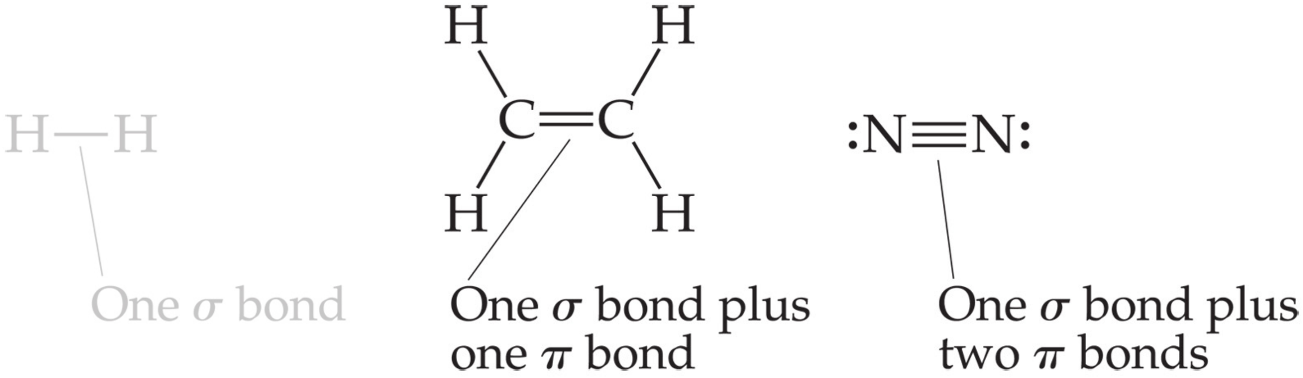
Single Bonds

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

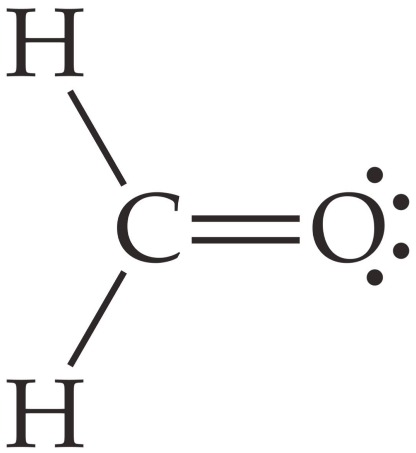


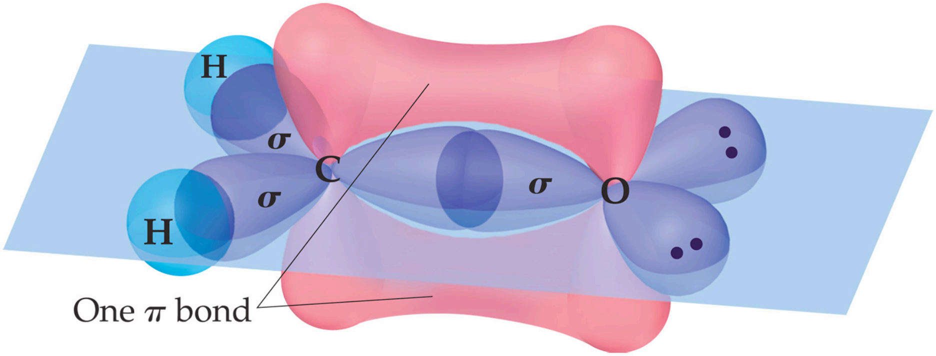
Multiple Bonds

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



Multiple Bonds

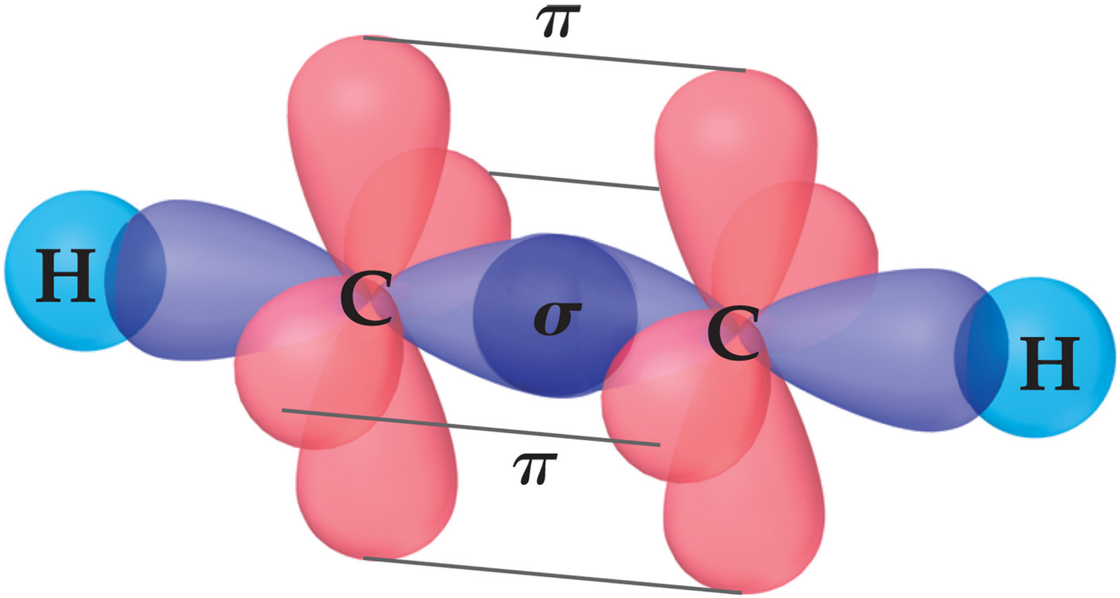




- Example: formaldehyde: an *sp*^{2} orbital on carbon overlaps in σ fashion with the corresponding orbital on the oxygen.
- The unhybridized *p* orbitals overlap in π fashion.

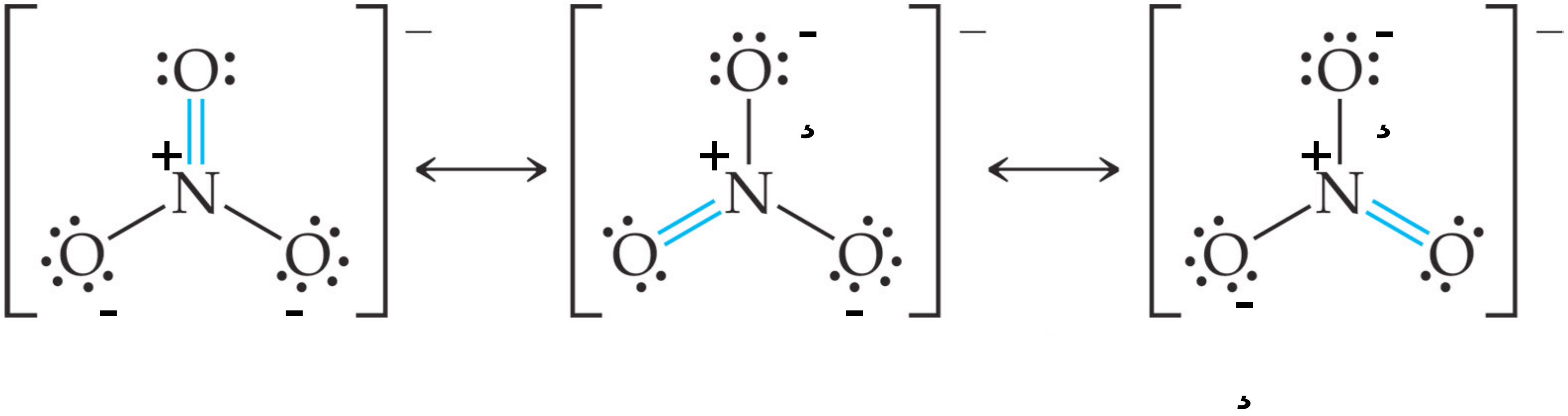
Multiple Bonds

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.

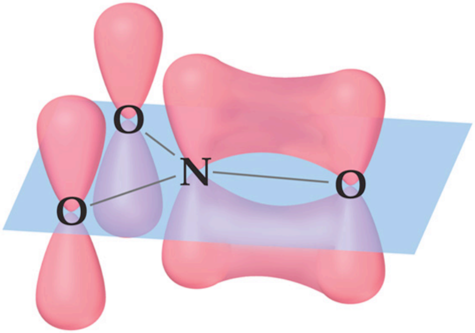


Delocalized Electrons: Resonance

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.

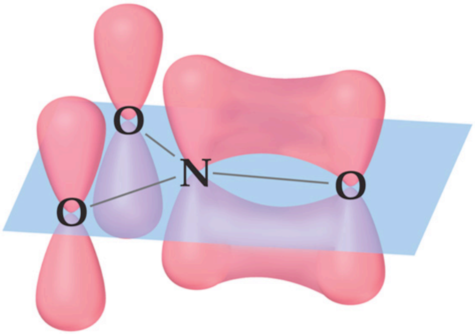


Delocalized Electrons: Resonance

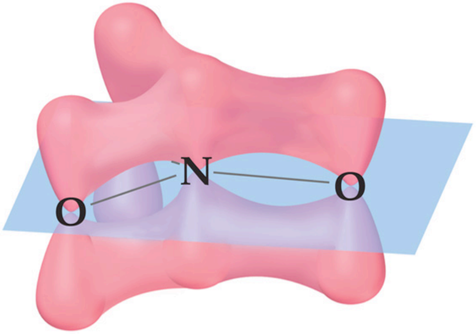


- each of the four atoms in the nitrate ion has a *p* orbital.
- The *p* orbitals on all three oxygens overlap with the *p* orbital on the central nitrogen.

Delocalized Electrons: Resonance

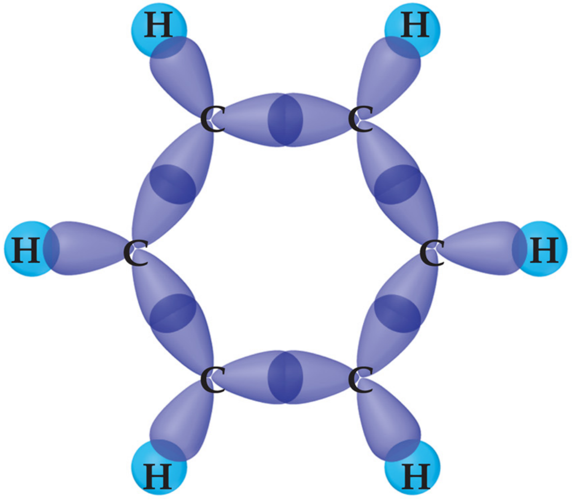


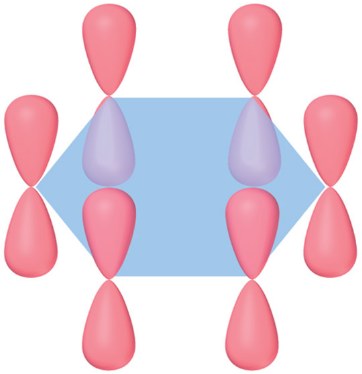
This means the π electrons are not localized between the nitrogen and one of the oxygens, but rather are delocalized throughout the ion.



Resonance

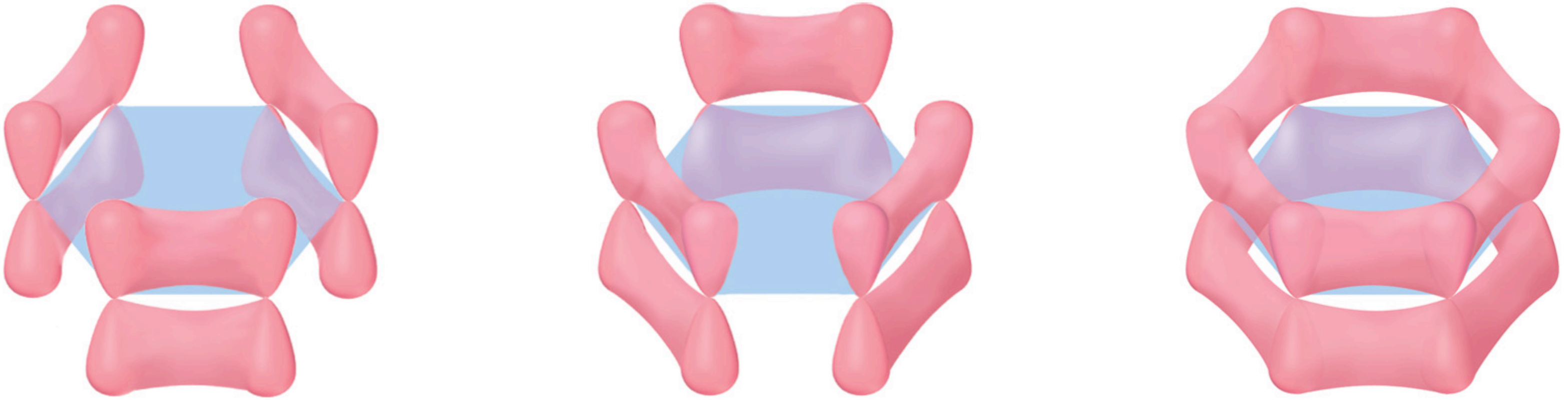
The organic molecule benzene has six σ bonds and a *p* orbital on each carbon atom.





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.

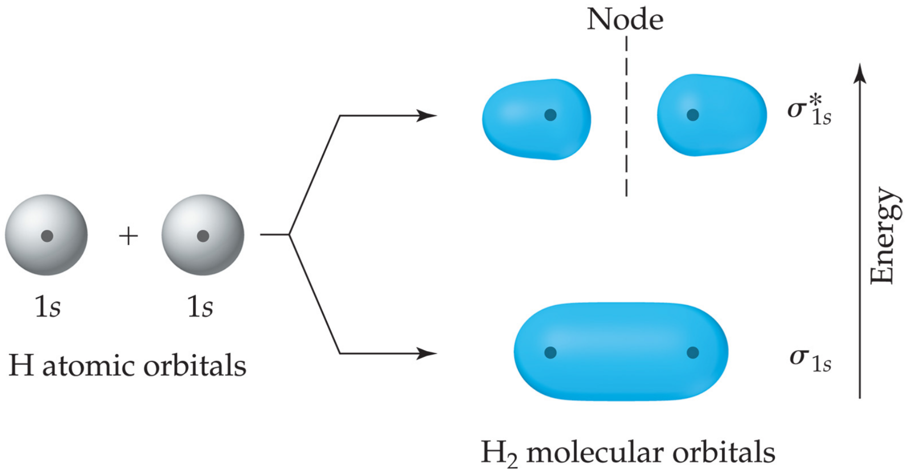


Valence bond theory

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

Molecular Orbital (MO) Theory

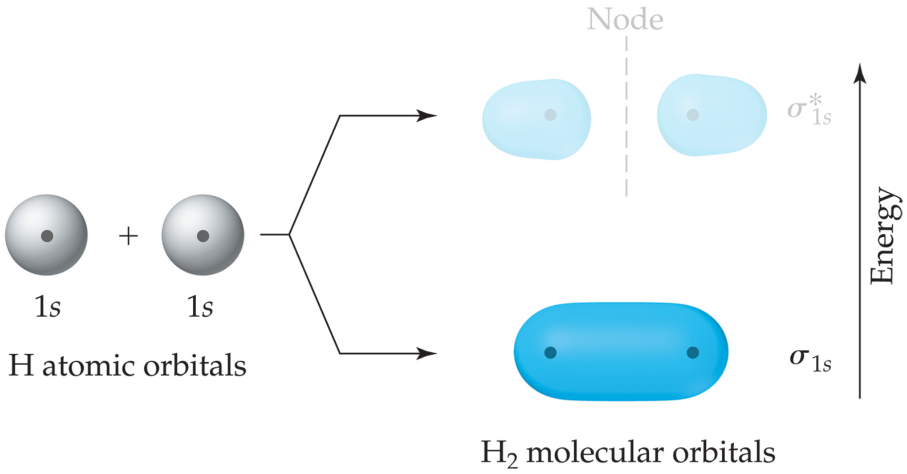
Valence bond theory works very well for most observed properties of ions and molecules, but there are some concepts better represented by molecular orbital theory.



Molecular Orbital (MO) Theory

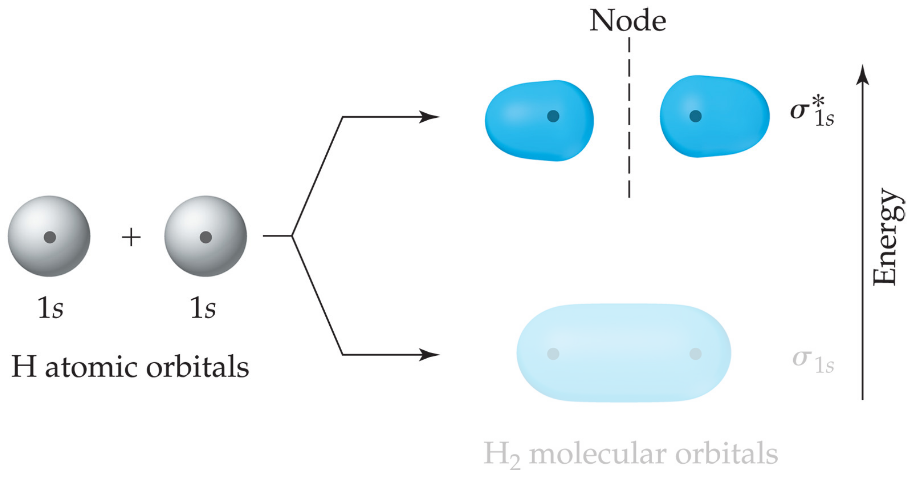
- In MO theory, we invoke the wave nature of electrons.

- If waves interact constructively, the resulting orbital is lower in energy: a bonding molecular orbital.



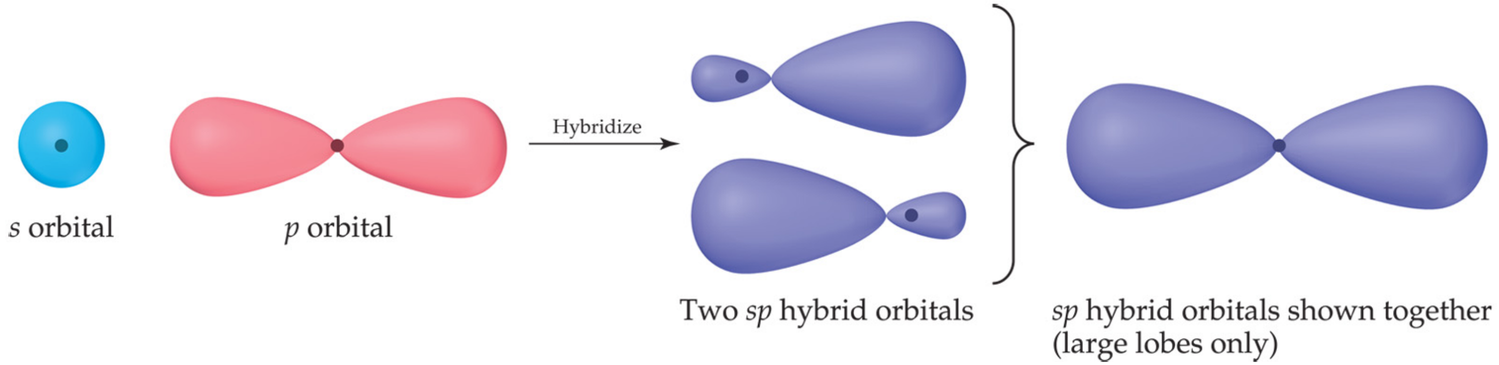
Molecular Orbital (MO) Theory

If waves interact destructively, the resulting orbital is higher in energy: an antibonding molecular orbital.

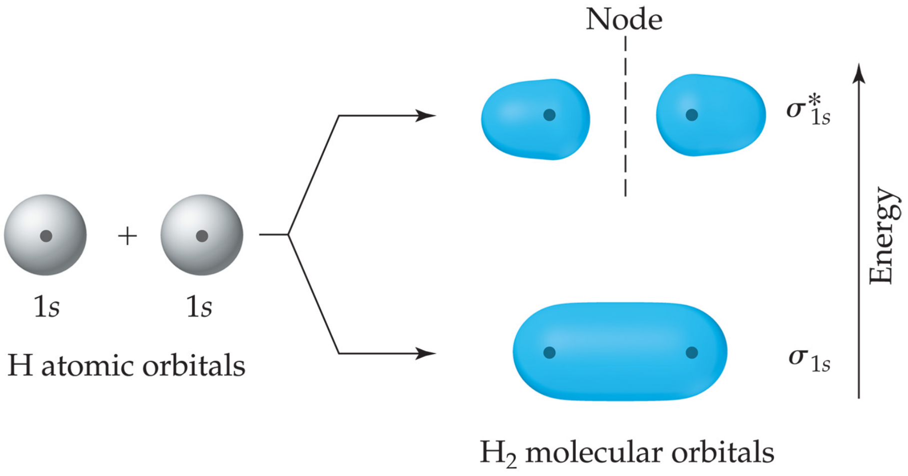


Molecular Orbital (MO) Theory

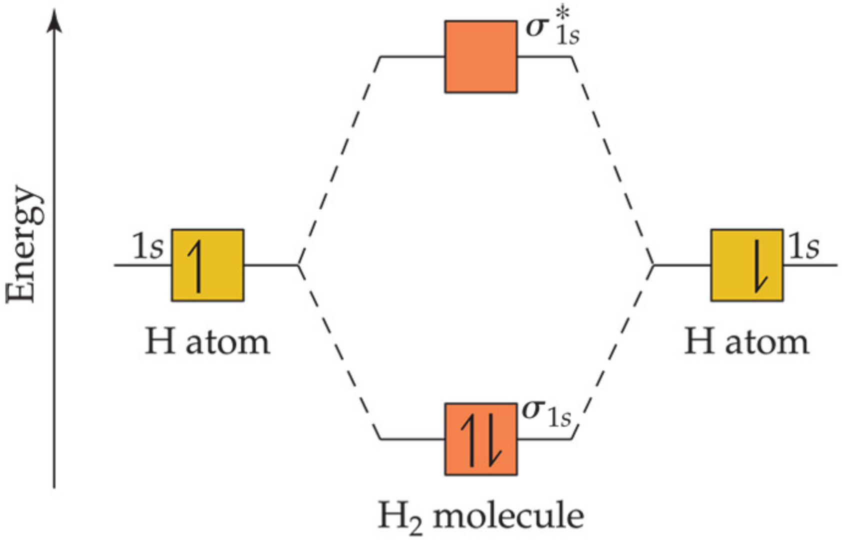
- Valence bond theory:
- atomic orbitals are mixed in each individual atom *before* bonding.



- Molecular orbital theory:
- no prebonding mixing. Molecular orbitals are computed *for the whole molecule*.

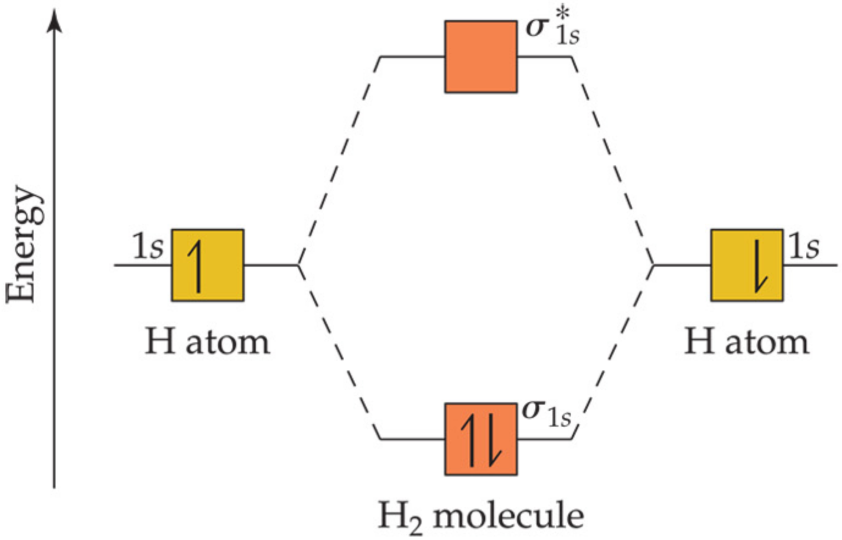


MO Theory



- In H_2 the two electrons go into the bonding molecular orbital.
- The bond order is one half the difference between the number of bonding and antibonding electrons.

MO Theory



For hydrogen, with two electrons in the bonding MO and none in the antibonding MO, the bond order is

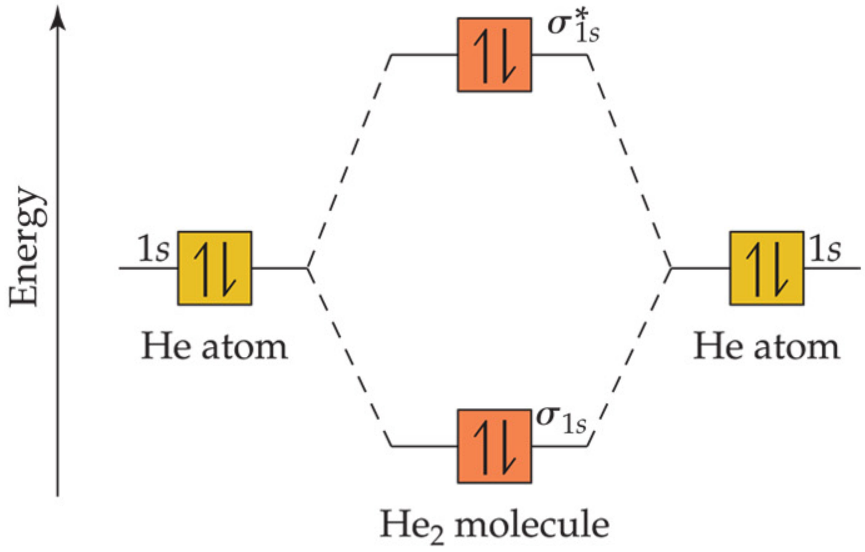
$$\frac{1}{2}(2 - 0) = 1$$

MO Theory

- In the case of He_2, the bond order would be

$$\frac{1}{2}(2 - 2) = 0$$

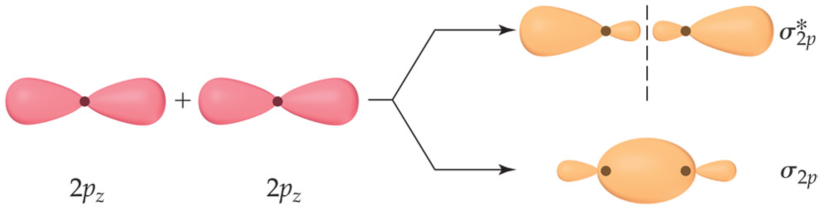
- Therefore, He_2 does not exist.

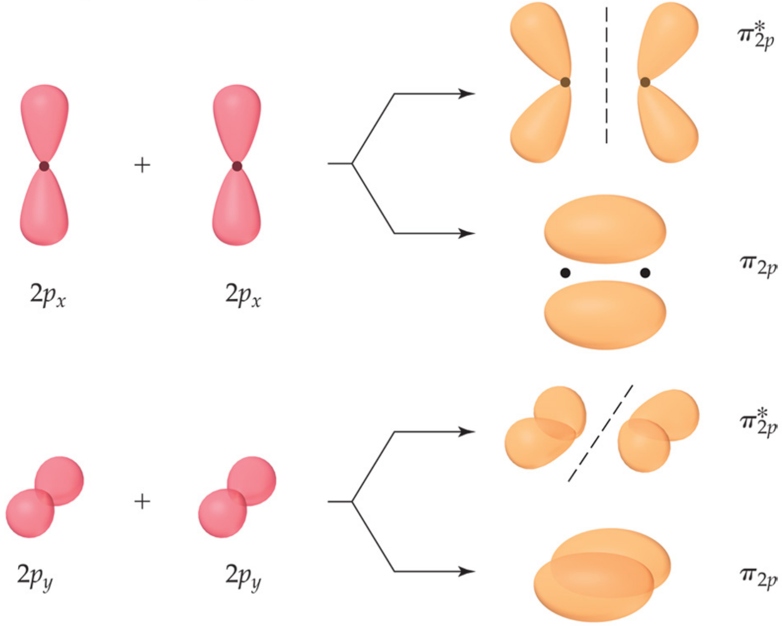


Rules for making and filling molecular orbitals

- 1. The number of MO's equals the # of Atomic orbitals
- 2. The overlap of two atomic orbitals gives two molecular orbitals, 1 bonding, one antibonding
- 3. Atomic orbitals combine with other atomic orbitals of *similar energy.*
- 4. Degree of overlap matters. More overlap means bonding orbital goes *lower* in E, antibonding orbital goes *higher* in E.
- 5. Each MO gets two electrons
- 6. Orbitals of the *same energy* get filled 1 electron at a time until they are filled.

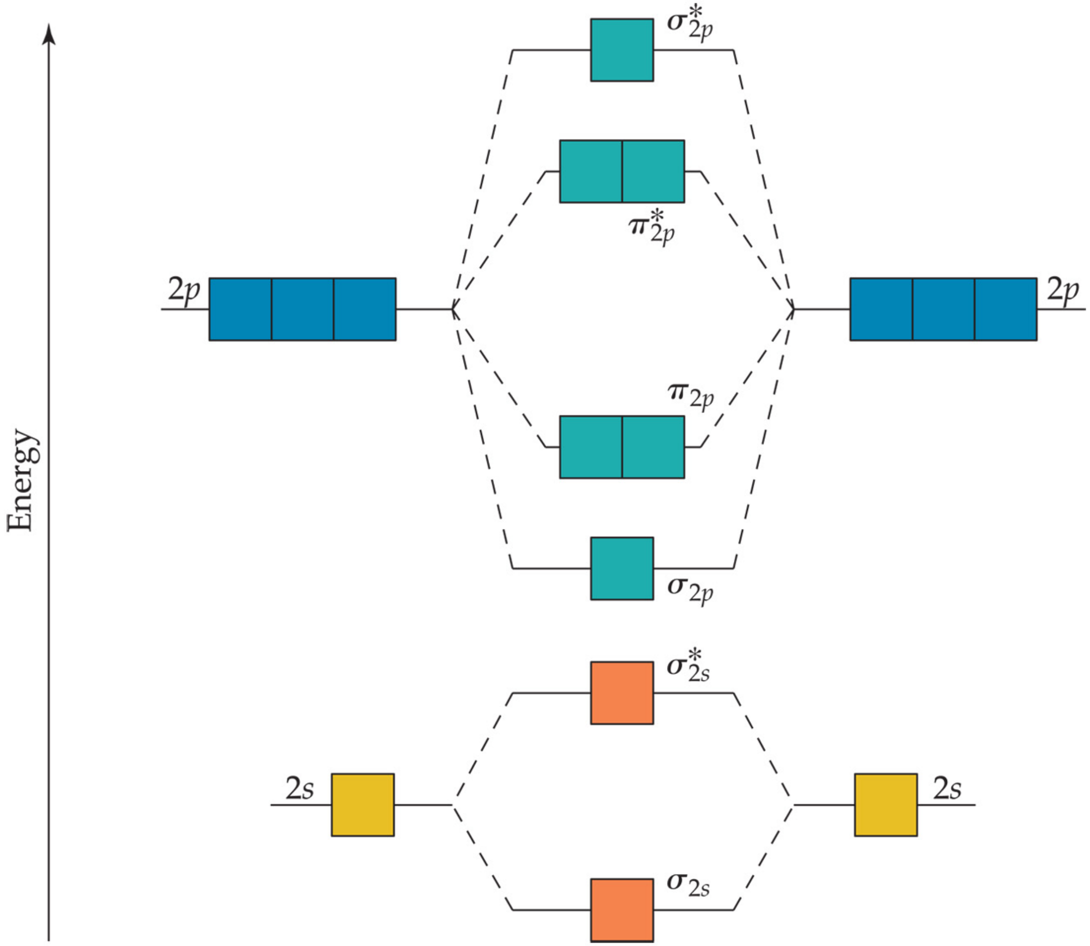
MO Theory


(a) “End-on” overlap of p orbitals forms σ and σ^* MOs.


(b) “Sideways” overlap of p orbitals forms two sets of π and π^* MOs.

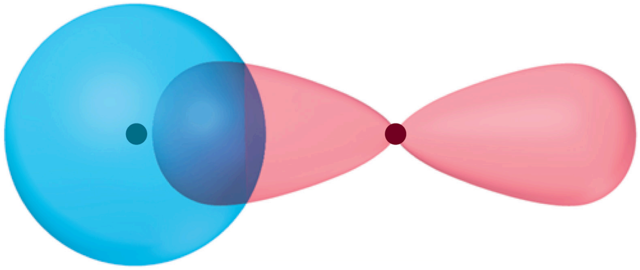
- For atoms *p* orbitals, there are two types of interactions:
  - The *p* orbitals that face each other overlap in σ fashion.
  - The other two sets of *p* orbitals overlap in π fashion.

MO Theory

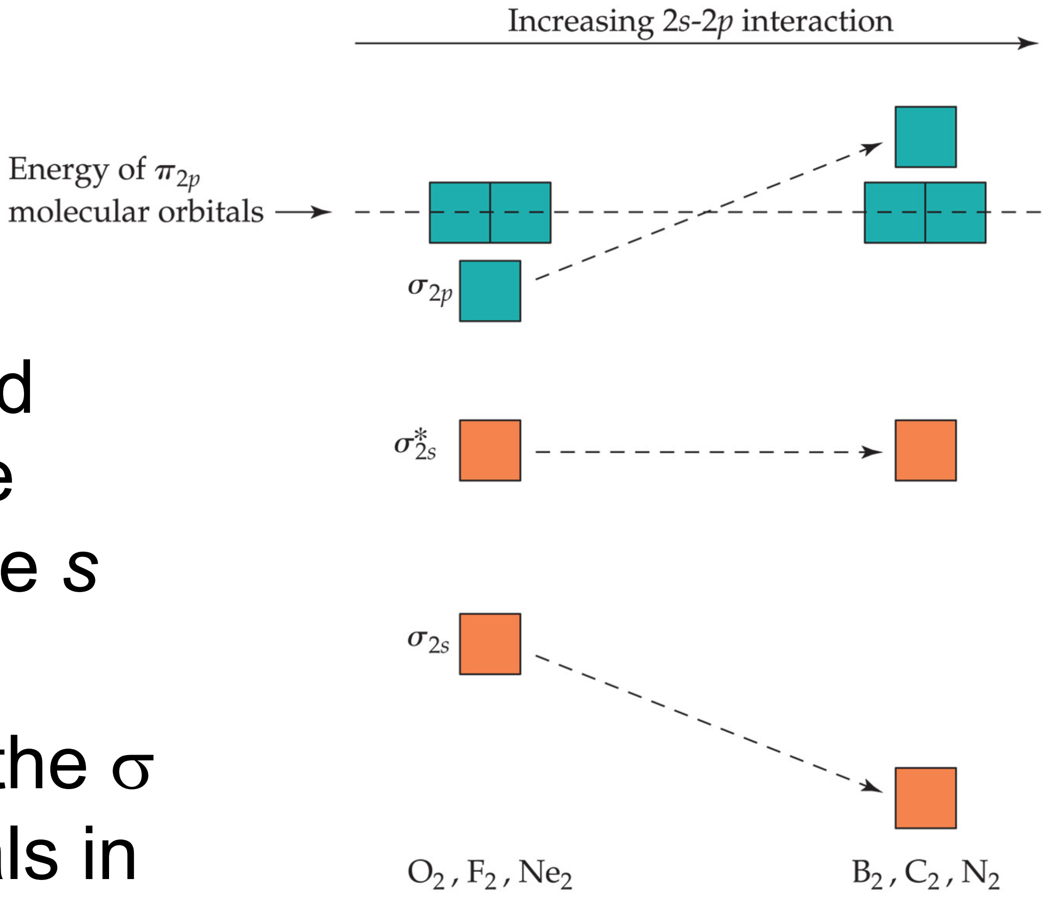


- The resulting MO diagram looks like this.
- There are both σ and π bonding molecular orbitals and σ* and π* antibonding molecular orbitals.
- We're assuming only 2 atomic orbitals mix to form an MO

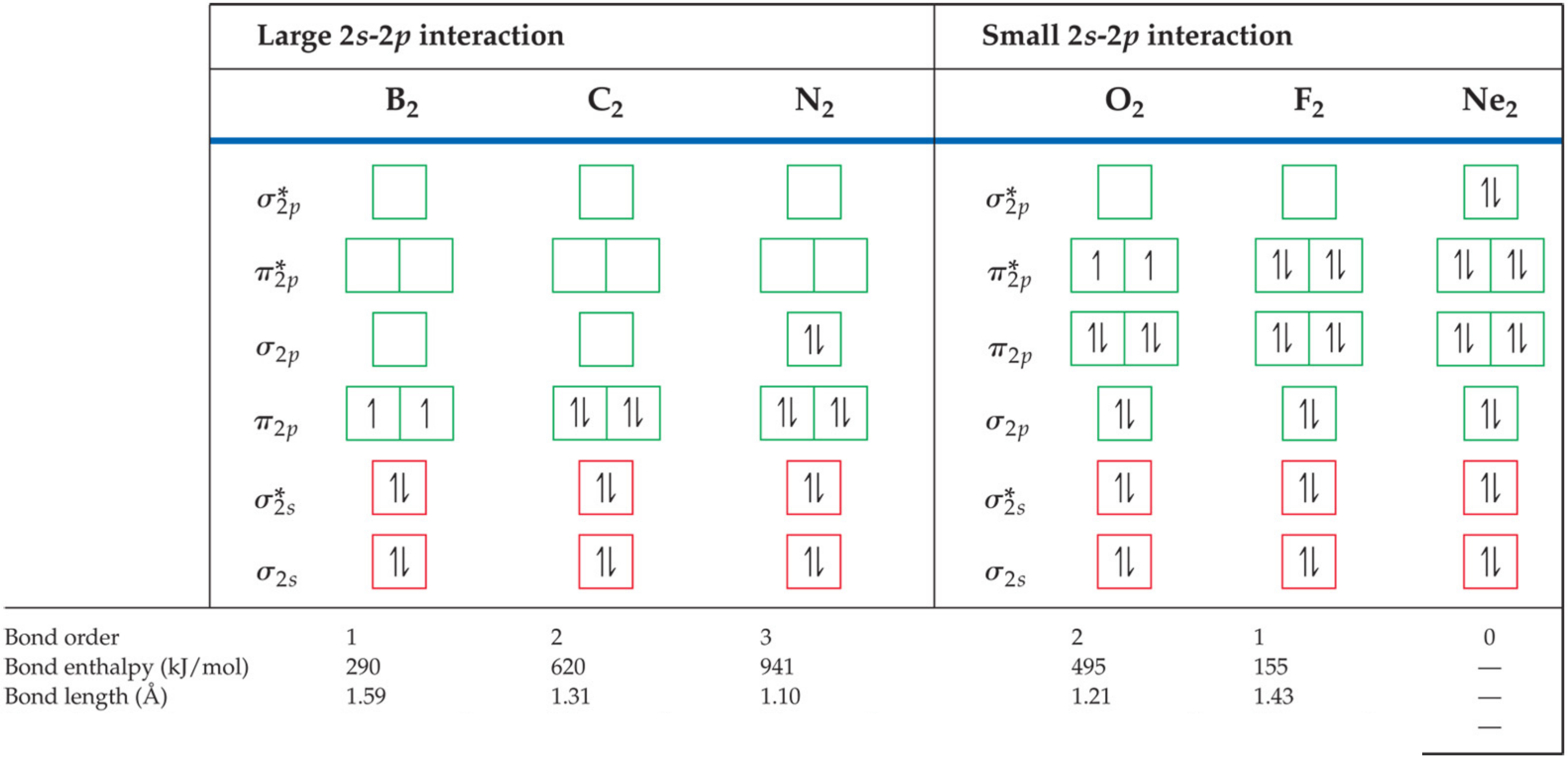
MO Theory



- The earlier *p*-block elements in the second period have a sizeable interaction between the *s* and *p* orbitals.
- This flips the order of the σ and π molecular orbitals in these elements.



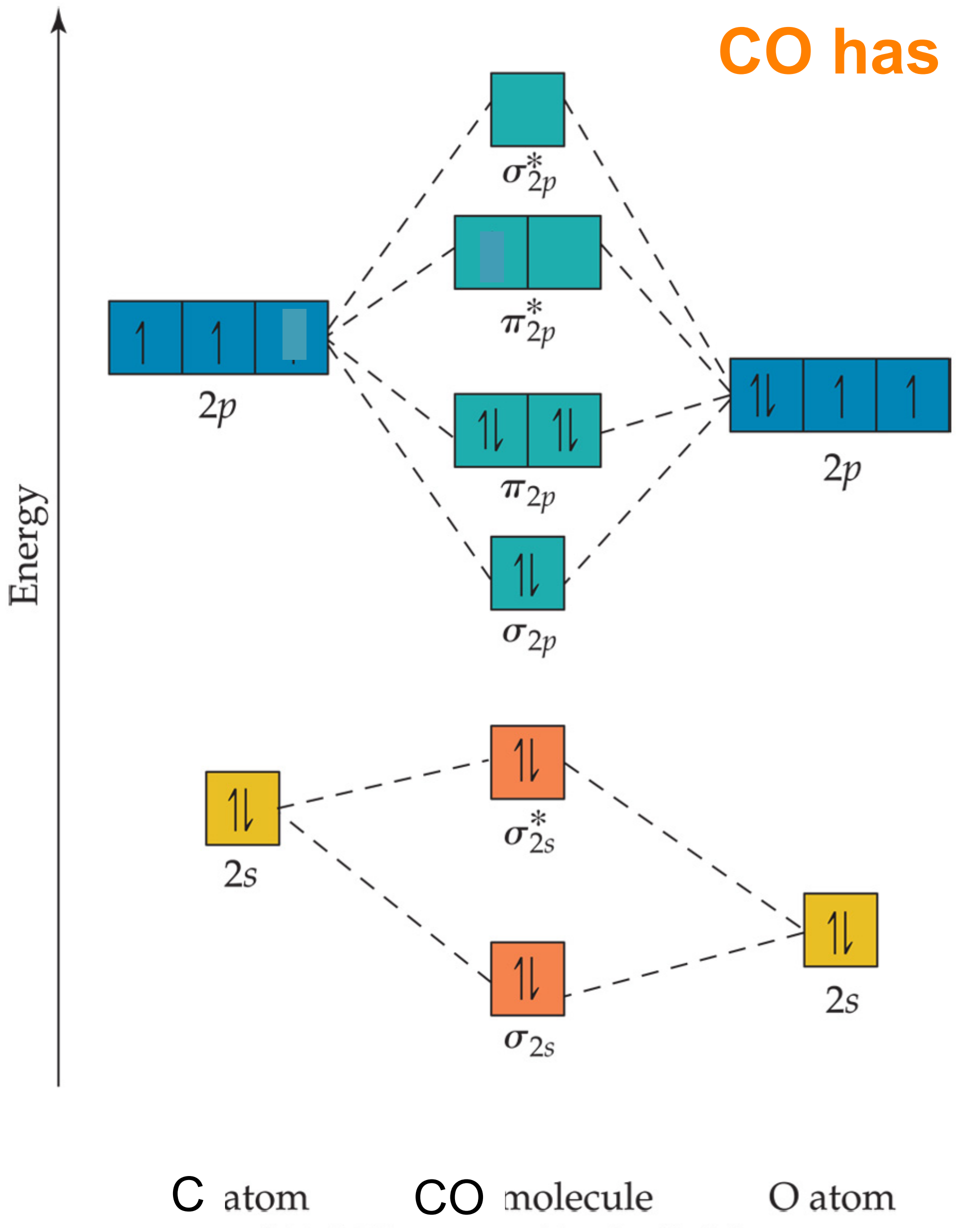
Second-Row MO Diagrams



	Large 2*s*-2*p* interaction				**Small 2*s*-2*p* interaction**		
	B_2	**C_2**	**N_2**		**O_2**	**F_2**	**Ne_2**
σ_{2p}^*	☐	☐	☐	σ_{2p}^*	☐	☐	↑↓
π_{2p}^*	☐☐	☐☐	☐☐	π_{2p}^*	↑ ↑	↑↓ ↑↓	↑↓ ↑↓
σ_{2p}	☐	☐	↑↓	π_{2p}	↑↓ ↑↓	↑↓ ↑↓	↑↓ ↑↓
π_{2p}	↑ ↑	↑↓ ↑↓	↑↓ ↑↓	σ_{2p}	↑↓	↑↓	↑↓
σ_{2s}^*	↑↓	↑↓	↑↓	σ_{2s}^*	↑↓	↑↓	↑↓
σ_{2s}	↑↓	↑↓	↑↓	σ_{2s}	↑↓	↑↓	↑↓
Bond order	1	2	3		2	1	0
Bond enthalpy (kJ/mol)	290	620	941		495	155	—
Bond length (Å)	1.59	1.31	1.10		1.21	1.43	—
							—

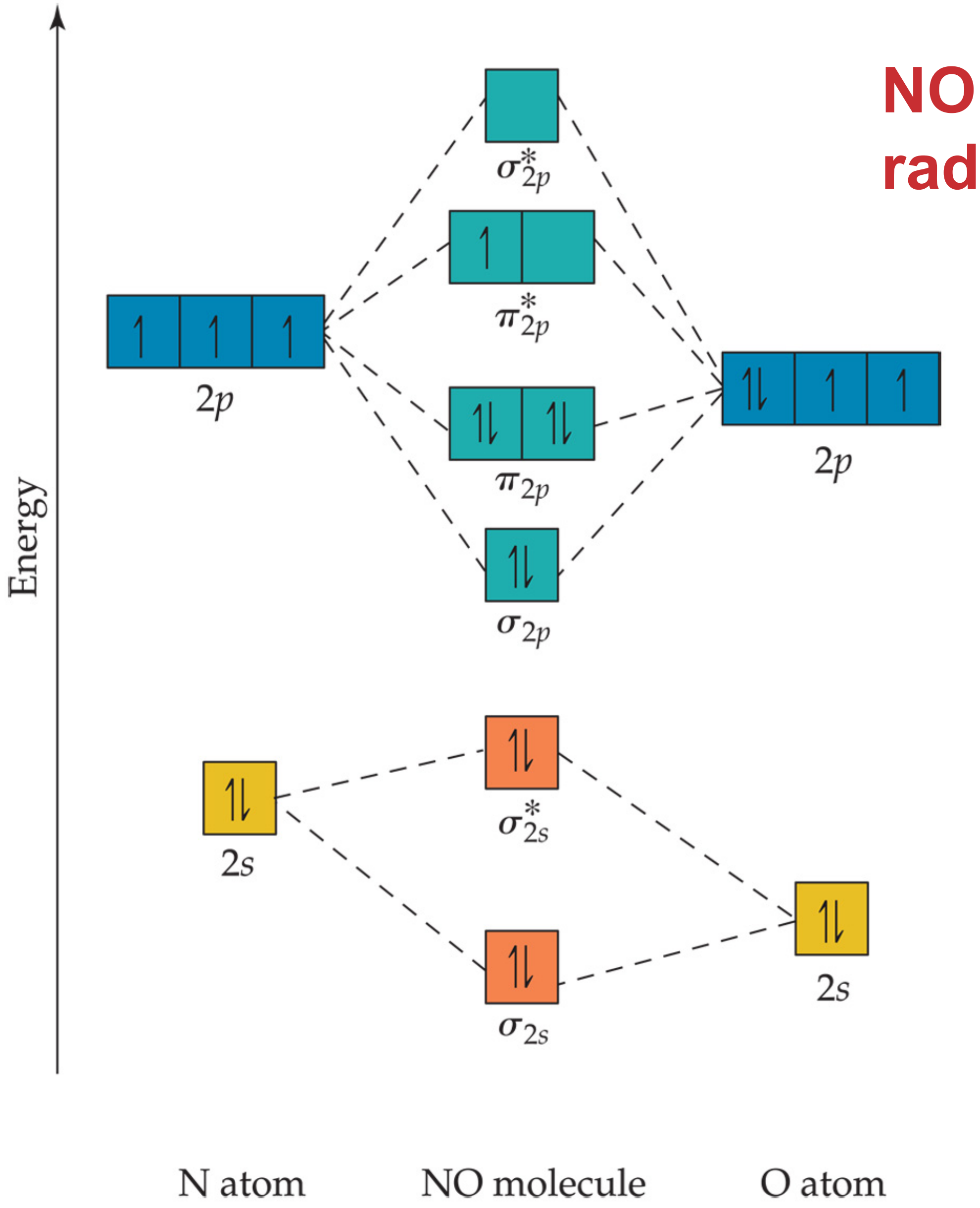
We will not be worrying about this switch in energy here.

Heterodiatomic molecules



CO has a triple bond

Heterodiatomic molecules



NO is paramagnetic radical

Why MO theory?

MO theory explains things that Valence Bond theory does not.

1. Magnetism
2. Color of molecules
3. Excited states of molecules.

Magnetism

We learned that electrons have magnetic quantum number m_s “spin”.

Electrons have magnetic moment.

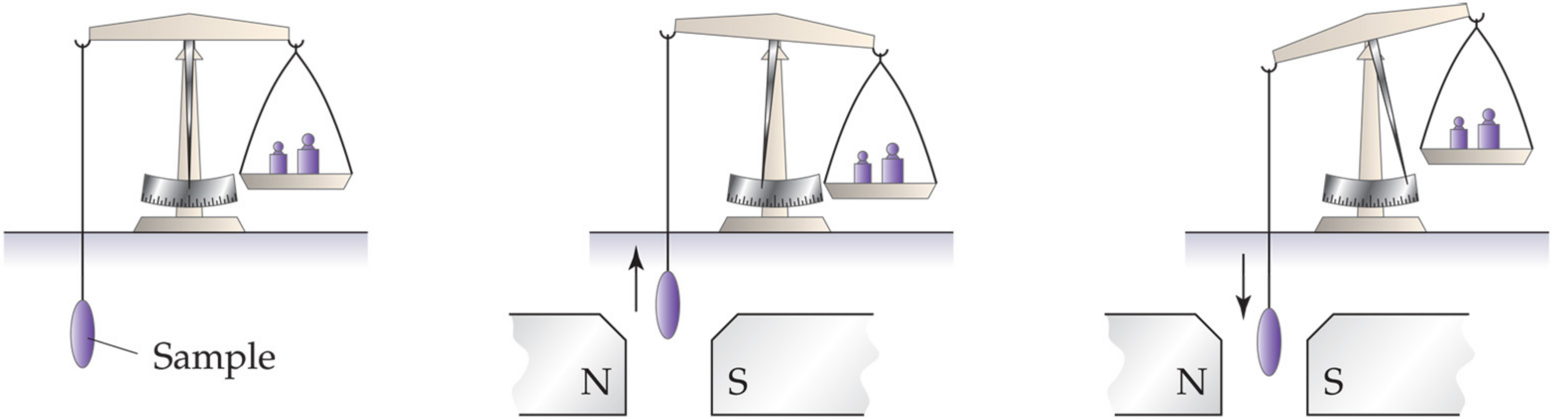
Electrons cause magnetism.

Three kinds of magnetism:

1. Diamagnetism
2. Paramagnetism
3. Ferromagnetism

Diamagnetic

Paramagnetic



(a) The sample is first weighed in the absence of a magnetic field.

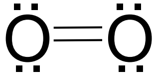
(b) When a field is applied, a diamagnetic sample moves out of the field and thus appears to have a lower mass.

(c) A paramagnetic sample is drawn into the field and thus appears to gain mass.

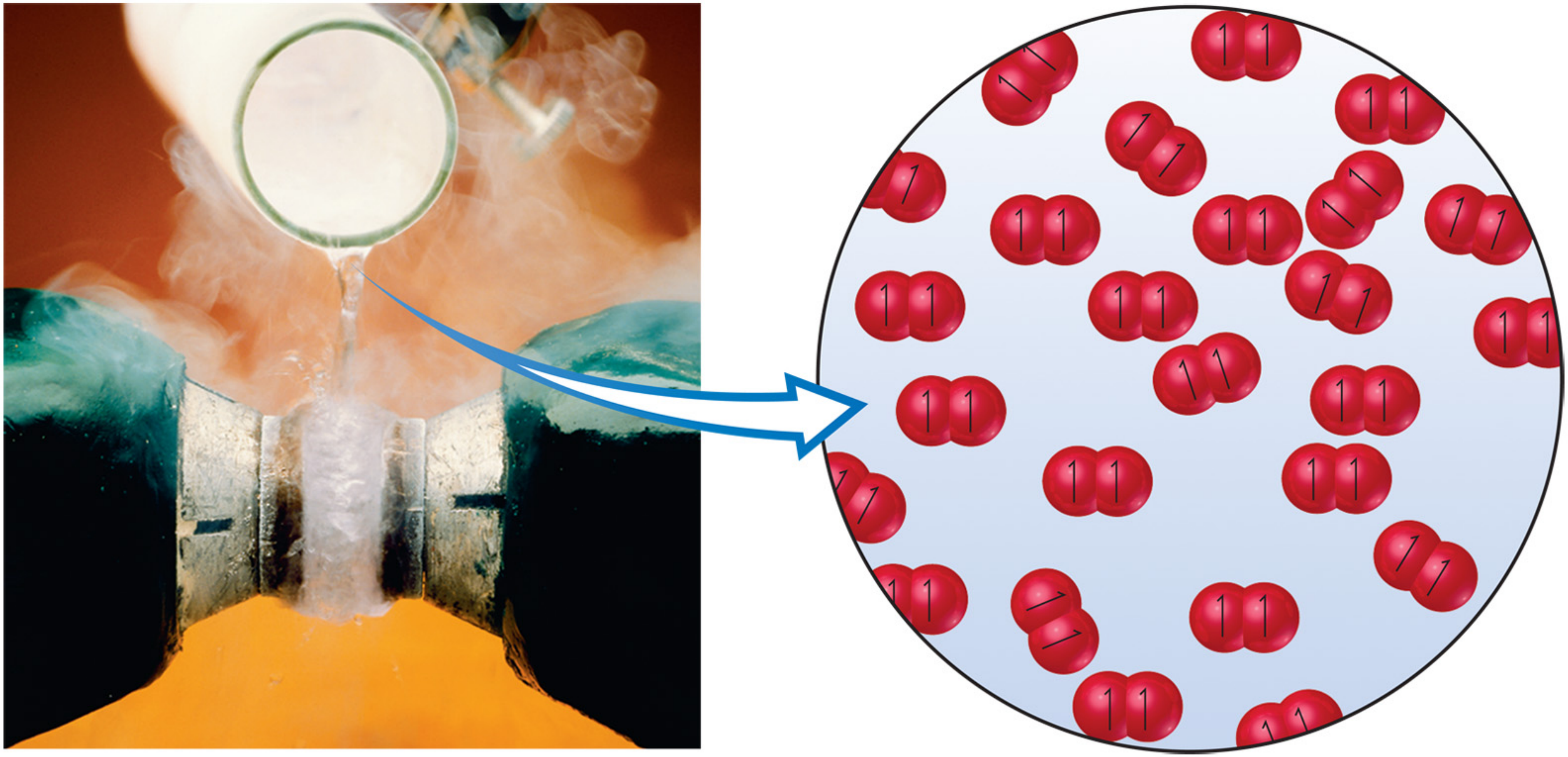
Electrons all paired

Unpaired electrons

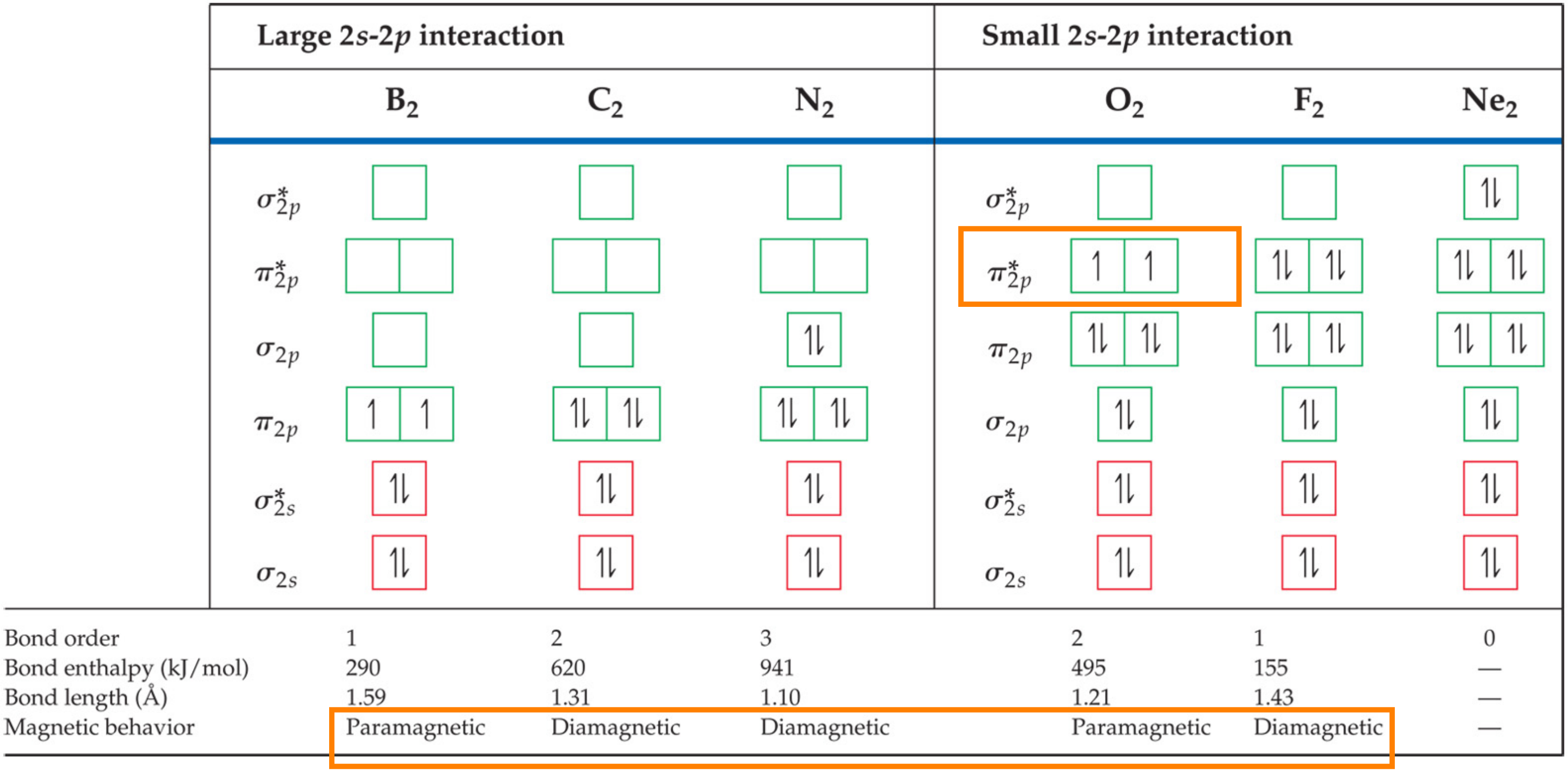
Oxygen O_2 is Paramagnetic!



Why?



MO to the rescue

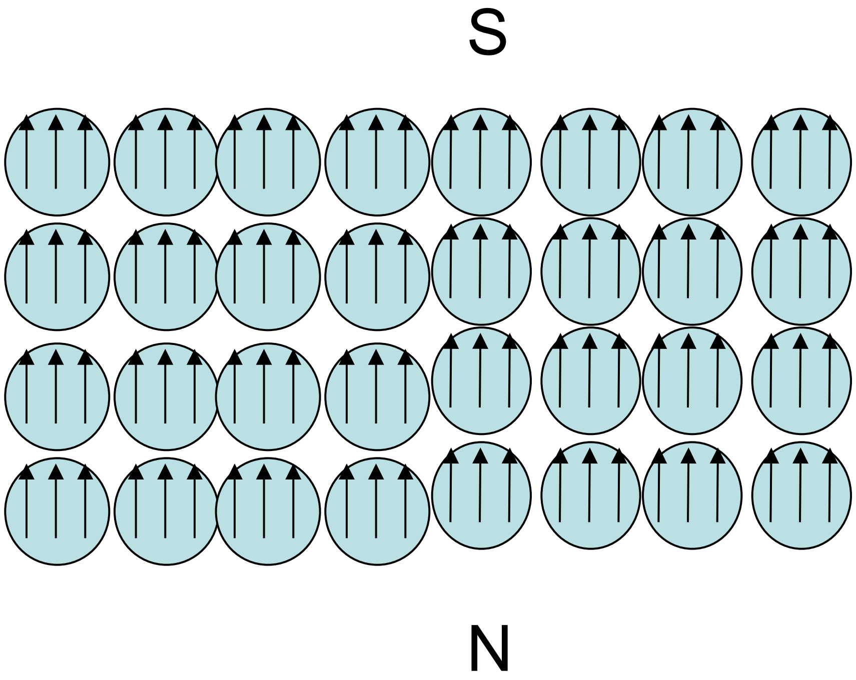


Large 2s-2p interaction				Small 2s-2p interaction			
	B_2	**C_2**	**N_2**		**O_2**	**F_2**	**Ne_2**
σ^*_{2p}				σ^*_{2p}			↑↓
π^*_{2p}				π^*_{2p}	↑ ↑	↑↓ ↑↓	↑↓ ↑↓
σ_{2p}			↑↓	π_{2p}	↑↓ ↑↓	↑↓ ↑↓	↑↓ ↑↓
π_{2p}	↑ ↑	↑↓ ↑↓	↑↓ ↑↓	σ_{2p}	↑↓	↑↓	↑↓
σ^*_{2s}	↑↓	↑↓	↑↓	σ^*_{2s}	↑↓	↑↓	↑↓
σ_{2s}	↑↓	↑↓	↑↓	σ_{2s}	↑↓	↑↓	↑↓
Bond order	1	2	3		2	1	0
Bond enthalpy (kJ/mol)	290	620	941		495	155	—
Bond length (Å)	1.59	1.31	1.10		1.21	1.43	—
Magnetic behavior	Paramagnetic	Diamagnetic	Diamagnetic		Paramagnetic	Diamagnetic	—

Ferromagnetism

Like iron, pulled to a magnet.

Long range order of spins in material

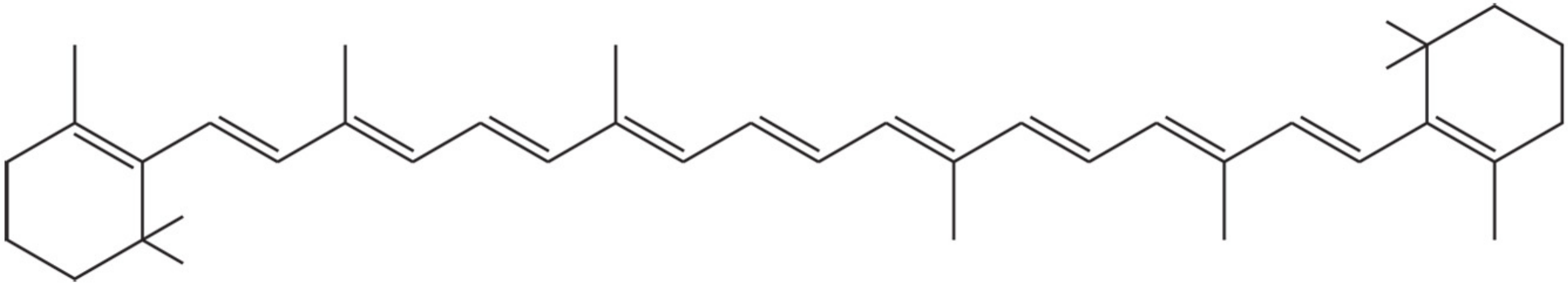


MO theory and color

Remember, elements produced color because of electrons
Moving from higher to lower ***atomic*** energy levels

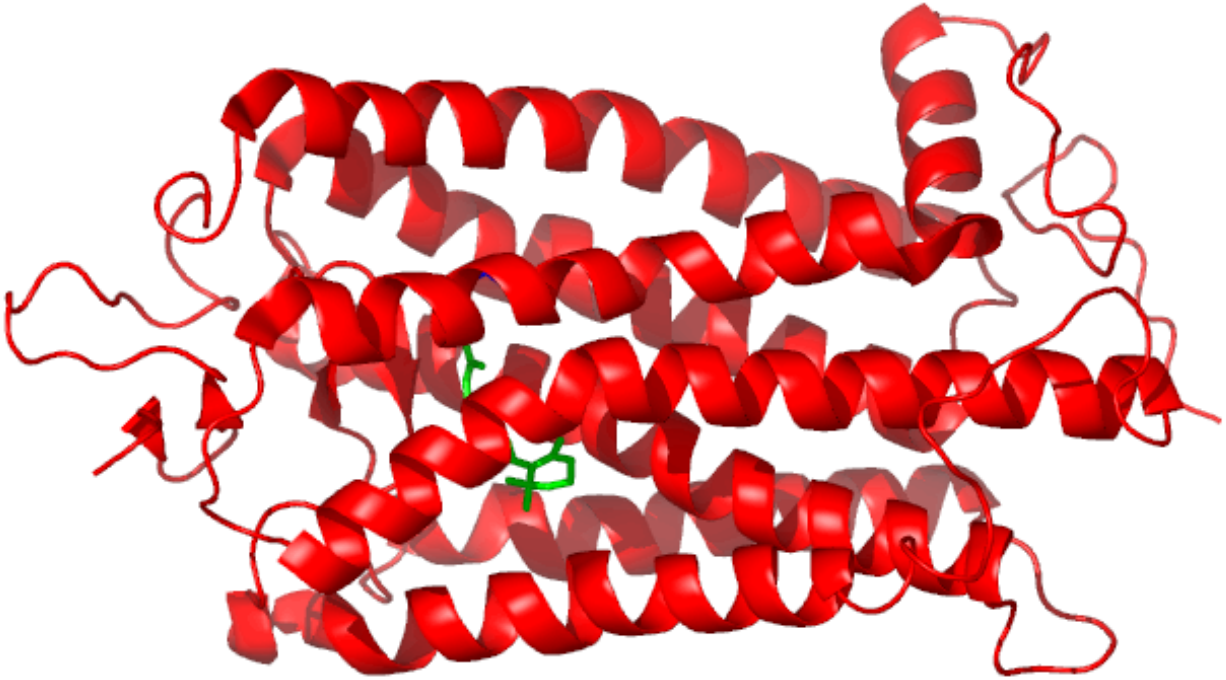
With MO theory, color of molecules is explained by electrons
Moving between ***molecular*** orbitals.

Conjugated polyenes have MO’s that give rise to colors, energy is absorbed, electrons go to higher energy levels.



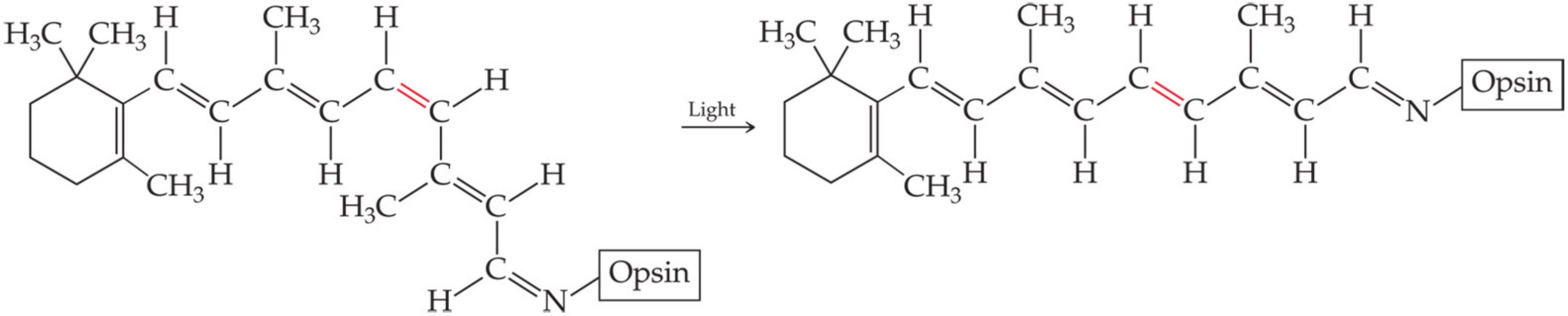
β-caroten

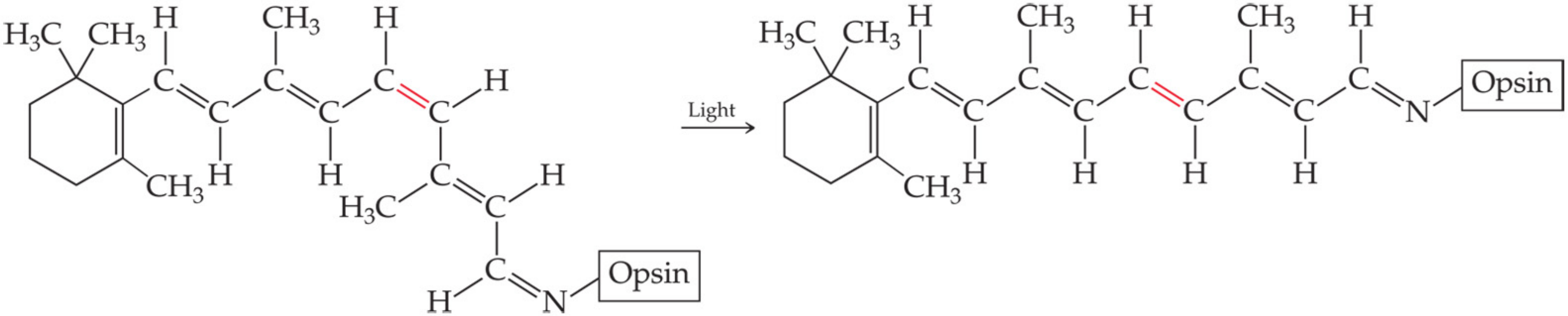
How do we see color?

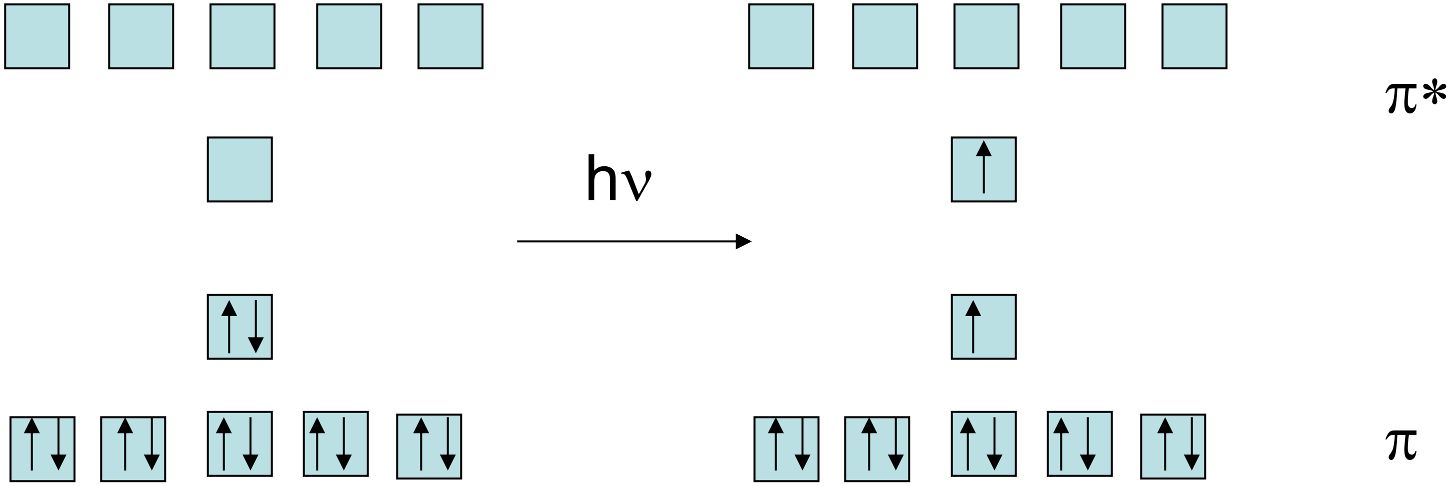


Isomerization wiggles the rest of the protein, sends nerve signal

Rhodopsin



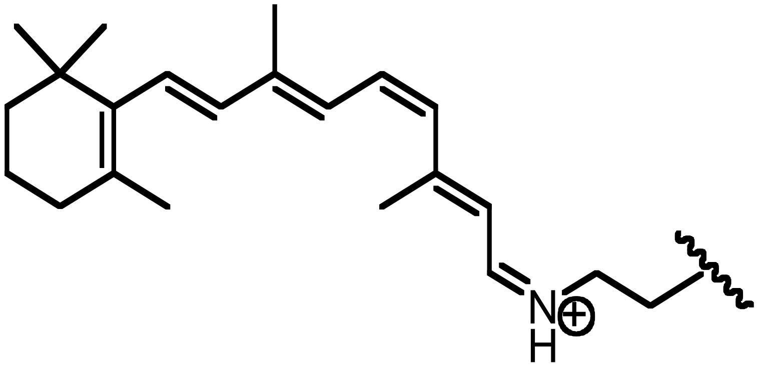


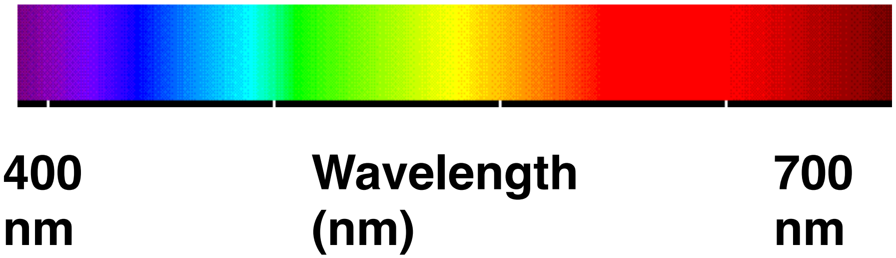


This weakens the pi bond so rotation can happen

How does Color Vision work?

Each rhodopsin (Rod, Blue, Green, Red) protein exhibits a different wavelength maxima as a result of 11*cis*-retinal binding as a protonated Schiff base (PSB) via a lysine residue. It is these interactions that lead to color vision and allow us to see the whole visible spectrum.





11-*cis*-retinal : ~ 380 nm

11-*cis*-retinal SB : ~ 365 nm

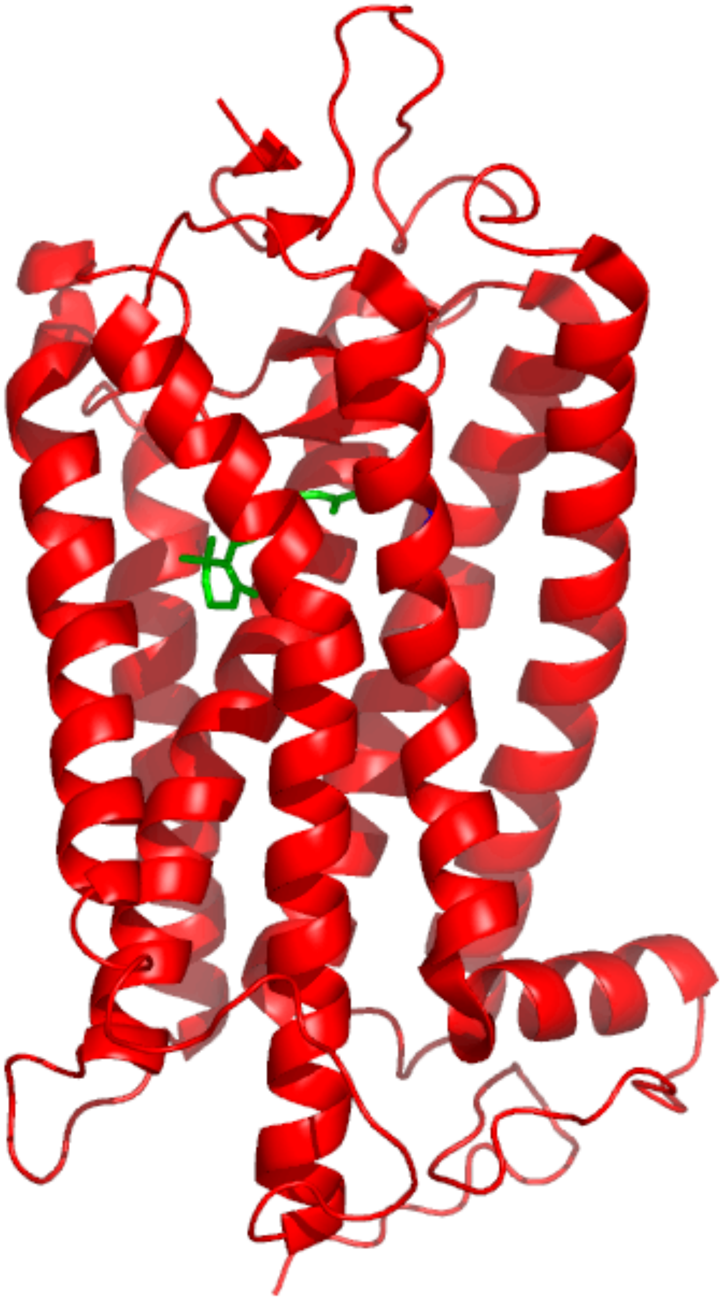
11-*cis*-retinal PSB : ~ 440 nm

PSB in **Blue** Rhodopsin : ~ 410 nm

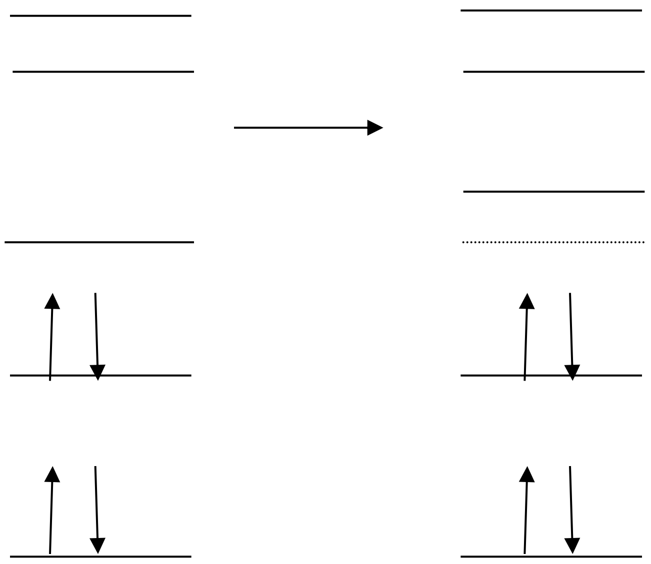
PSB in **Green** Rhodopsin : ~ 530 nm

PSB in **Red** Rhodopsin : ~ 560 nm

PSB in **Rod** Rhodopsin : ~ 500 nm



You can change the energy of the MO’s of retinal by changing the environment around the molecule.



Exam 3 topics

- Chapter 7, periodic properties,
  - Effective nuclear charge
  - Electronegativity
  - Electron affinity
  - Ionization energy
  - Periodic properties (less emphasized)
- Chapter 8,
  - covalent and ionic bonding
  - Electronegativity
  - polar bonds
- Chapter 8, Lewis structures
  - standard lewis structures
  - formal charge
  - resonance
  - less than an octet
  - more than an octet

Exam 3 topics

- Chapter 9, geometry and shape of molecules
- Chapter 9, polarity/dipole moments of whole molecules
- Chapter 9, introduction to covalent bonding, diatomics
- Chapter 9, hybridization sp, sp^2, sp^3, sp^3d, sp^3d^2
- Chapter 9, Valence Bond Theory

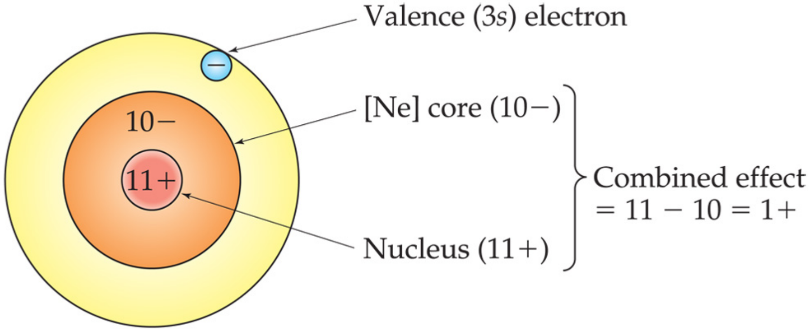
- Not covered:
  - Molecular Orbital Theory

Chapter 7

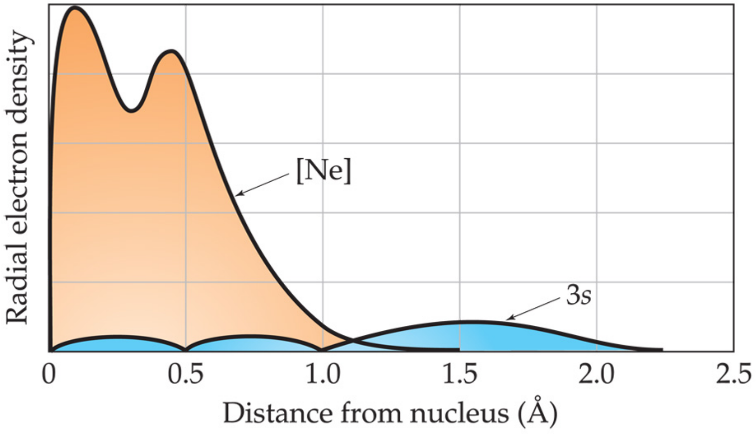
- Periodic trends
- Effective nuclear charge
- Ionization energy, trends
- electron affinity, trends.

Effective Nuclear Charge

Na



(a)



The effective nuclear charge, Z_{eff}, is:

$Z_{eff} = Z - S$

where Z = atomic number S = screening constant, usually close to the number of inner (n-1) electrons.

Valence electrons:

How many valence electrons in:

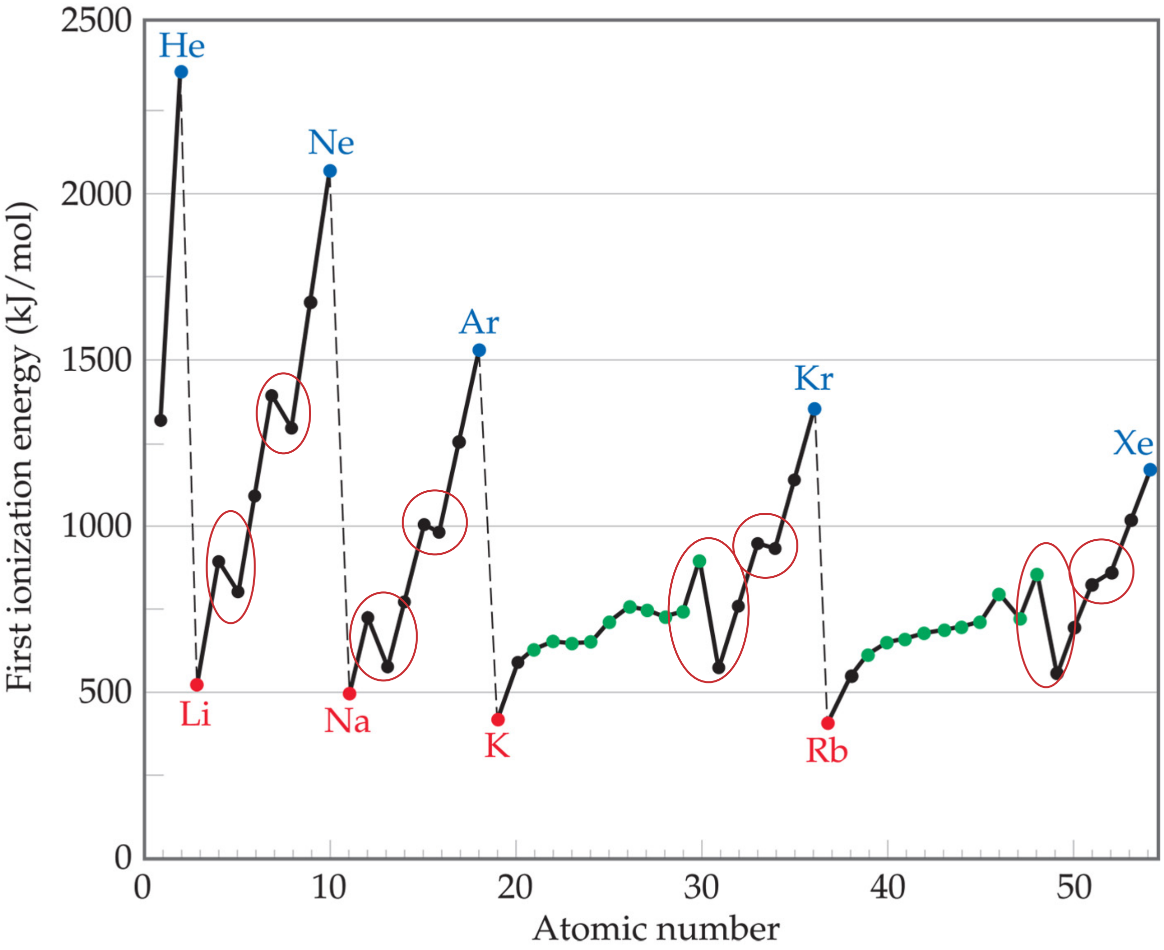
O
O^{2-}
Co
Co^{2+}

Valence electrons:

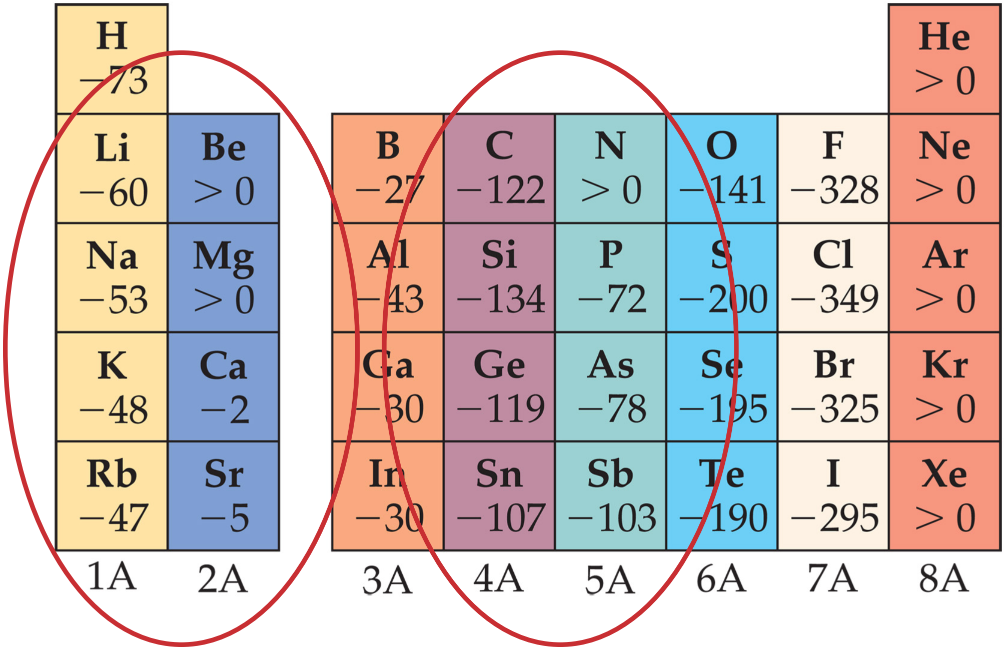
- all electrons in outer most shell
- all electrons in an unfilled subshell.

Trends in First Ionization Energies

On a smaller scale, there are two jags in each line. Why?



Trends in Electron Affinity



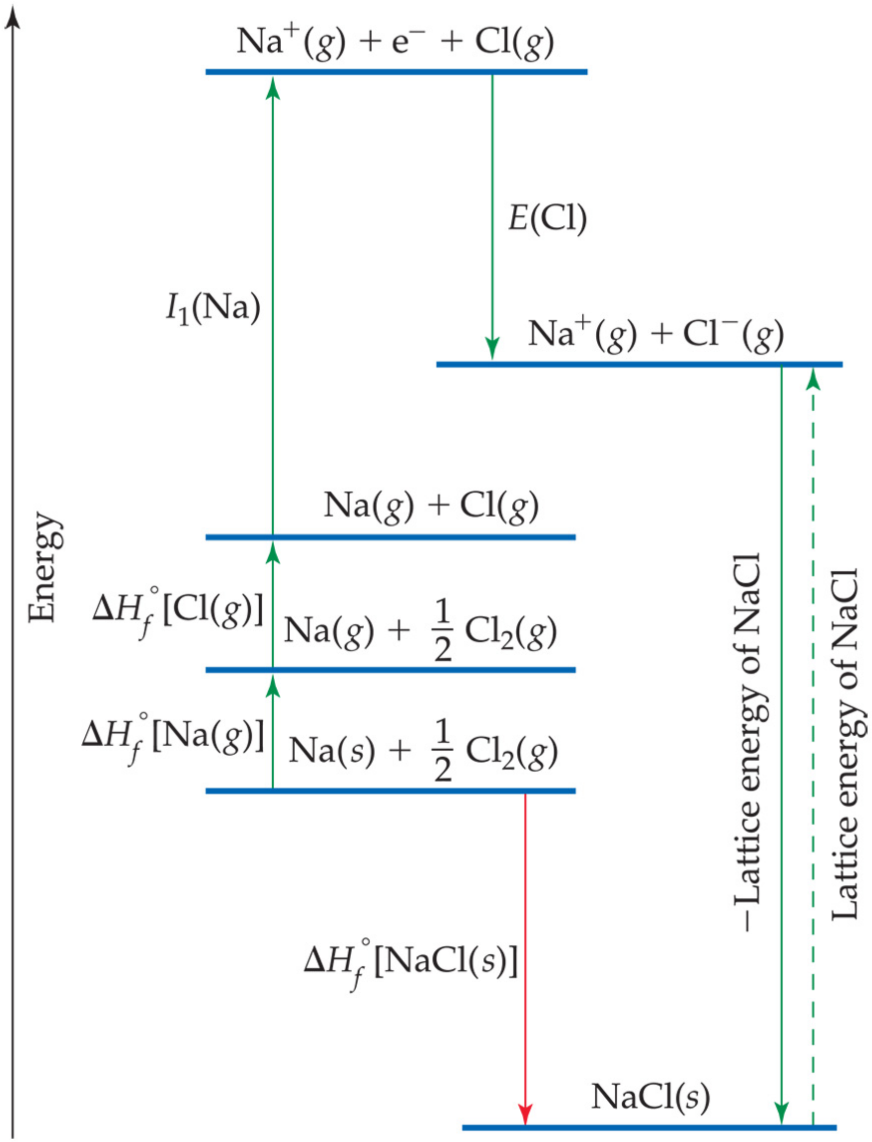
1A	2A	3A	4A	5A	6A	7A	8A
H −73							**He** > 0
Li −60	**Be** > 0	**B** −27	**C** −122	**N** > 0	**O** −141	**F** −328	**Ne** > 0
Na −53	**Mg** > 0	**Al** −43	**Si** −134	**P** −72	**S** −200	**Cl** −349	**Ar** > 0
K −48	**Ca** −2	**Ga** −30	**Ge** −119	**As** −78	**Se** −195	**Br** −325	**Kr** > 0
Rb −47	**Sr** −5	**In** −30	**Sn** −107	**Sb** −103	**Te** −190	**I** −295	**Xe** > 0

There are also two discontinuities in this trend.

Why?????

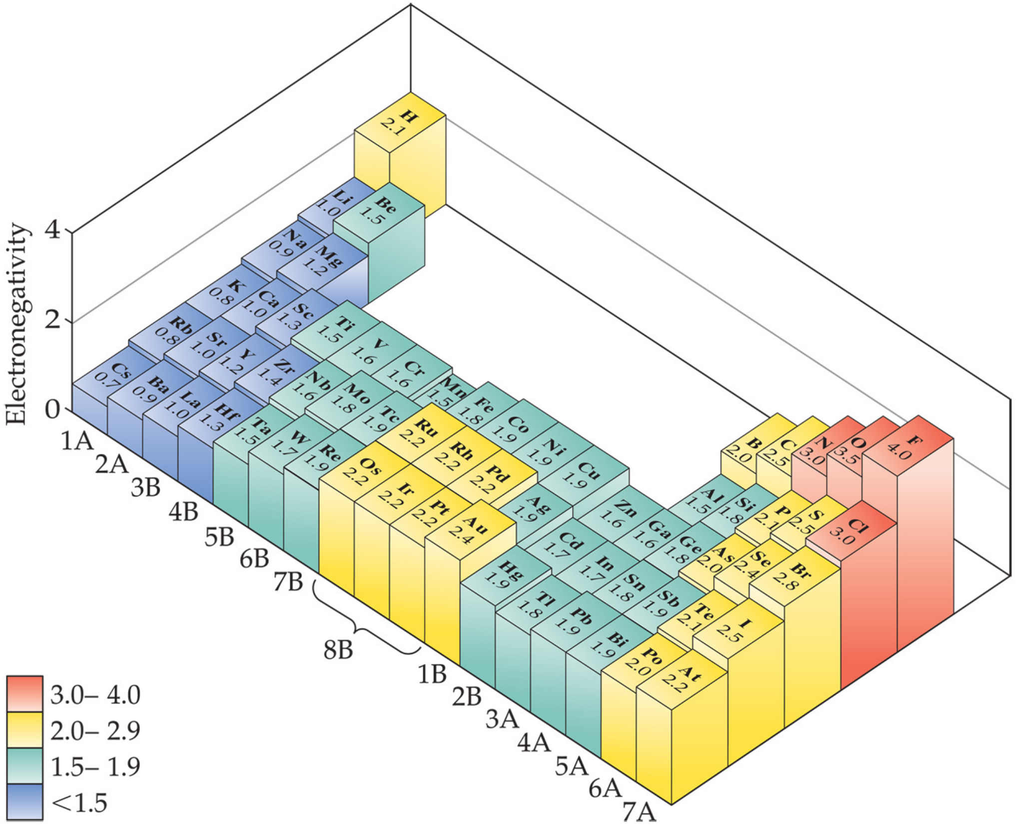
Exam 3 topics

- Chapter 8, covalent and ionic bonding
  - What is ionic bonding? What holds the atoms together?
  - Energetics of ionic bonding
  - Lattice energy
  - What effects the size of the lattice energy?
    - Ion size
    - Ion charge



Exam 3 topics

- Chapter 8, electronegativity
  - What is electronegativity?
  - What are the trends on the periodic table?
- Chapter 8, polar bonds



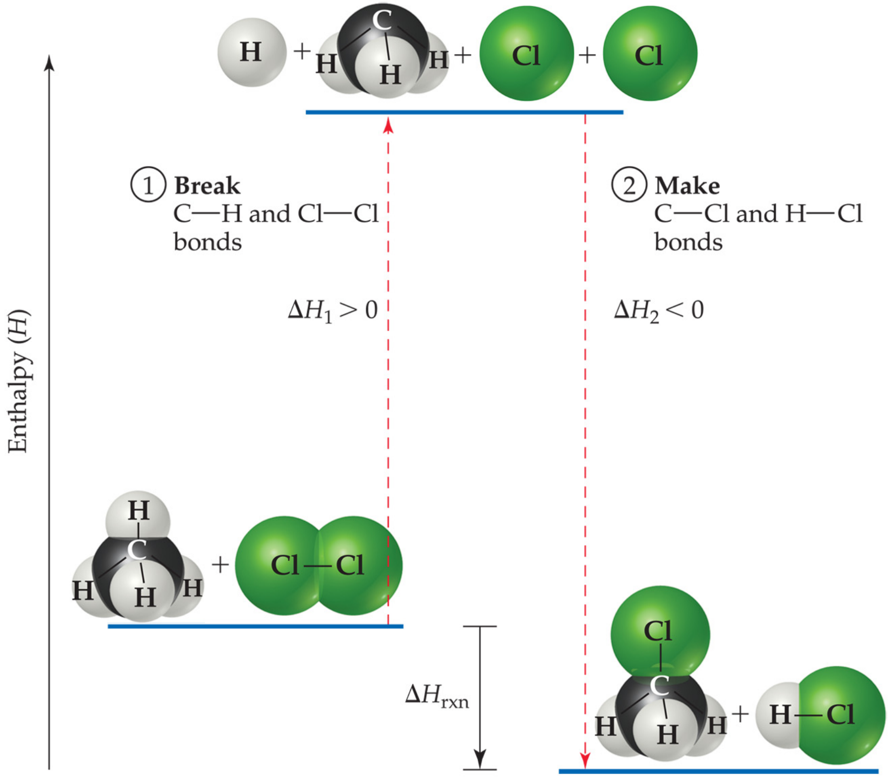
Exam 3 topics

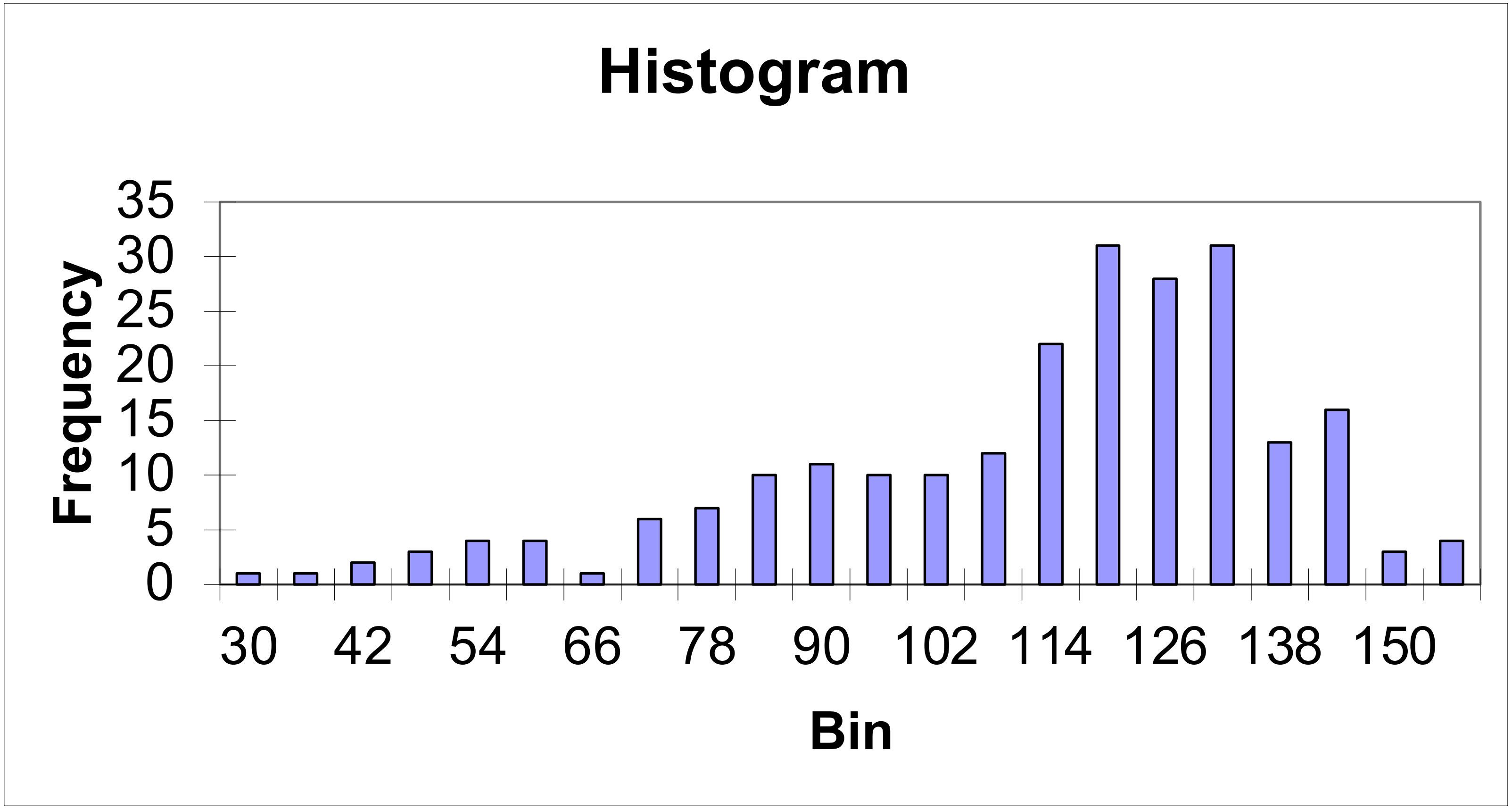
- Chapter 8, Lewis structures
  - standard lewis structures
  - formal charge
  - resonance
  - less than an octet
  - more than an octet

XeF_2 XeF_6, CO_3^-, NO_2, ClO_4^-, SbF_5, SO_2, SO_3^{2-}, H_2O_2

Exam 3 topics

- Chapter 8, bond enthalpies
  - use bond enthalpy table to calculate a ΔH of reaction
  - bonds broken - bonds made = enthapy of reaction.




Histogram
Frequency
35
30
25
20
15
10
5
0
30
42
54
66
78
90
102
114
126
138
150
Bin

Bin	*Frequency*
30	1
36	1
42	2
48	3
54	4
60	4
66	1
72	6
78	7
84	10
90	11
96	10
102	10
108	12
114	22
120	31
126	28
132	31
138	13
144	16
150	3
156	4

Exam 3 topics

- Chapter 9, geometry and shape of molecules, VSEPR.
- Chapter 9, polarity/dipole moments of whole molecules

- Give the geometry, shape and predict the dipole moment of each:

- XeF_2, ClO_4^-, SF_4, BrO_2^-

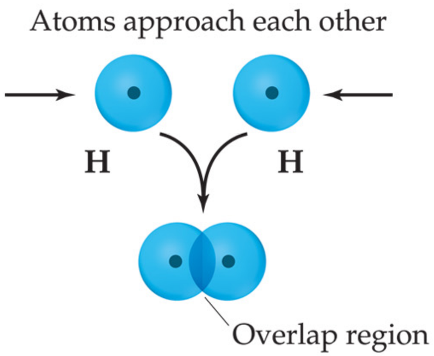
Valence bond theory

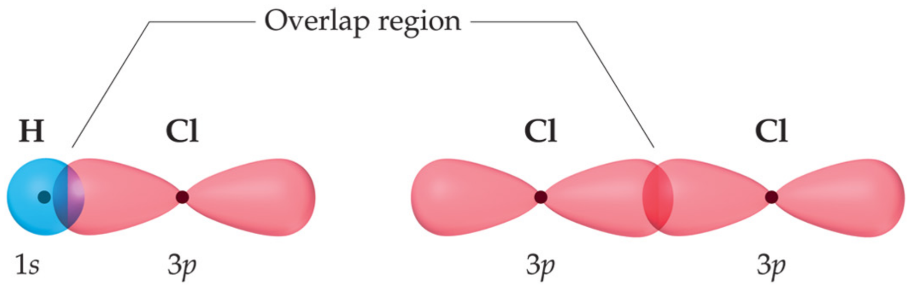
- Hybridization only

Exam 3 topics

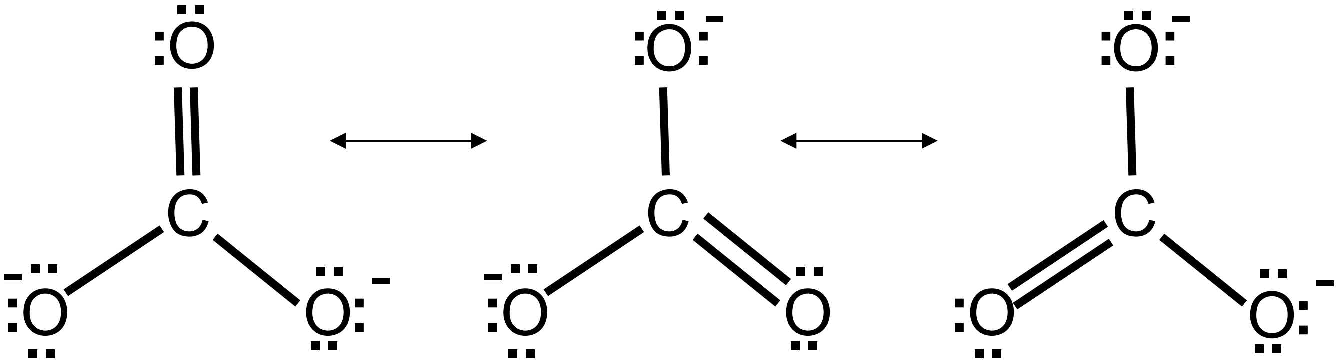
Chapter 9, introduction to covalent bonding, diatomics

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





15.



trigonal planar,trigonal planar, nonpolar