

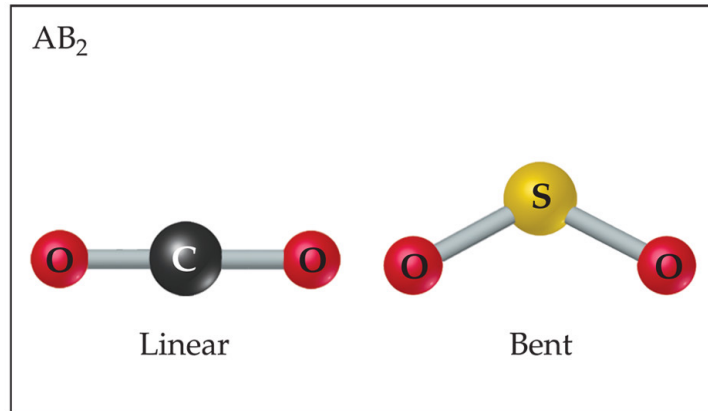
Chapter 9

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.

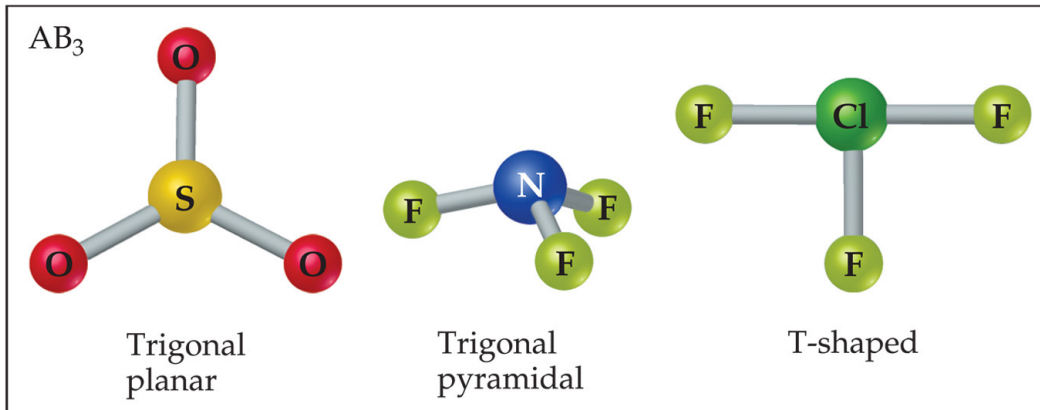
Molecular Shapes



- geometry & shape of molecule critical
- we can easily predict the 3D structure of a molecule just by

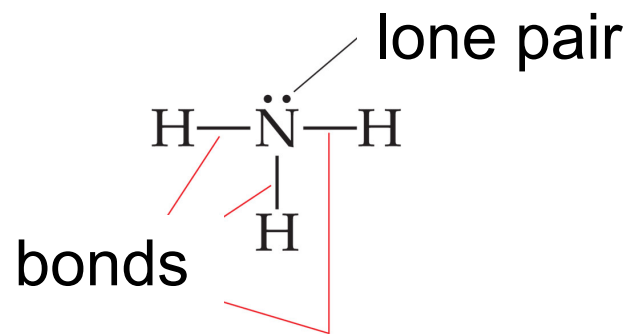
adding up:

- **bound atoms + lone pairs**

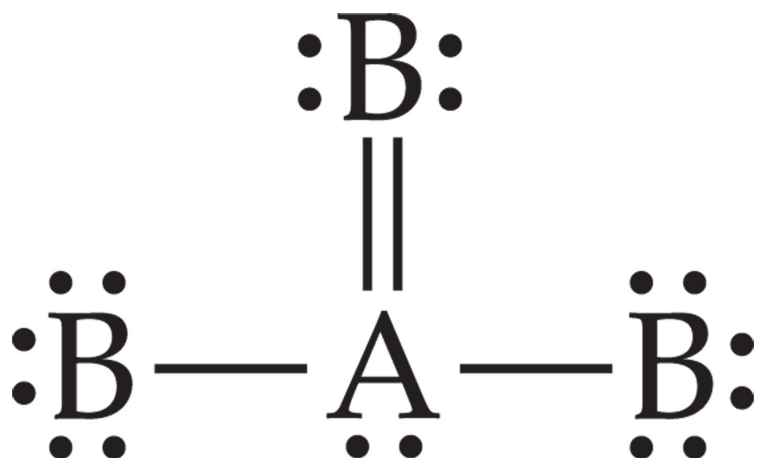


What Determines the Shape of a Molecule?

- 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”



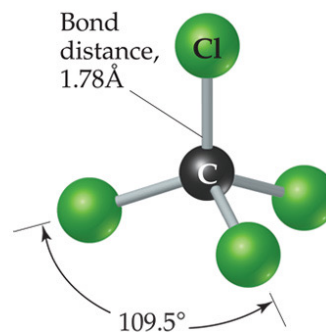
- The central atom has four “things” around it. A “thing” is an **atom** or a **lone pair** of electrons.
- # things = **atoms plus lone pairs**

Valence Shell Electron Pair Repulsion Theory (VSEPR)

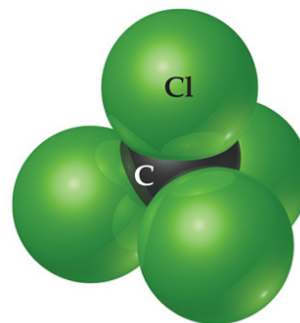
“The best arrangement of a given number of things is the one that minimizes the repulsions among them.”



(a)



(b)

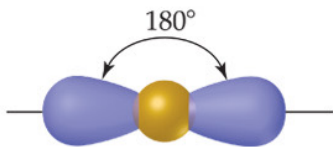


(c)

number of things arrangement geometry bond angles

Geometries

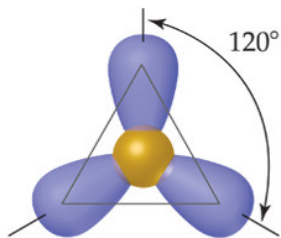
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Linear

180°

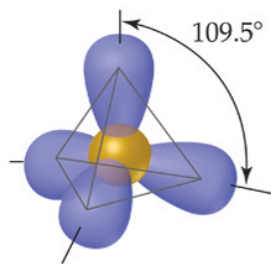
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Trigonal planar

120°

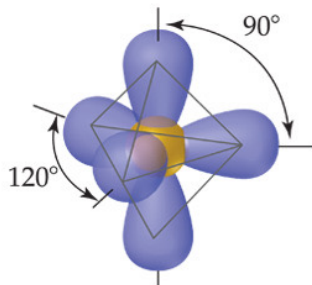
4



Tetrahedral

109.5°

5

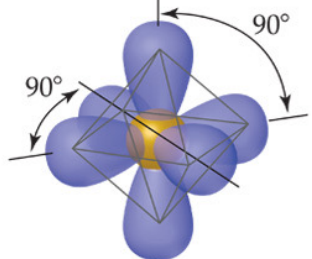


Trigonal bipyramidal

120°

90°

6



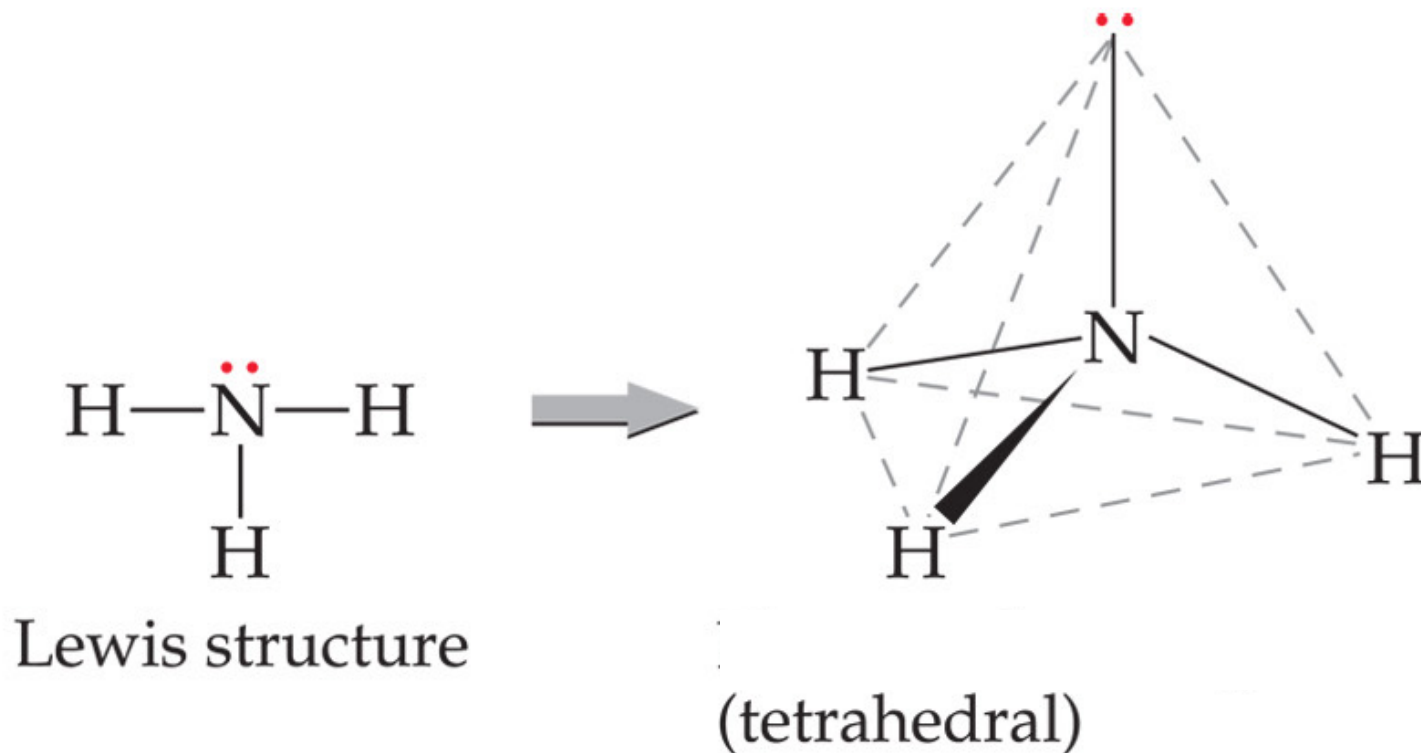
Octahedral

90°

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

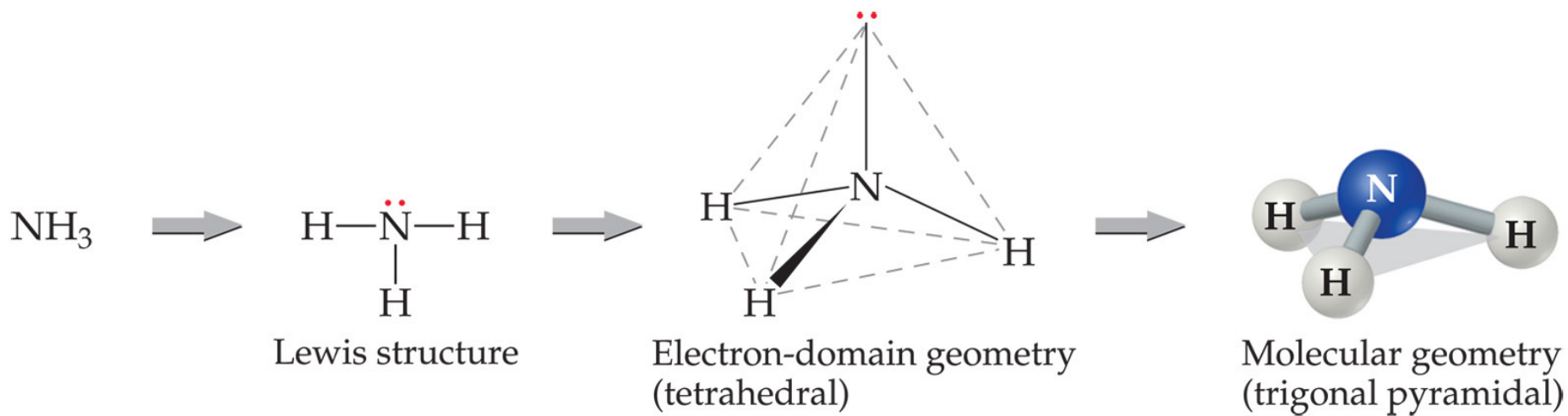
You must learn these!

GEOMETRIES



- 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



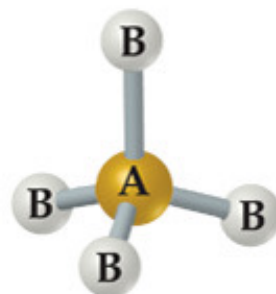
- The geometry is often *not* the **shape** of the molecule, however.
- The “**shape**” is defined by the positions of **only the atoms in the molecules, not the lone pairs.**

Geometries vs. shape

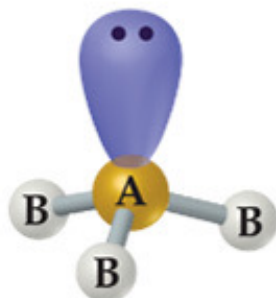
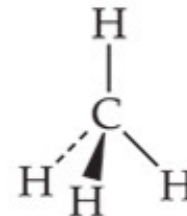
Within each **geometry**, there might be more than one **shape**.

All three have tetrahedral *geometry*

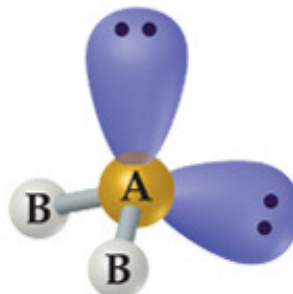
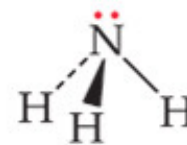
But 3 different *shapes*.



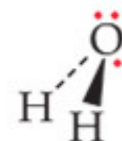
Tetrahedral shape



Trigonal pyramidal shape



Bent shape



Linear geometry two things

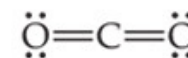
things geometry atoms lone pairs shape example

2



2

0

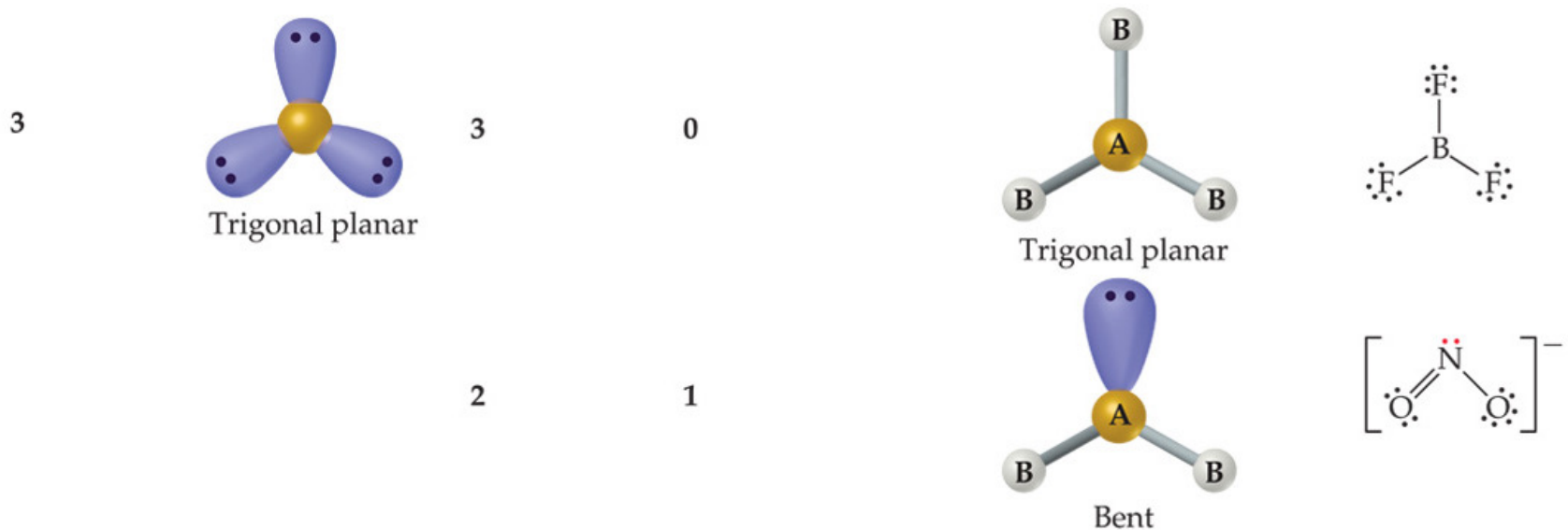


- In this geometry, there is only one molecular geometry: linear.
- NOTE: If there are only two atoms in the molecule, the molecule will be linear no matter what the geometry is.

Trigonal Planar geometry

3 things

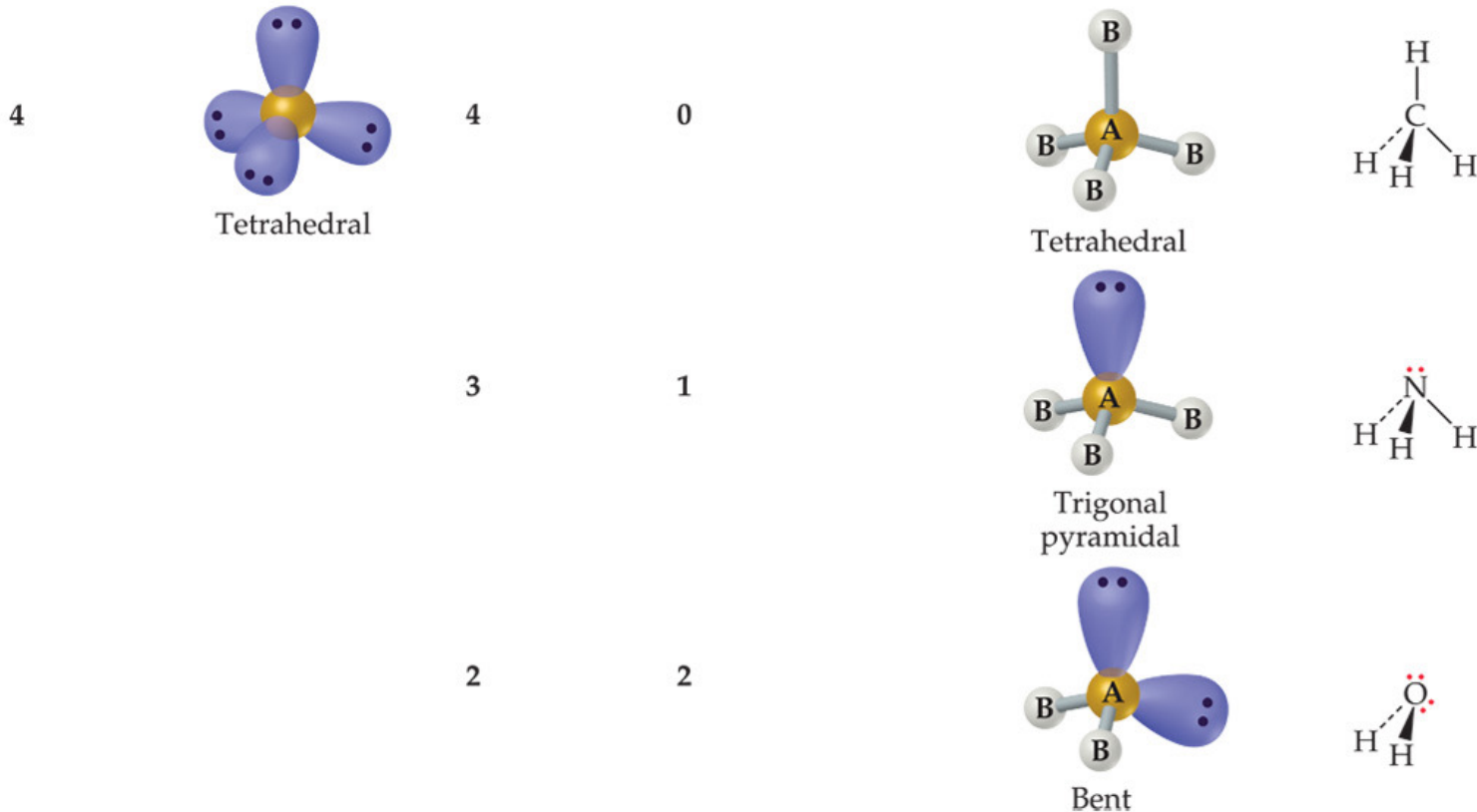
things geometry atoms lone pairs shape example



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

Tetrahedral geometry 4 things

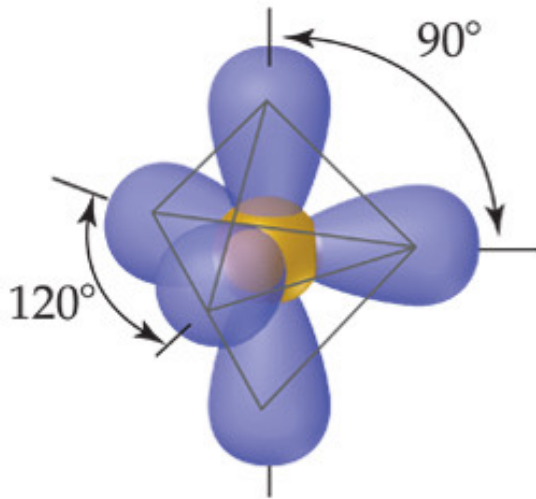
Things geometry atoms lone pairs shape example



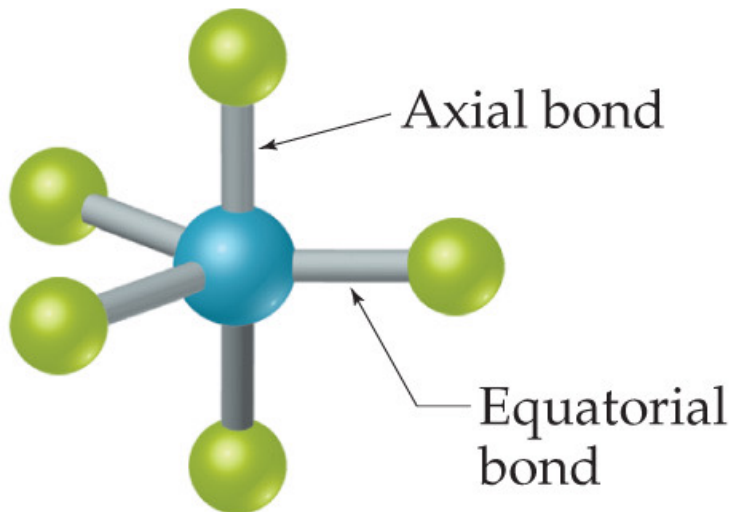
- There are three molecular geometries:
 - Tetrahedral, if no lone pairs
 - Trigonal pyramidal if one is a lone pair
 - Bent if there are two lone pairs

Trigonal Bipyramidal geometry

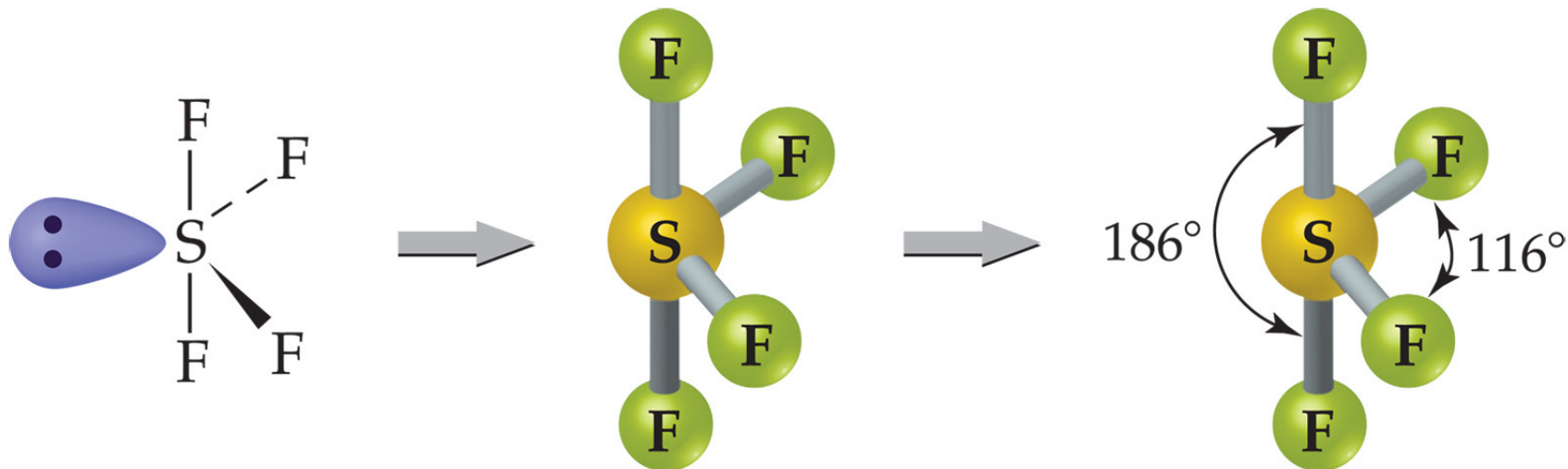
5 things



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



Trigonal Bipyramidal geometry

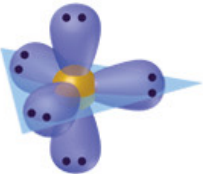
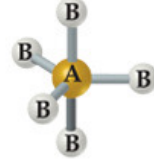
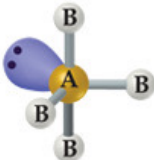
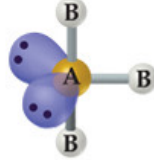
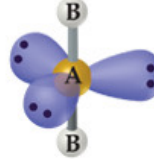


Lower-energy conformations result from having lone pairs in equatorial, rather than axial, positions in this geometry.

Lone pairs are fatter than atoms, take up more space.

Trigonal Bipyramidal geometry

Things geometry atoms lone pairs shape example

5	 <p>Trigonal bipyramidal</p>	5	0	 <p>Trigonal bipyramidal</p>	PCl ₅
		4	1	 <p>Seesaw</p>	SF ₄
		3	2	 <p>T-shaped</p>	ClF ₃
		2	3	 <p>Linear</p>	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
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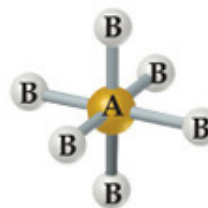
6



Octahedral

6

0

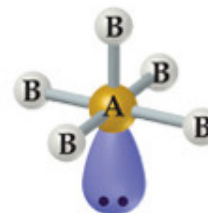


Octahedral

SF₆

5

1

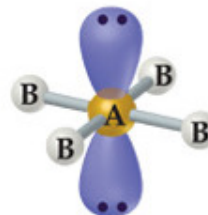


Square pyramidal

BrF₅

4

2



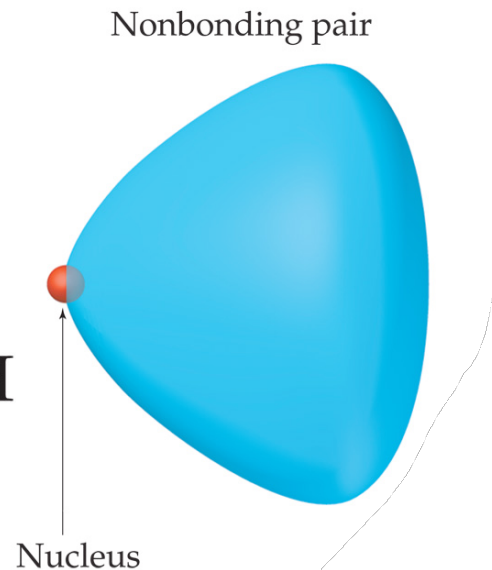
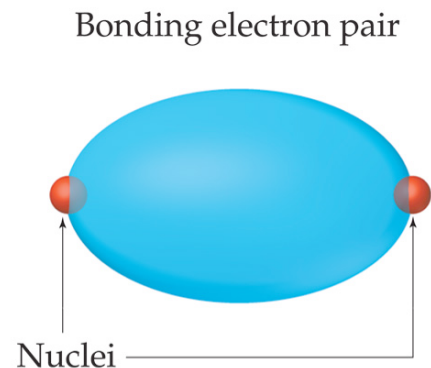
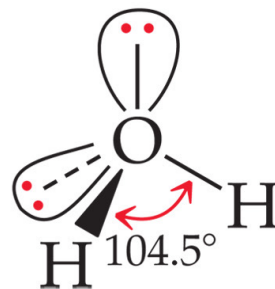
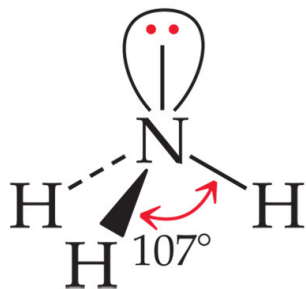
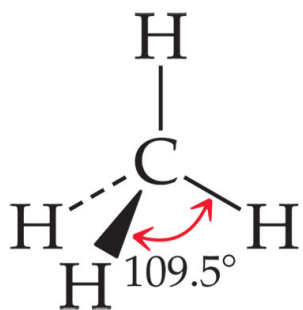
Square planar

XeF₄

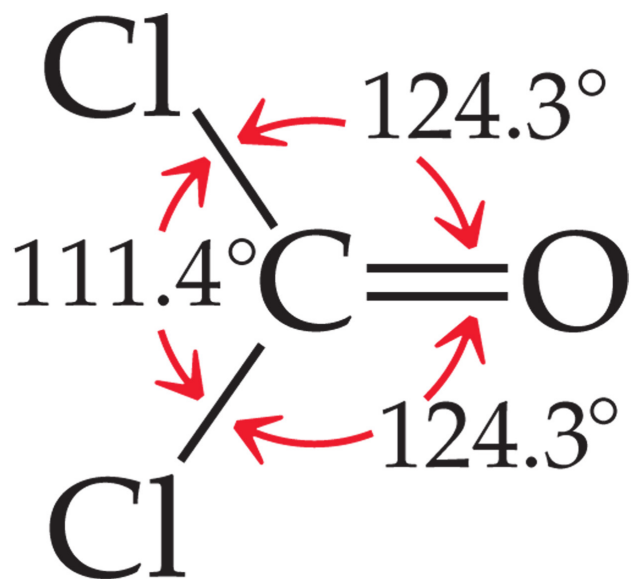
- All positions are equivalent in the octahedral domain.
- There are three molecular geometries:

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.



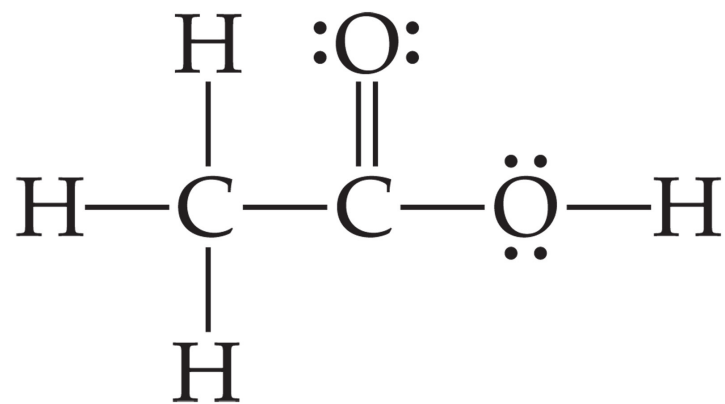
Multiple Bonds and Bond Angles



- 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.

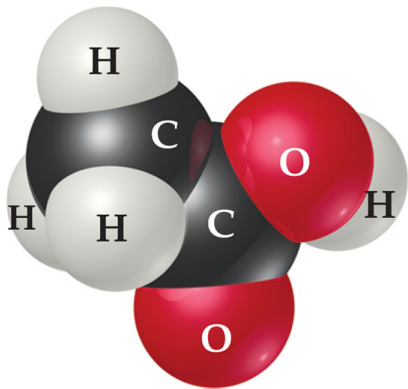
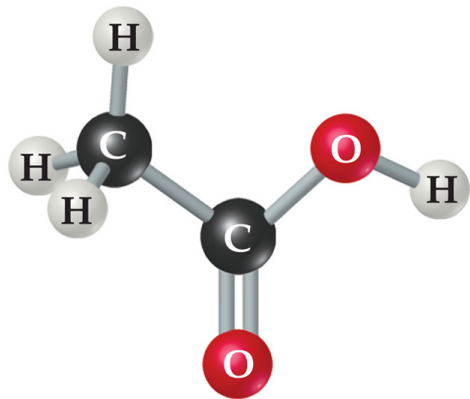
Larger Molecules

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



	$ \begin{array}{c} \text{H} \\ \\ \text{H}-\text{C} \\ \\ \text{H} \end{array} $	$ \begin{array}{c} \text{:O:} \\ \\ \text{C} \end{array} $	$ \begin{array}{c} \ddot{\text{O}}-\text{H} \end{array} $
Number of electron domains	4	3	4
Electron-domain geometry	Tetrahedral	Trigonal planar	Tetrahedral
Predicted bond angles	109.5°	120°	109.5°

Larger Molecules

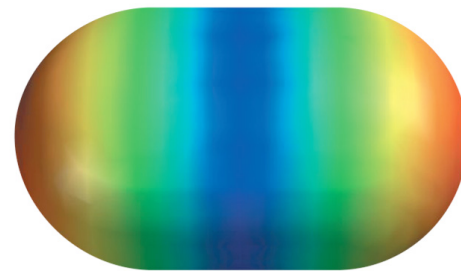
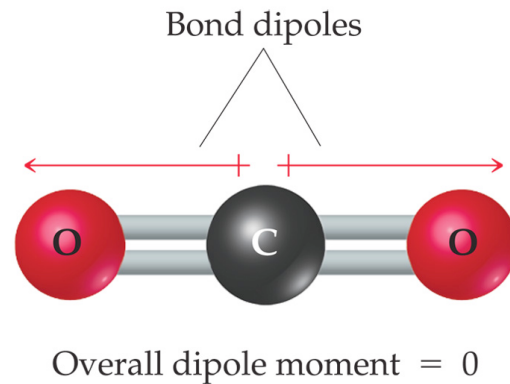


The geometry about each atom follows the same rules!

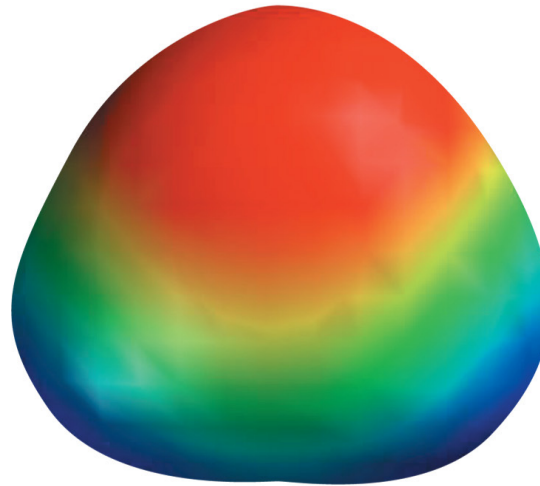
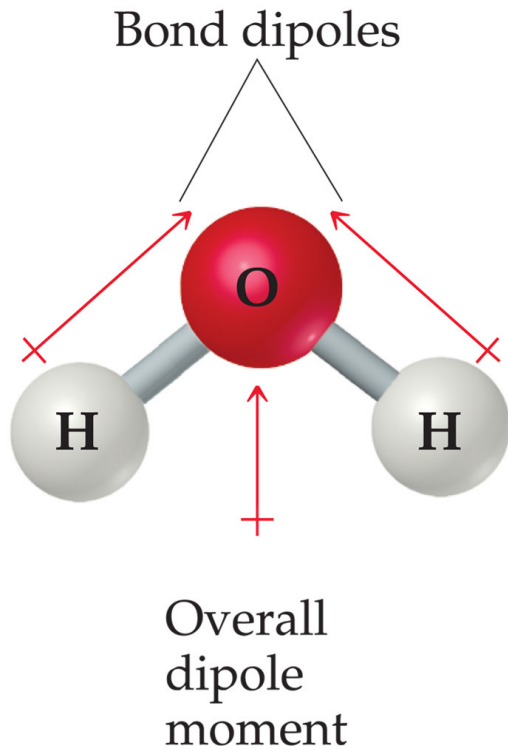
The molecular structure is the result.

Polarity

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



Polarity

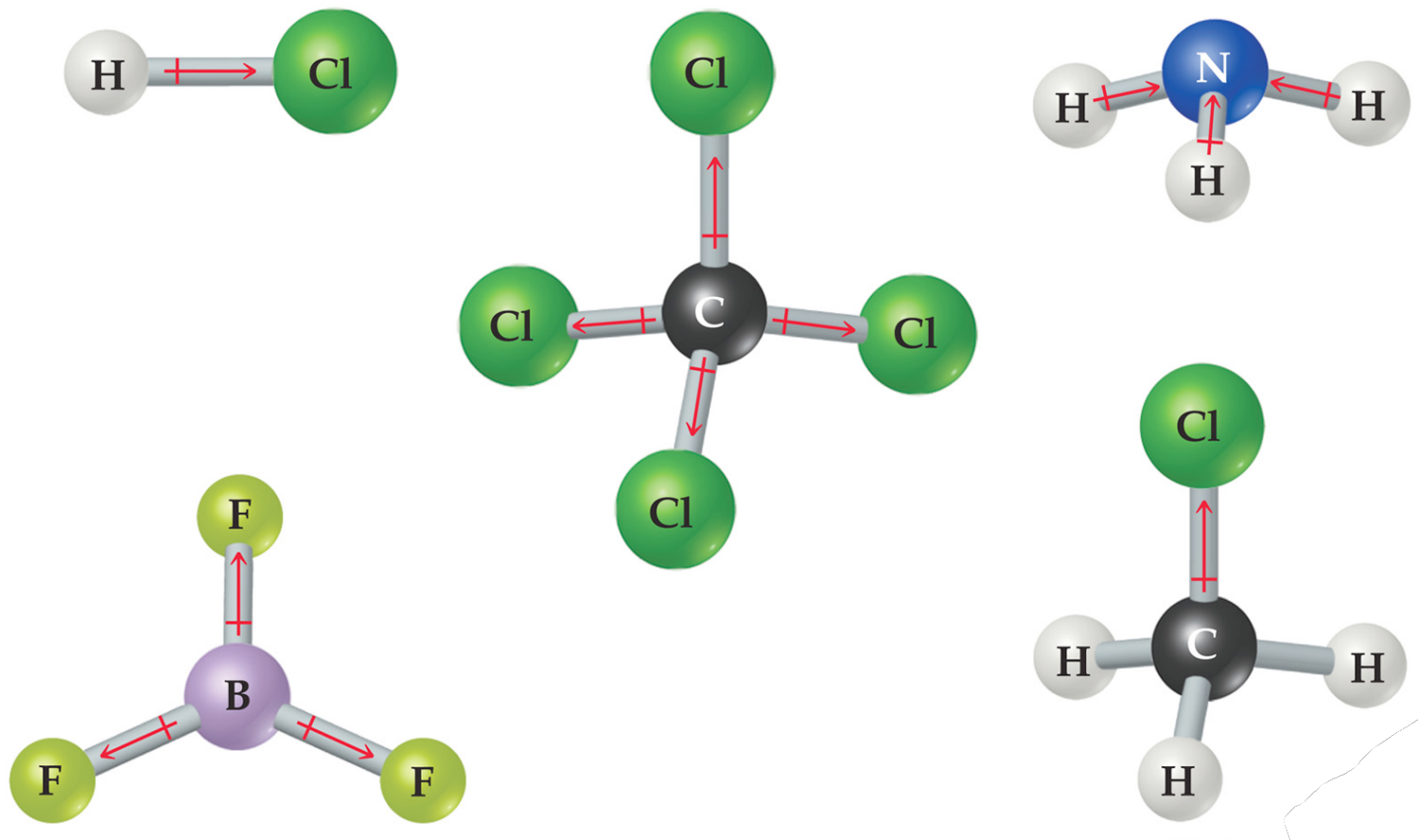


By adding the individual bond dipoles, one can determine the overall dipole moment for the molecule.

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

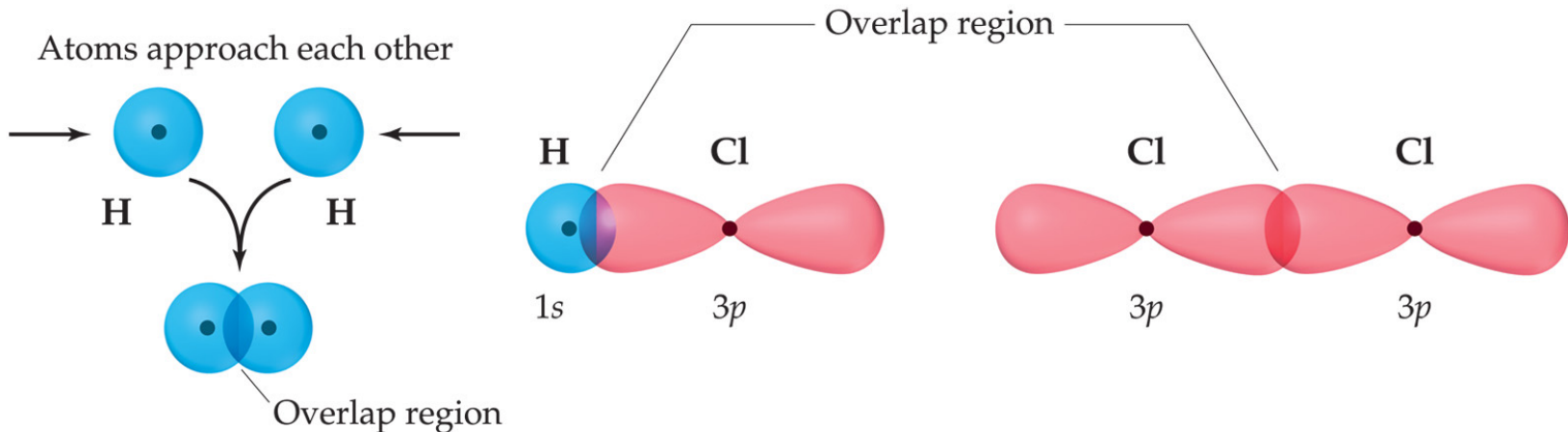
Polarity

“The tractor pull in space”



Overlap and Bonding

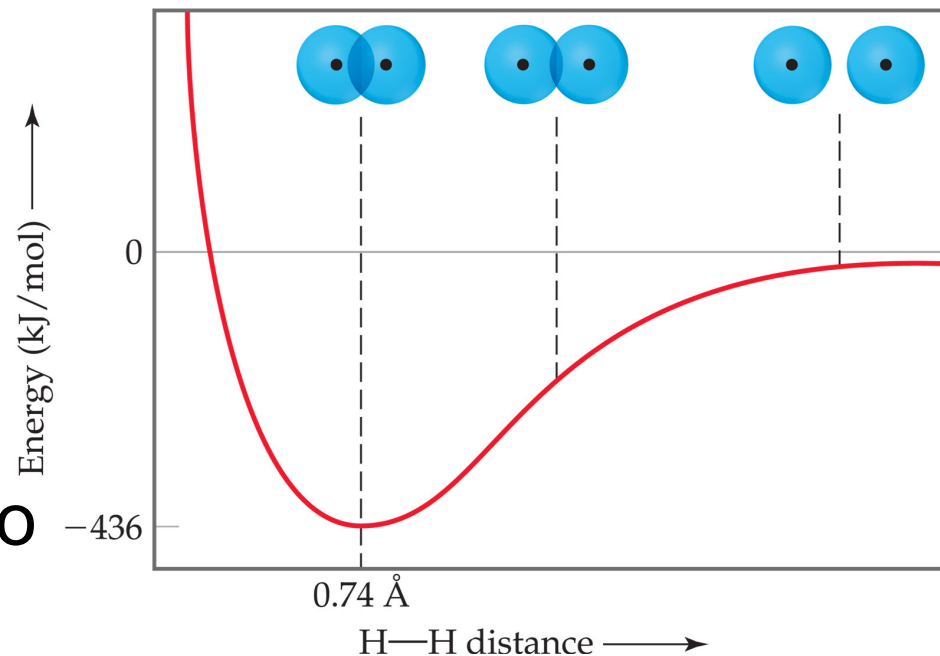
- covalent bonds form when electrons are “shared.”
- But what does that mean? What’s the relationship between an atom’s atomic orbitals and bonding?
- 1. 2 Atomic orbitals
 - one from each atom
 - each occupied with one electron,
 - overlap, electrons go in these overlapped orbitals



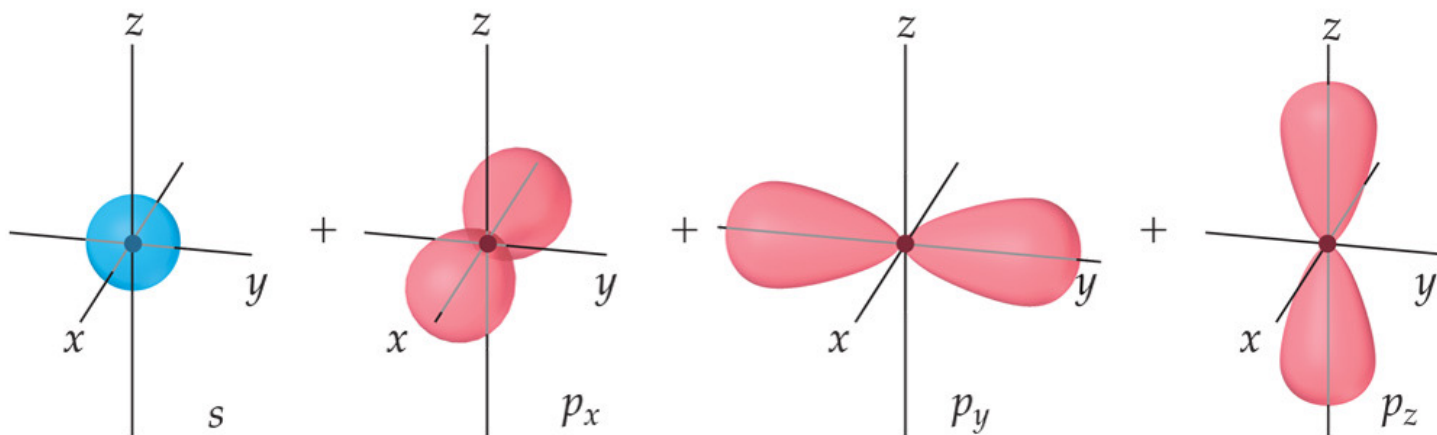
- 2. Atomic orbitals from each atom combine to make new orbitals called “molecular orbitals” and valence electrons go in those orbitals.

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.



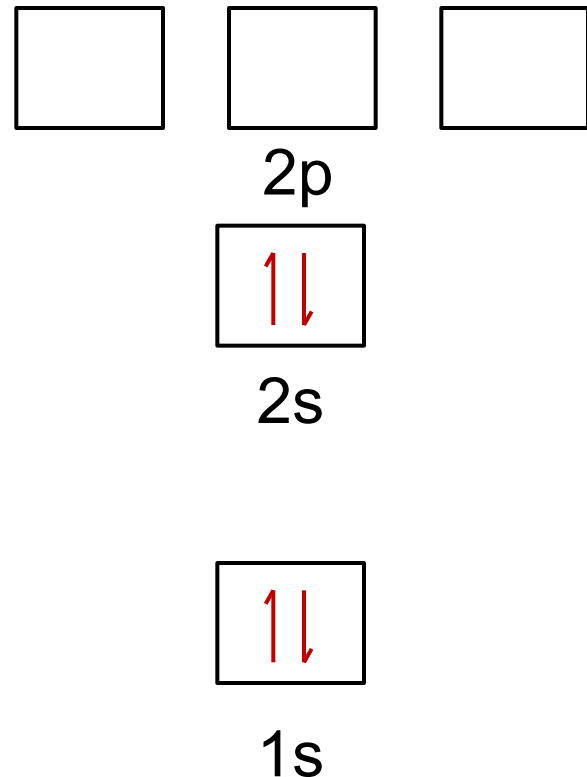
Hybrid Orbitals



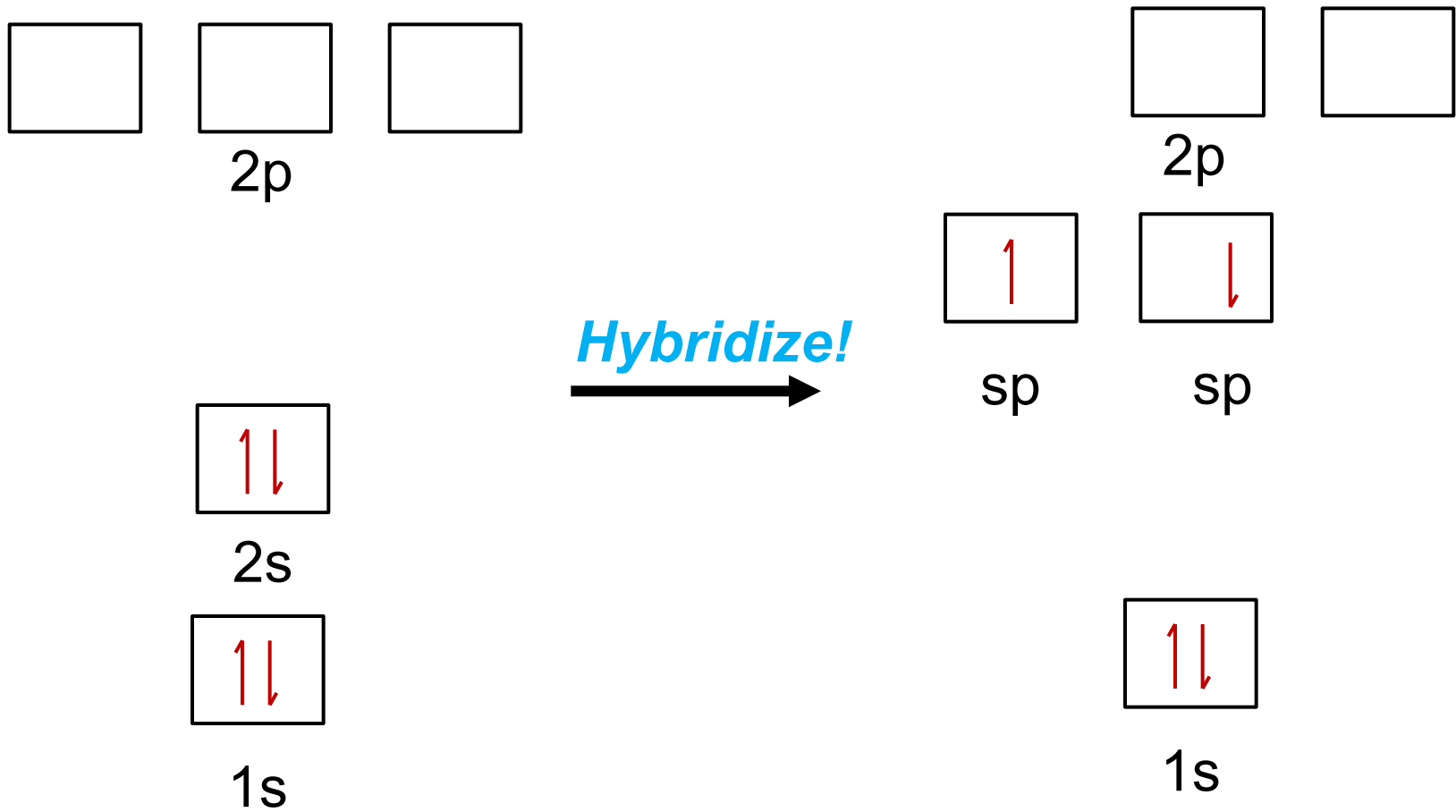
But how do you get tetrahedral, trigonal bipyramidal, and other geometries when the atomic orbitals seem to be at right angles from each other?

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!



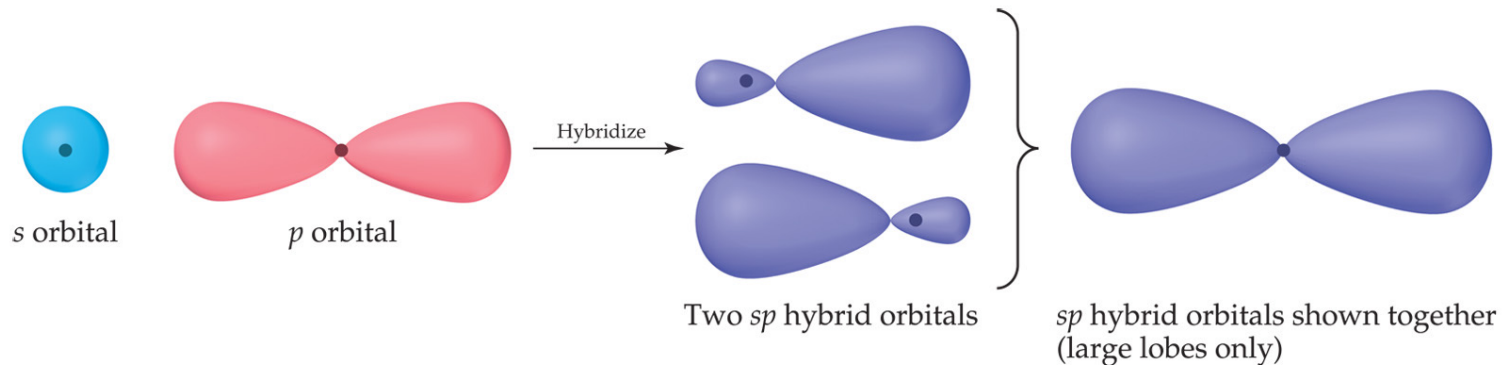
Hybrid Orbitals



Hybrid Orbitals

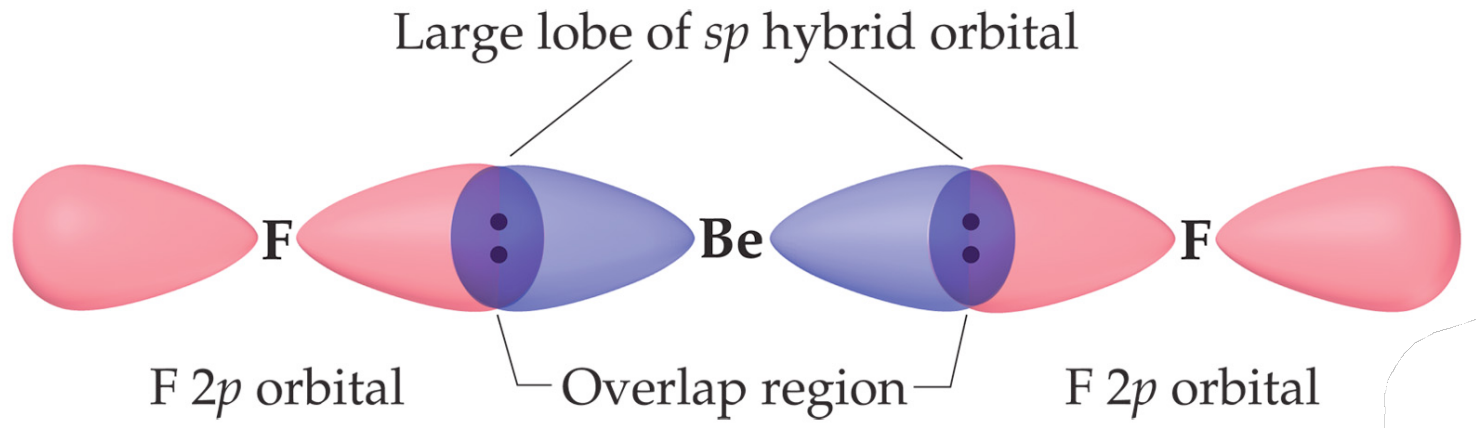
What do they look like?

- 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.



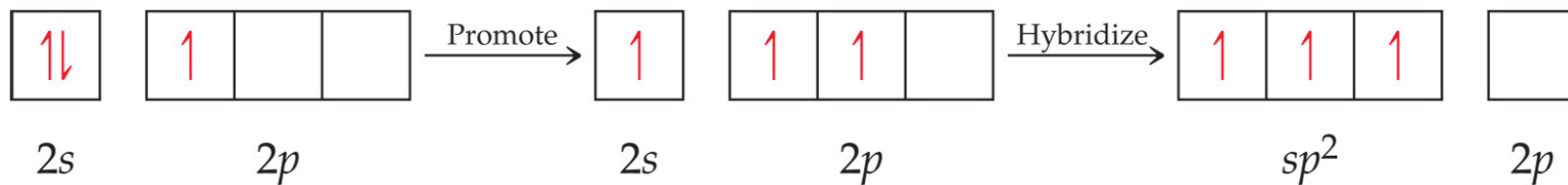
Hybrid Orbitals

- 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...

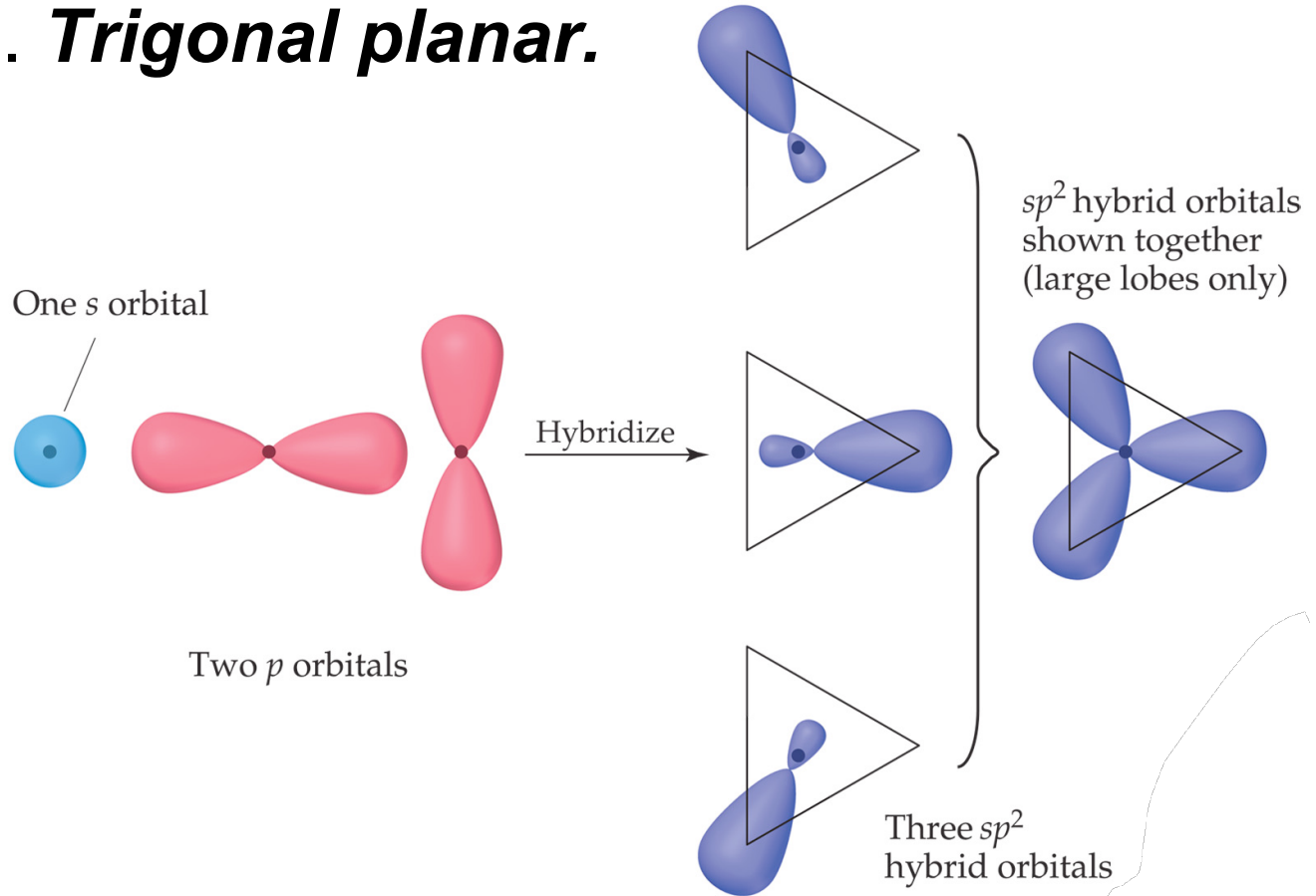


Three hybrid orbitals, one for each H bound to the central Boron atom

Hybrid Orbitals

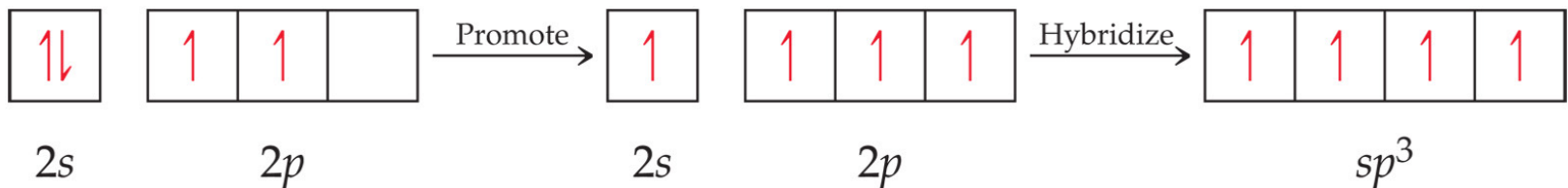
...three degenerate sp^2 orbitals.

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



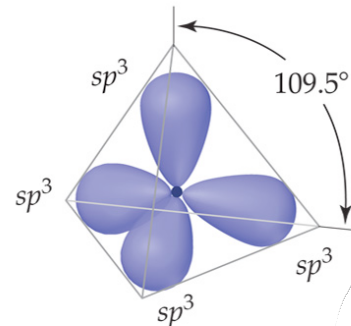
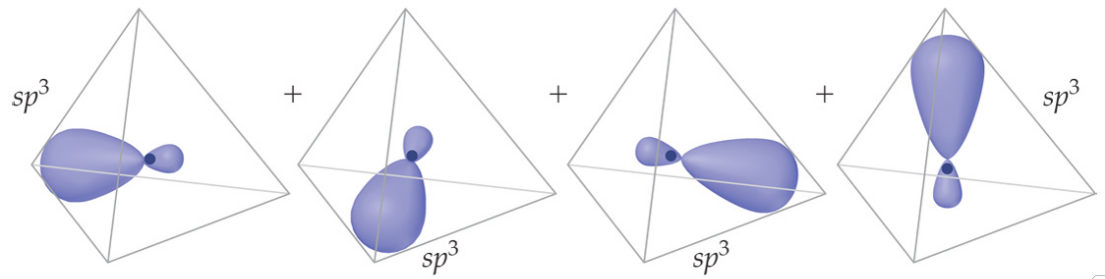
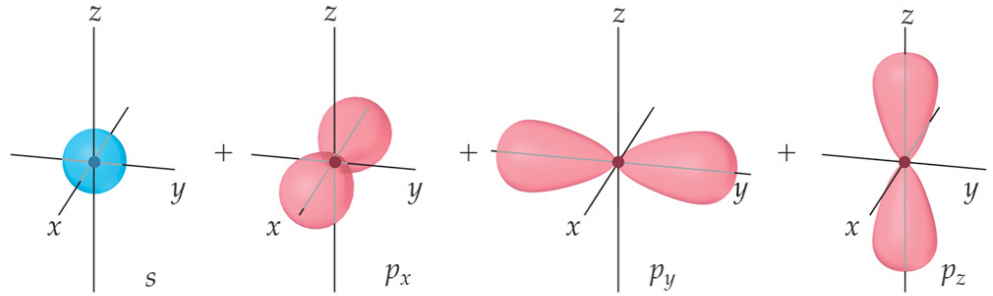
Hybrid Orbitals

With carbon in methane CH_4 we get...



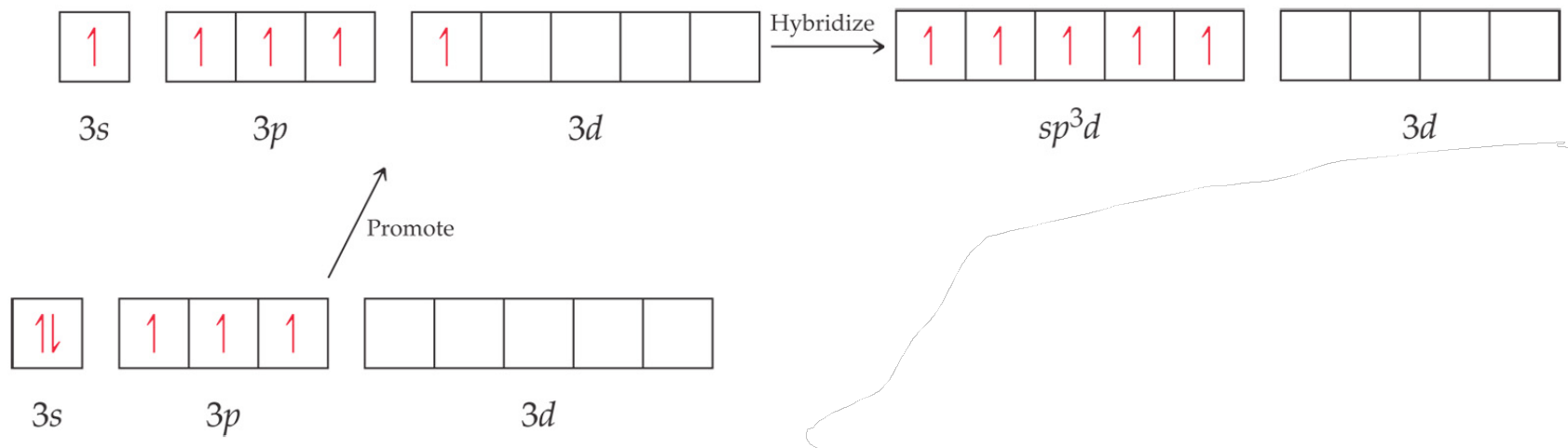
Hybrid Orbitals

...four degenerate sp^3 orbitals.

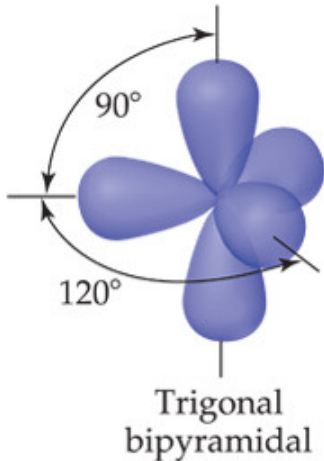


Hybrid Orbitals

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



Hybrid Orbitals

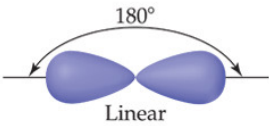
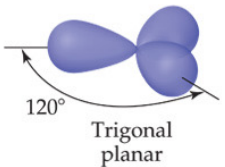
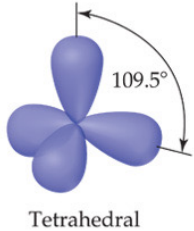
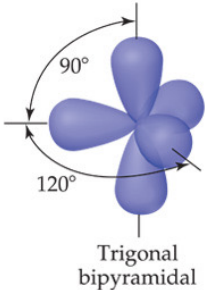
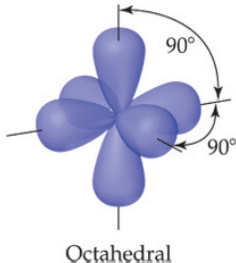


This leads to five degenerate sp^3d orbitals...

...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	 <p>Linear</p>	$\text{BeF}_2, \text{HgCl}_2$
s, p, p	Three sp^2	 <p>Trigonal planar</p>	BF_3, SO_3
s, p, p, p	Four sp^3	 <p>Tetrahedral</p>	$\text{CH}_4, \text{NH}_3, \text{H}_2\text{O}, \text{NH}_4^+$
s, p, p, p, d	Five sp^3d	 <p>Trigonal bipyramidal</p>	$\text{PF}_5, \text{SF}_4, \text{BrF}_3$
s, p, p, p, d, d	Six sp^3d^2	 <p>Octahedral</p>	$\text{SF}_6, \text{ClF}_5, \text{XeF}_4, \text{PF}_6^-$

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

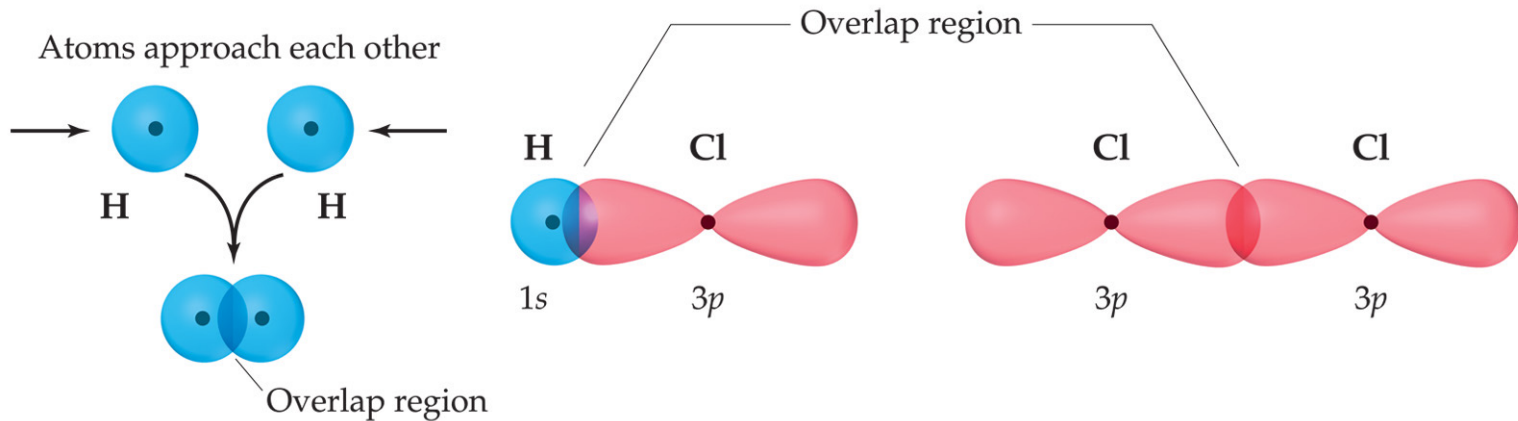
The exam

- 1 size trend
- 1 Effective nuclear charge
- 1 electron affinity
- 1 lattice energy
- 2 Ion. energy trend
- 2 periodic trends in chemical behavior
 - (metals vs. nonmetals)
- 1 electronegativity
- 15-20 questions will be about 8-9 Lewis structures:
 - Lewis structures, polarity, VSEPR.

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.

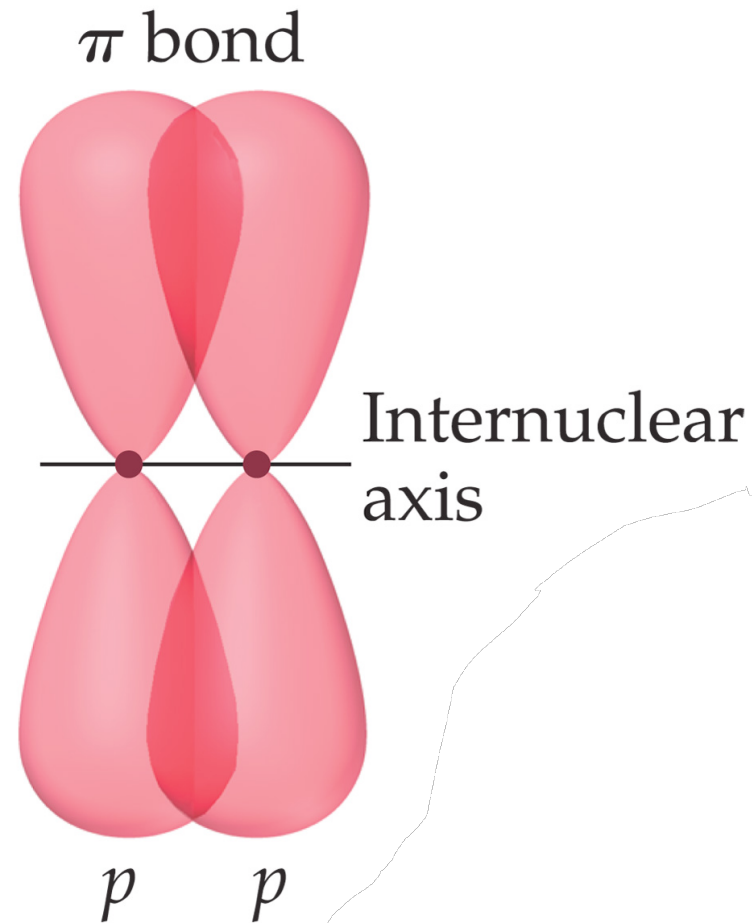
Sigma (σ) Bonds



- 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.

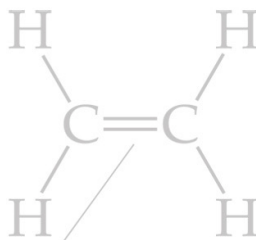


Single Bonds

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



One σ bond



One σ bond plus
one π bond



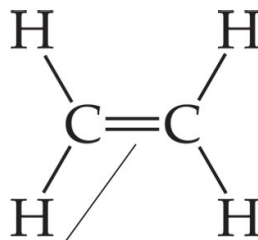
One σ bond plus
two π bonds

Multiple Bonds

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



One σ bond

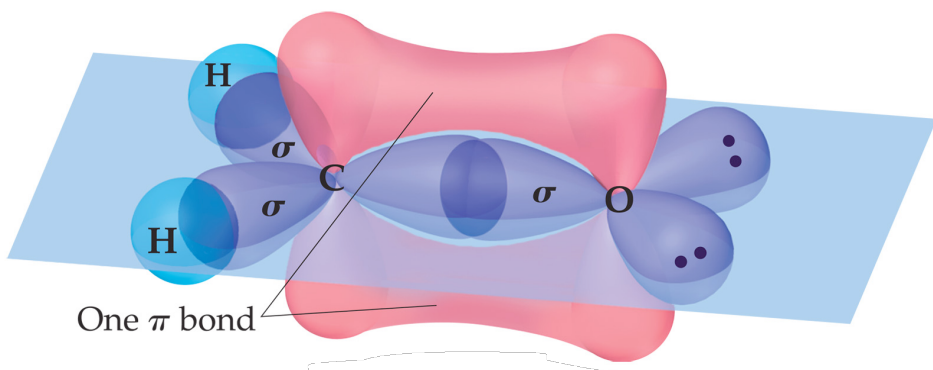
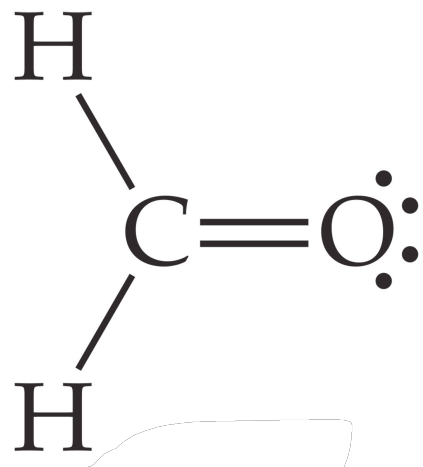


One σ bond plus
one π bond



One σ bond plus
two π bonds

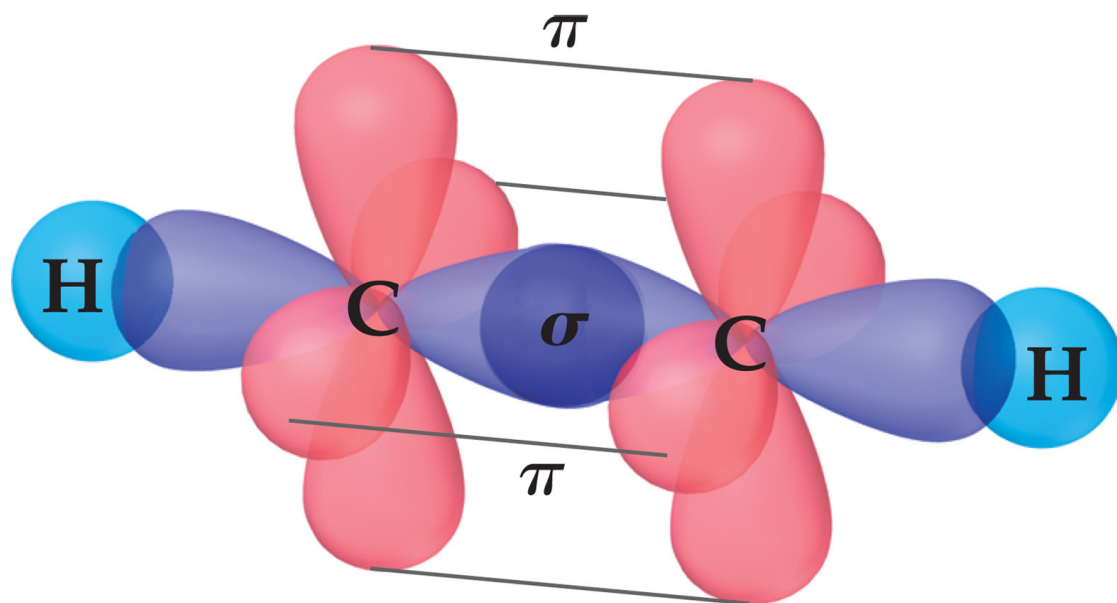
Multiple Bonds



- 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.

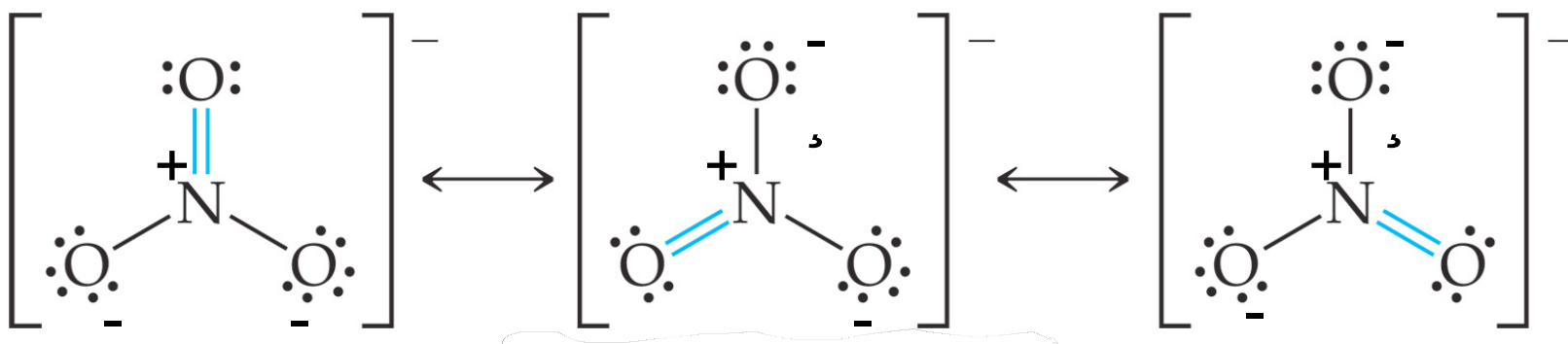
Multiple Bonds

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.

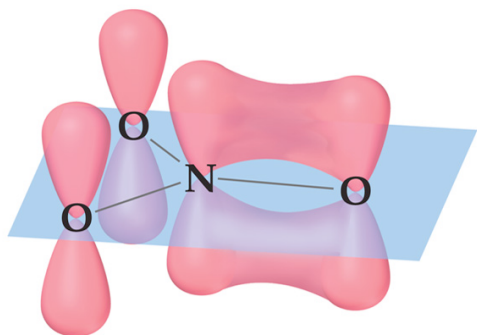


Delocalized Electrons: Resonance

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.

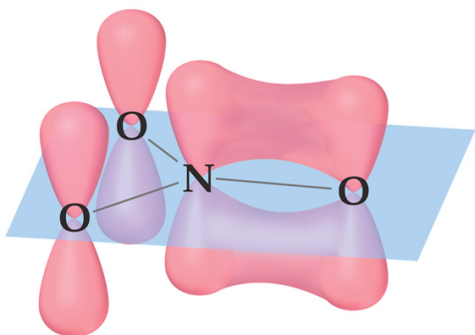


Delocalized Electrons: Resonance

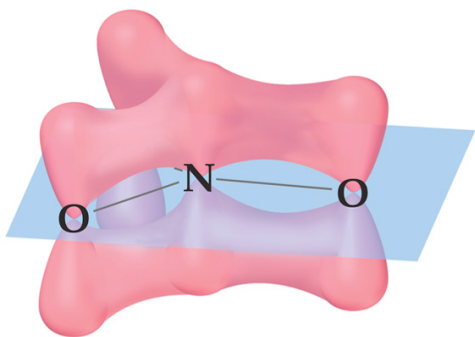


- each of the four atoms in the nitrate ion has a p orbital.
- The p orbitals on all three oxygens overlap with the p orbital on the central nitrogen.

Delocalized Electrons: Resonance

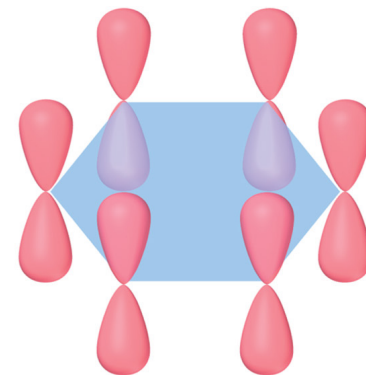
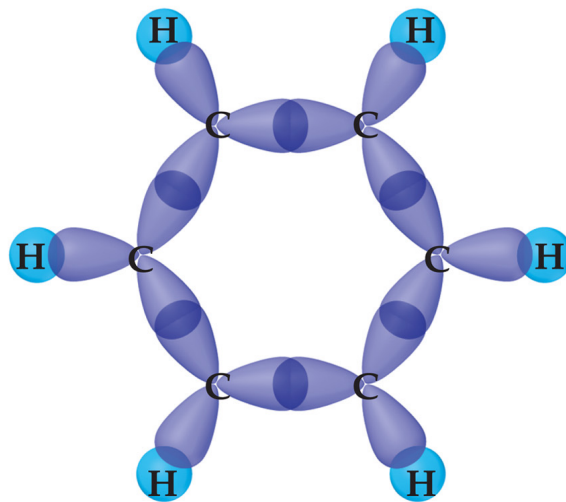
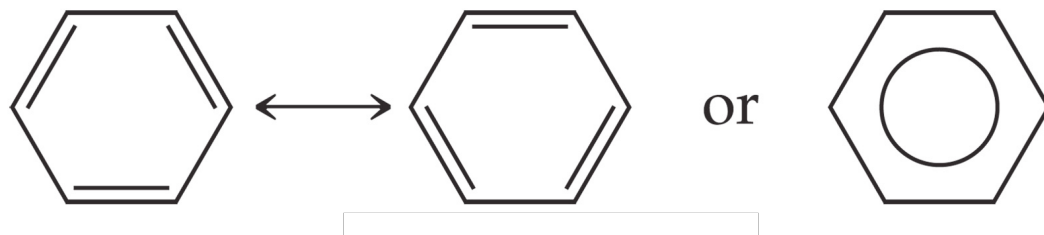


This means the π electrons are not localized between the nitrogen and one of the oxygens, but rather are **delocalized** throughout the ion.



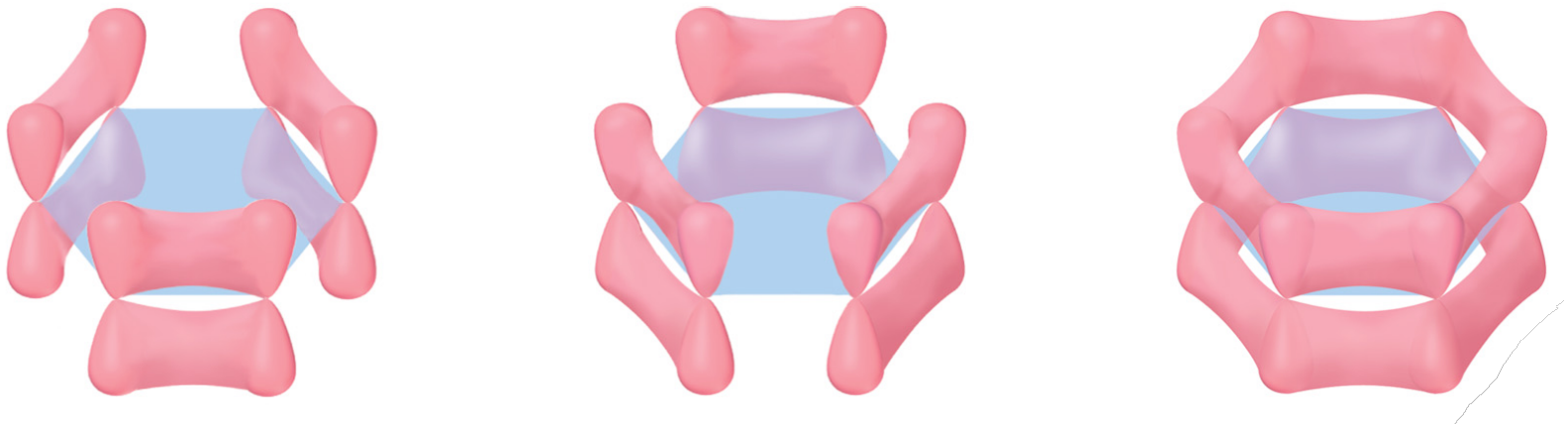
Resonance

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.

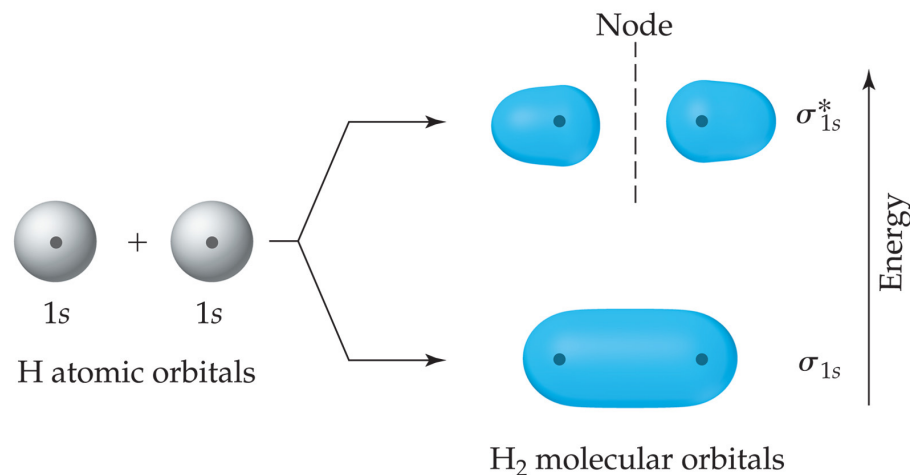


Valence bond theory

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

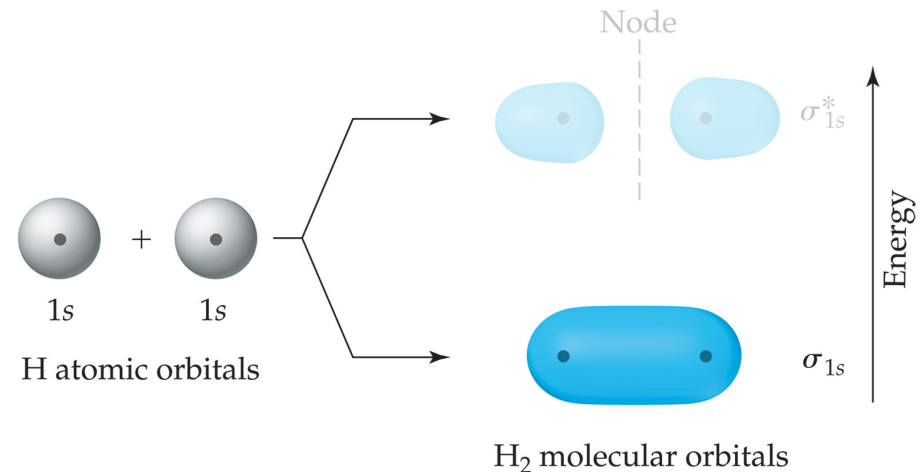
Molecular Orbital (MO) Theory

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.



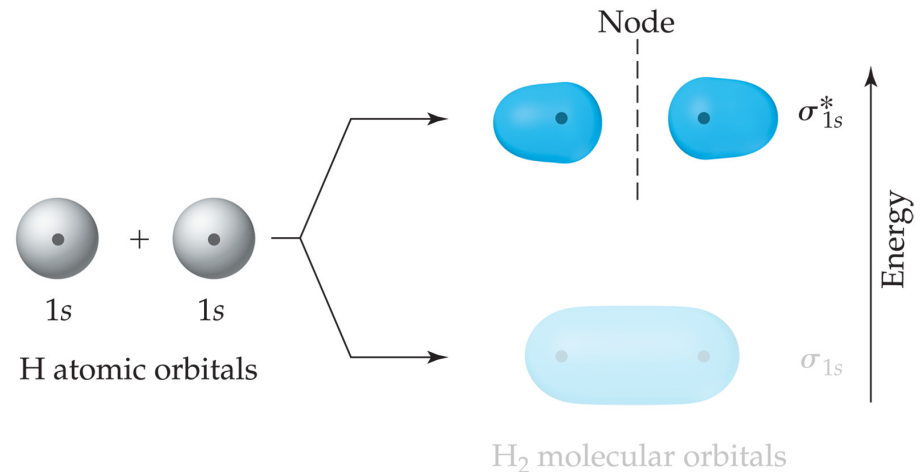
Molecular Orbital (MO) Theory

- 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.



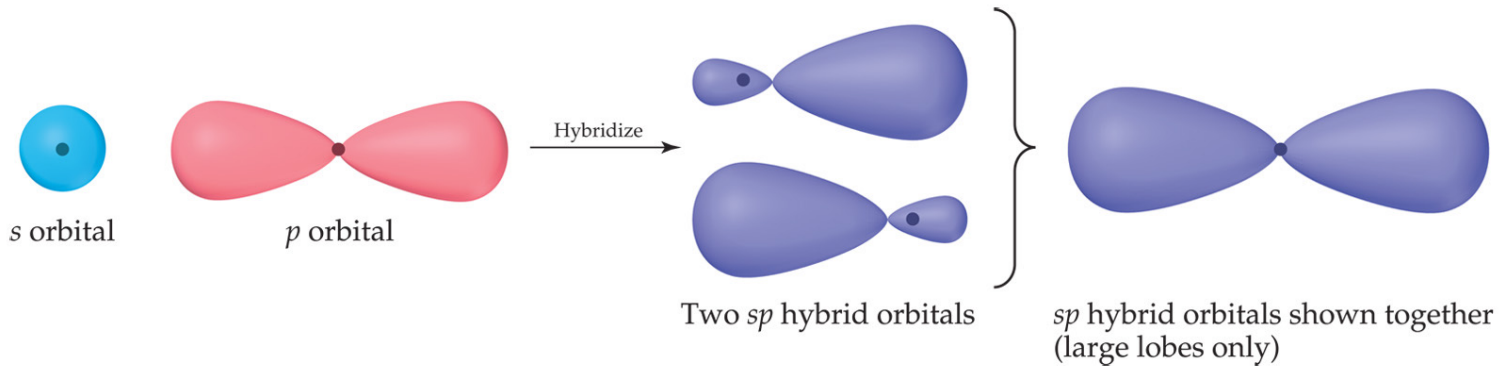
Molecular Orbital (MO) Theory

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

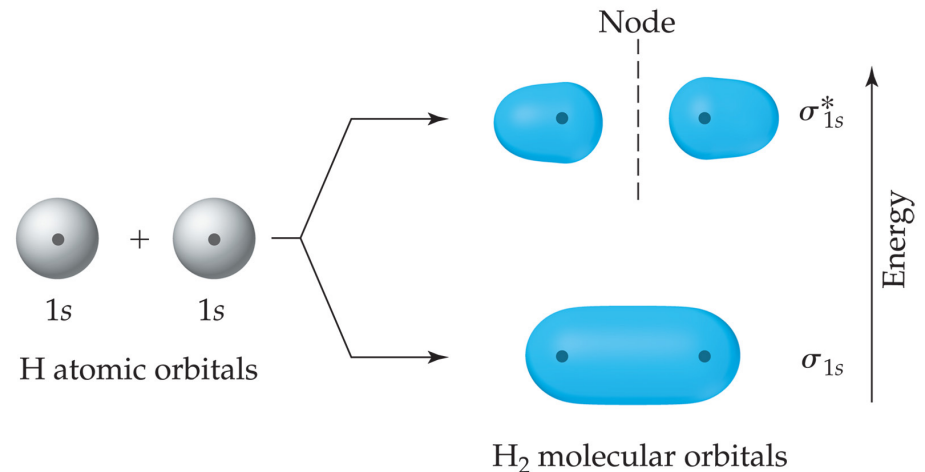


Molecular Orbital (MO) Theory

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

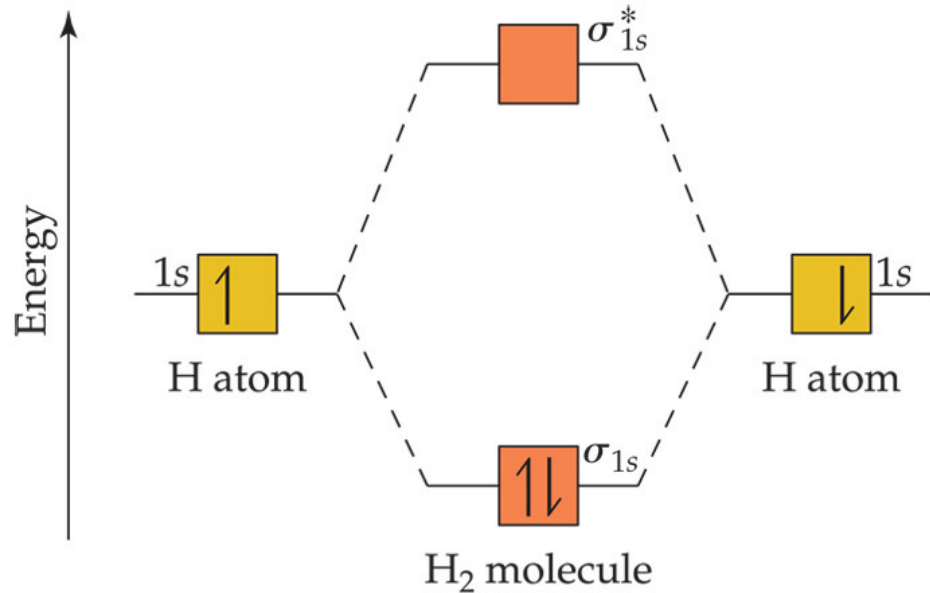


- Molecular orbital theory:
 - All of the atomic orbitals from all of all the atoms are mixed together.



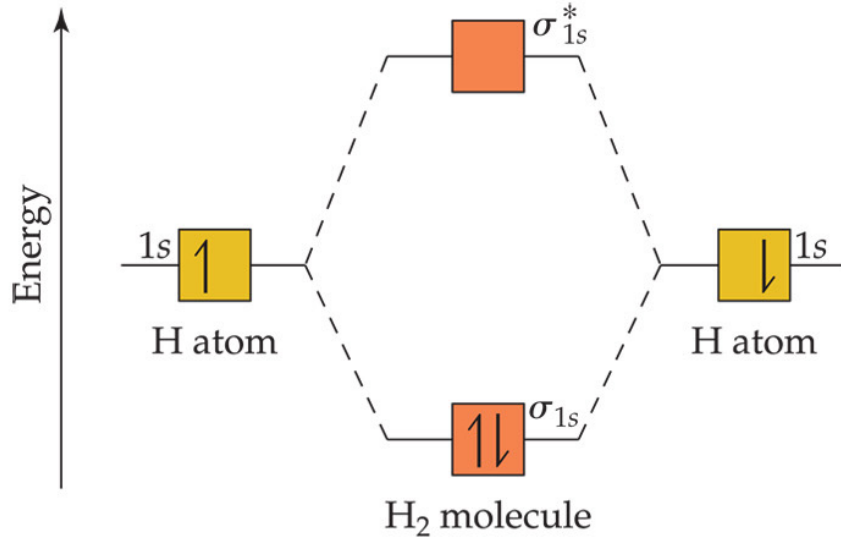
MO Theory

Example 1, H₂



- In H₂ 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

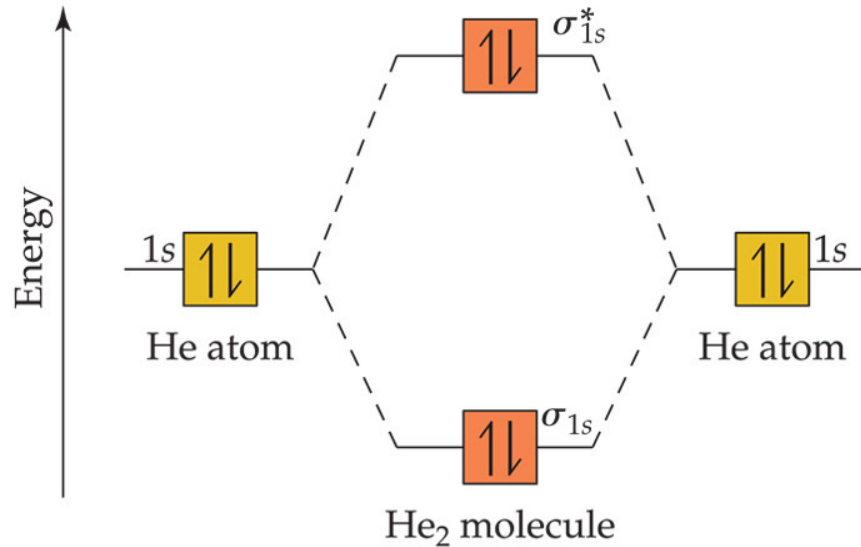
$$\frac{1}{2} (2 - 0) = 1$$

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.

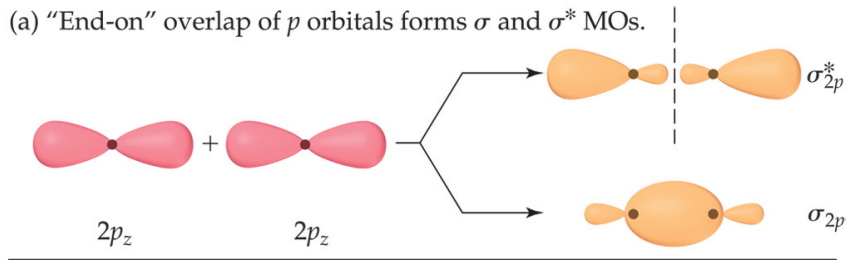


Rules for making and filling molecular orbitals

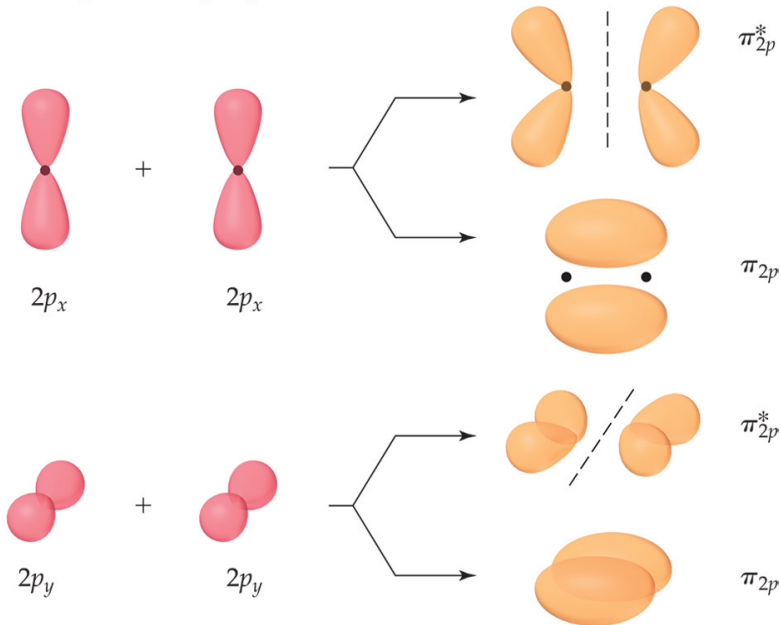
- 1. The number of MO's equals the # of Atomic orbitals
- 2. The overlap of two atomic orbitals gives two molecular orbitals, 1 bonding, one antibonding
- 3. Atomic orbitals combine with other atomic orbitals of *similar energy*.
- 4. Degree of overlap matters. More overlap means bonding orbital goes *lower* in E, antibonding orbital goes *higher* in E.
 - Less overlap, orbital more like an atomic orbital. Electrons in that orbital will be localized to one atom.
- 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.

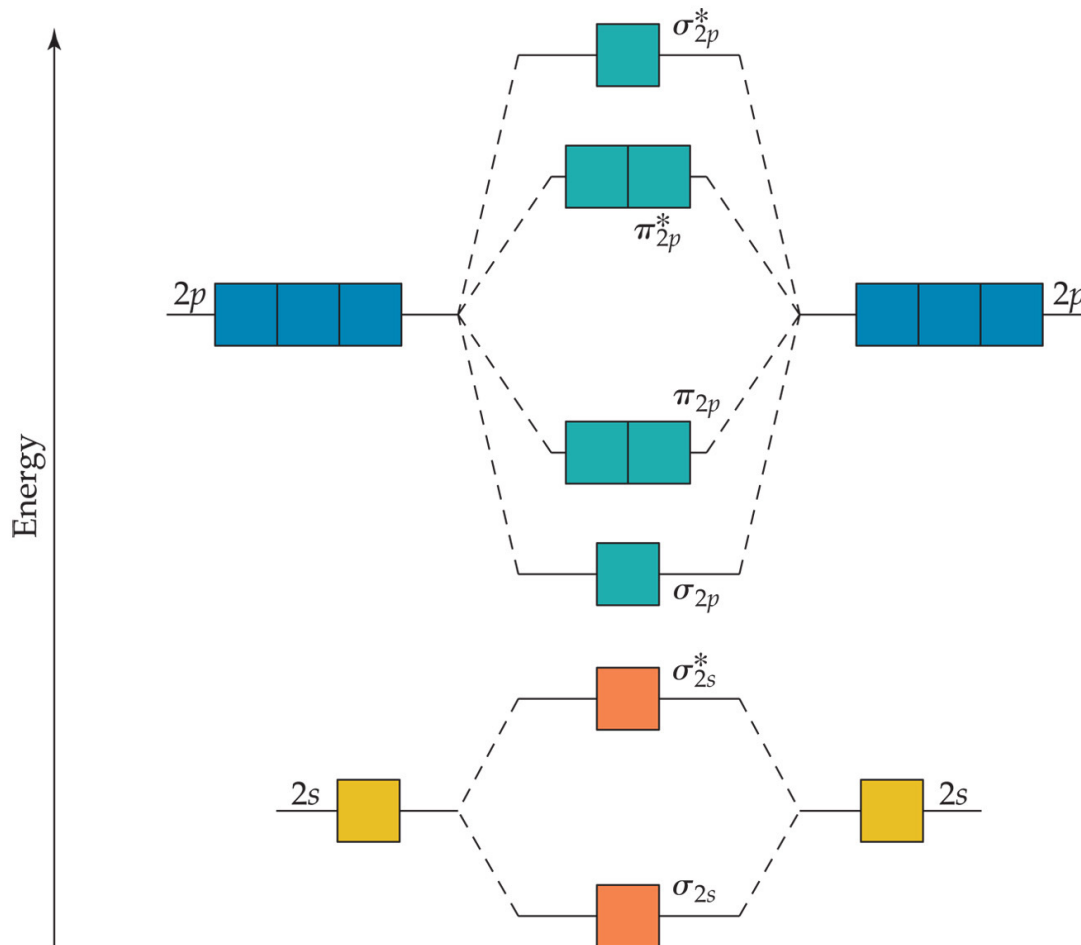


(b) "Sideways" overlap of p orbitals forms two sets of π and π^* MOs.



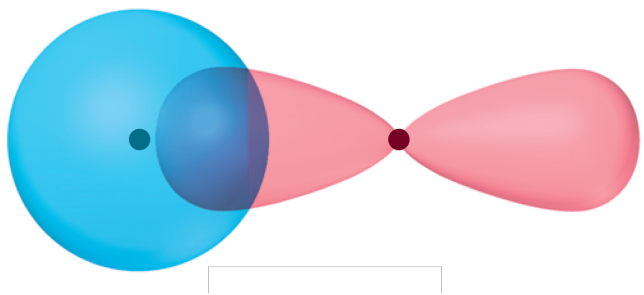
- For p orbitals, there are two types of interactions:
 - The p orbitals that face each other overlap in σ fashion.
 - The other two sets of p orbitals overlap in π fashion.

MO Theory

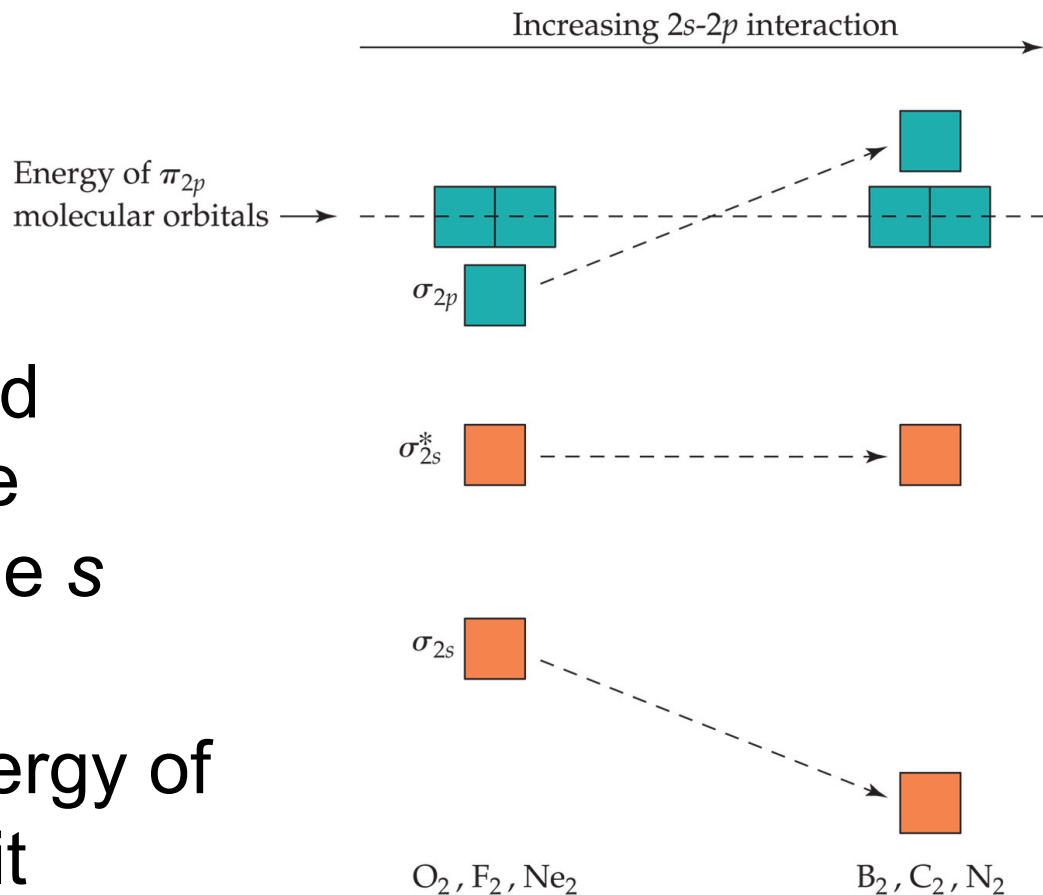


- The resulting MO diagram looks like this.
- There are both σ and π bonding molecular orbitals and σ^* and π^* antibonding molecular orbitals.
- We're assuming only 2 atomic orbitals mix to form an MO

MO Theory



- The earlier p -block elements in the second period have a sizeable interaction between the s and p orbitals.
- This increases the energy of the σ orbital, making it higher in E than the π molecular orbitals in these elements.



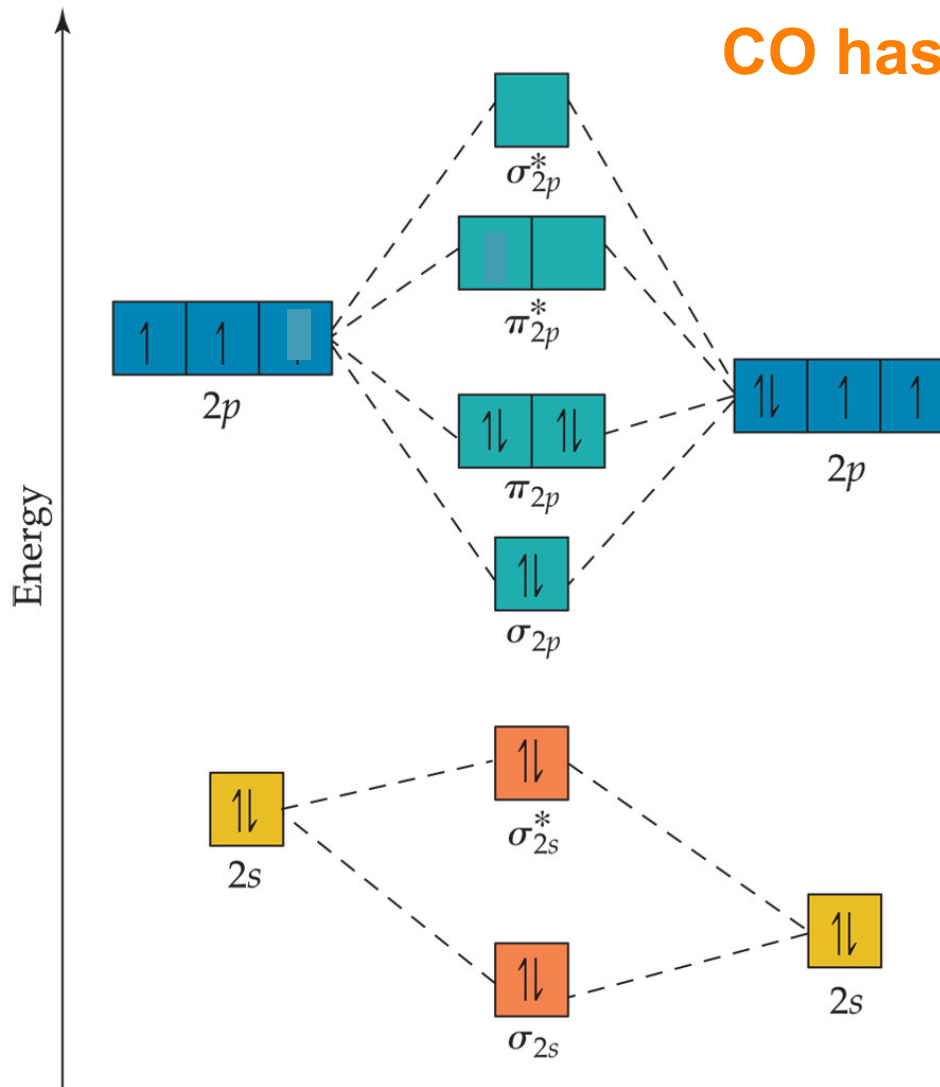
Second-Row MO Diagrams

	Large 2s-2p interaction			Small 2s-2p interaction		
	B ₂	C ₂	N ₂	O ₂	F ₂	Ne ₂
σ_{2p}^*						
π_{2p}^*						
σ_{2p}						
π_{2p}						
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 emphasizing this switch in energy on the exam.

Heterodiatomic molecules

CO has a triple bond

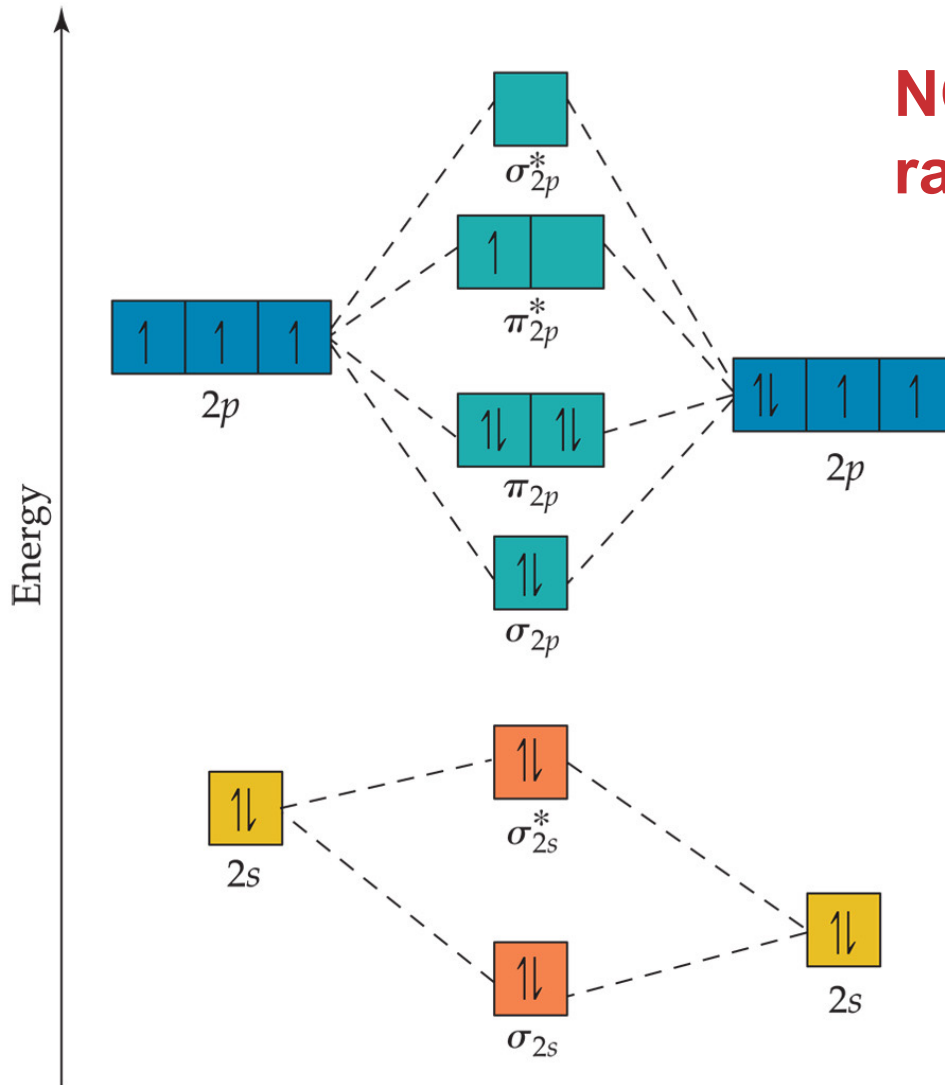


C atom

CO molecule

O atom

Heterodiatomic molecules



NO is paramagnetic radical

N atom NO molecule O atom

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.

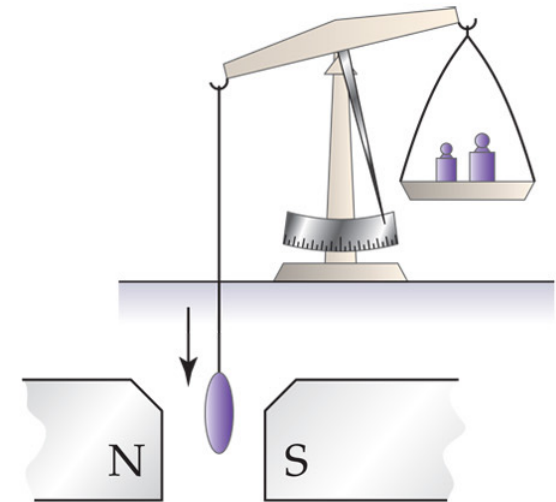
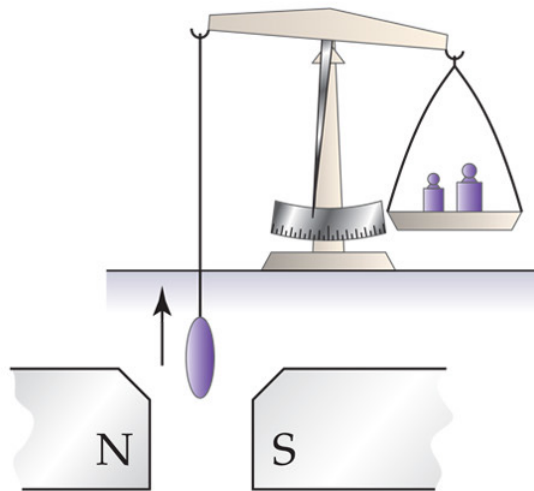
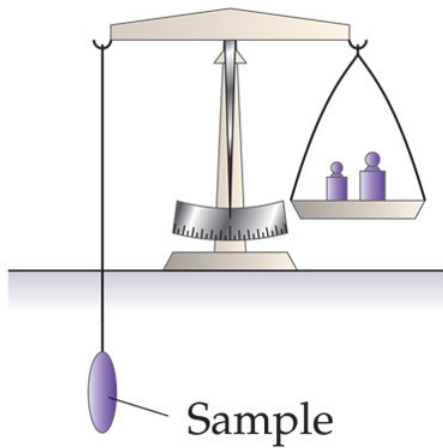
Electrons cause magnetism.

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.

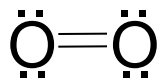
(c) A paramagnetic sample is drawn into the field and thus appears to gain mass.

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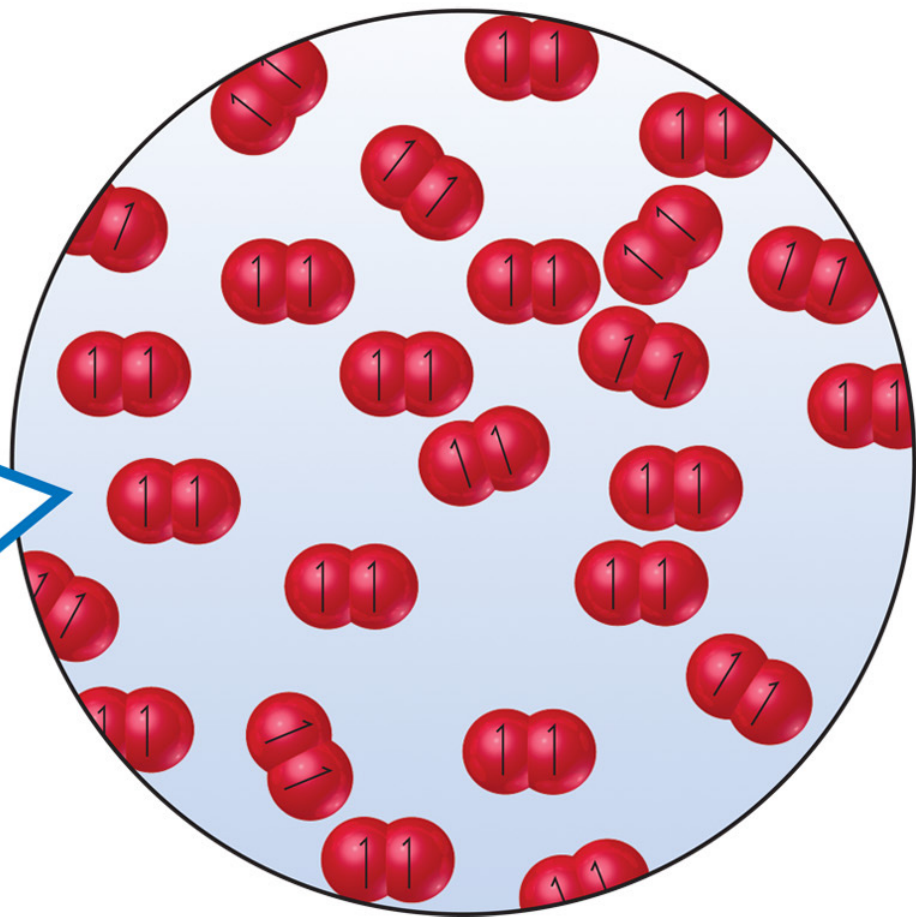
Electrons all paired

Unpaired electrons

Oxygen O₂ is Paramagnetic!



Why?



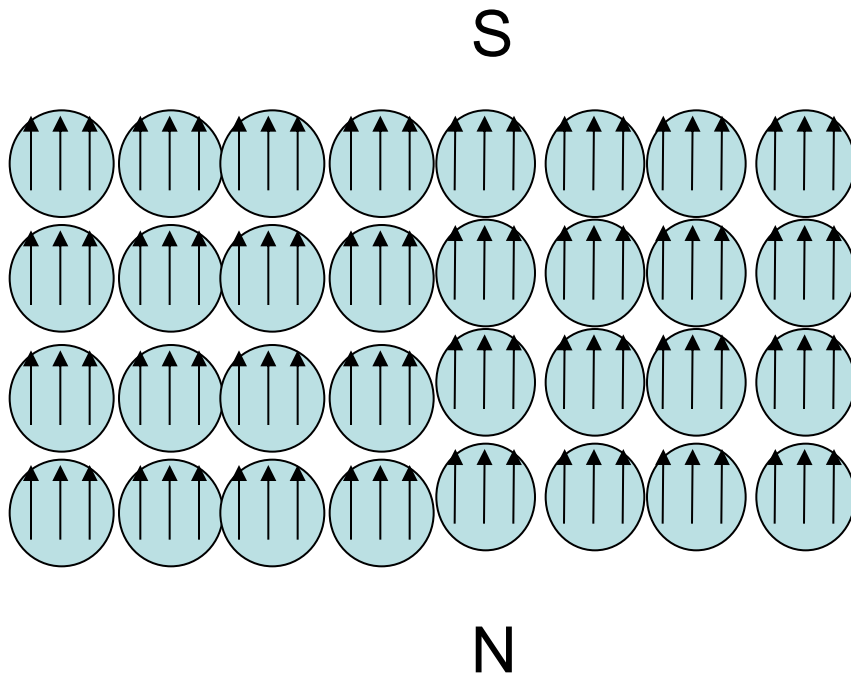
MO to the rescue

	Large 2s-2p interaction			Small 2s-2p interaction		
	B ₂	C ₂	N ₂	O ₂	F ₂	Ne ₂
σ_{2p}^*						
π_{2p}^*						
σ_{2p}						
π_{2p}						
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

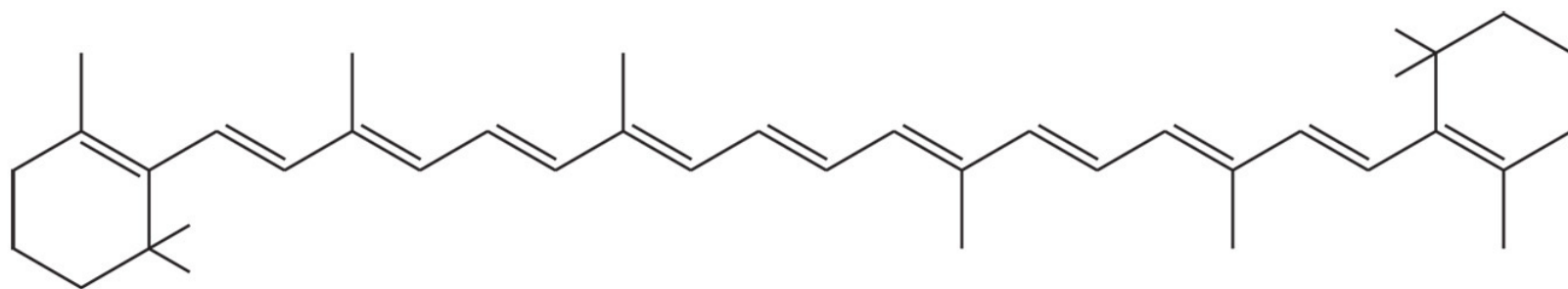


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Remember, elements produced color because of electrons
Moving from higher to lower **atomic** energy levels

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.

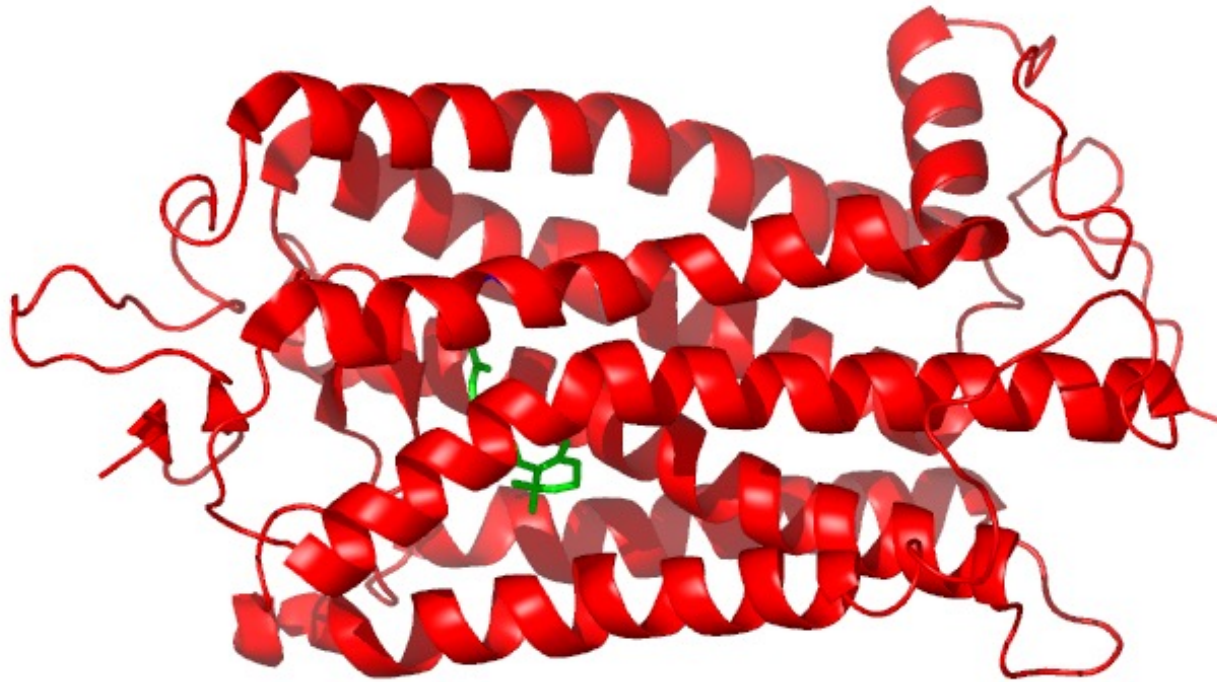


β -carotene

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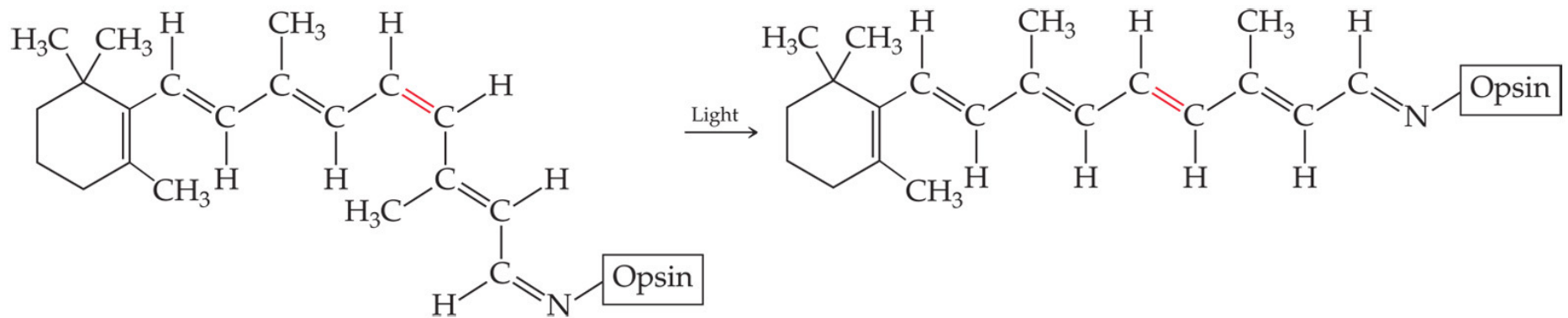
In a molecule like this...
there is a lot of overlap of the p atomic orbitals for all the carbons.

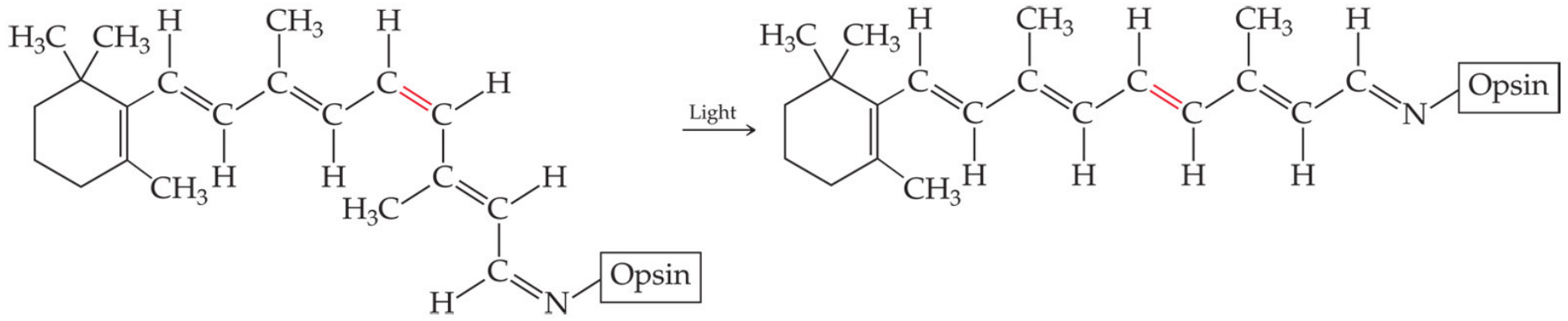
How do we see color?



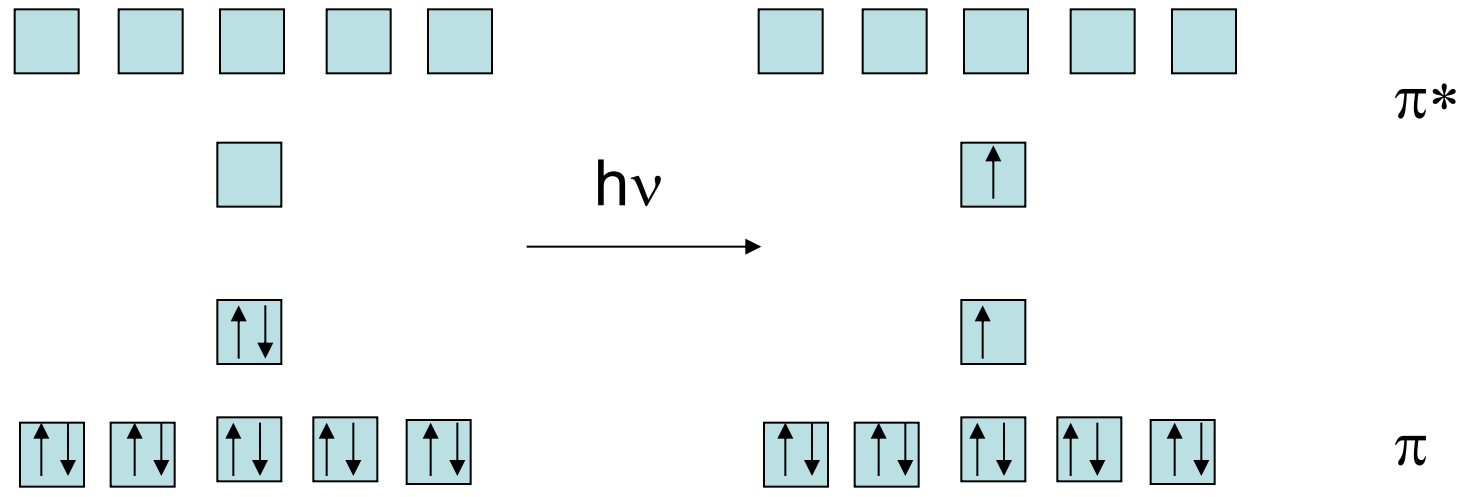
Isomerization
wiggles the rest of
the protein, sends
nerve signal

Rhodopsin





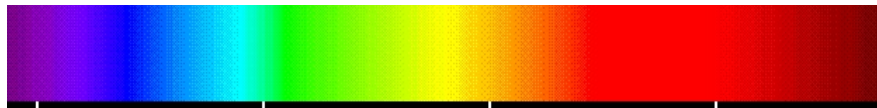
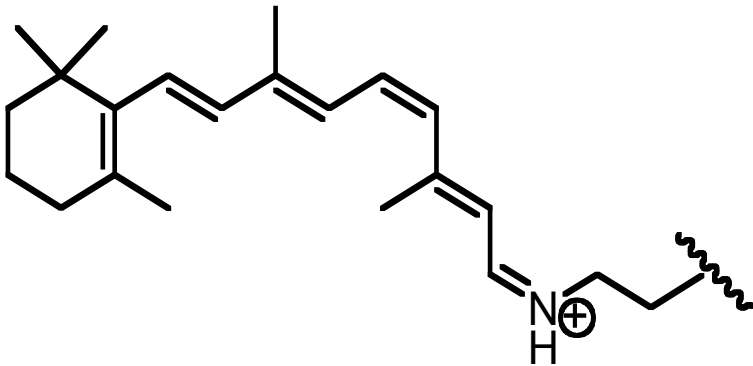
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This weakens the pi bond so rotation can happen

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.



400
nm

Wavelength
(nm)

700
nm

11-*cis*-retinal : ~ 380 nm

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

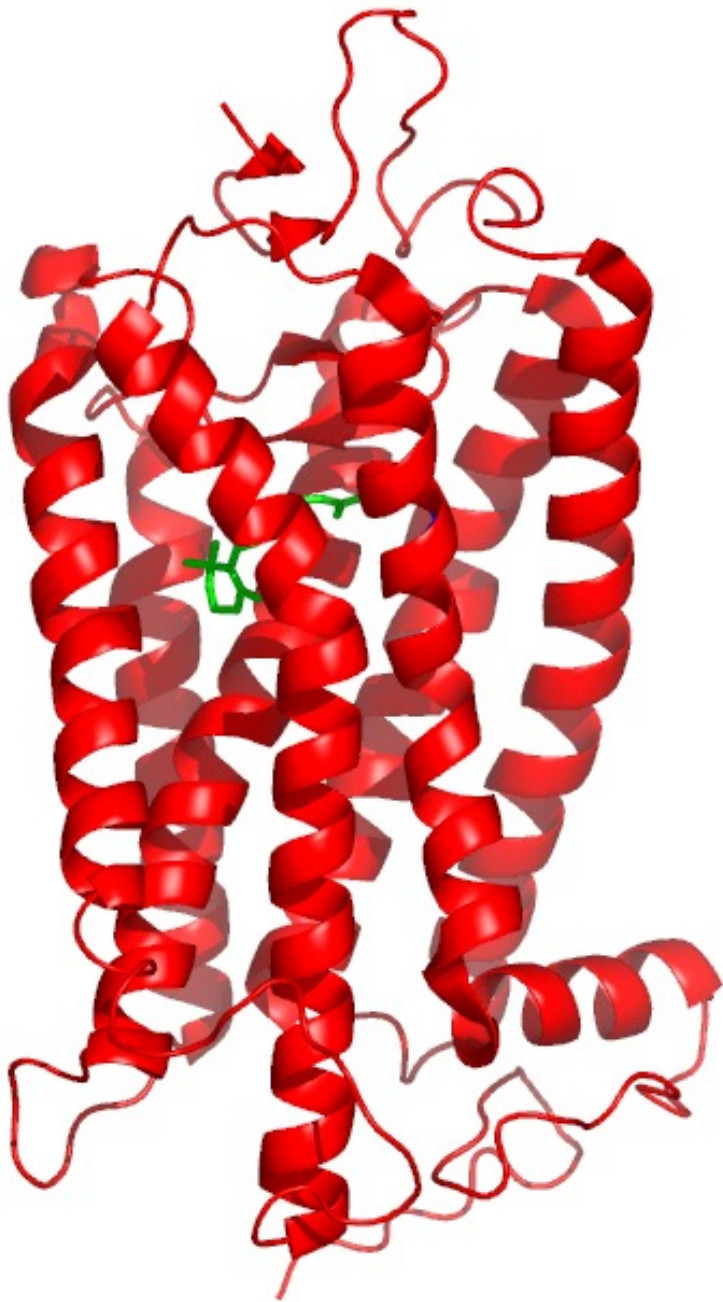
11-*cis*-retinal PSB : ~ 440 nm

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

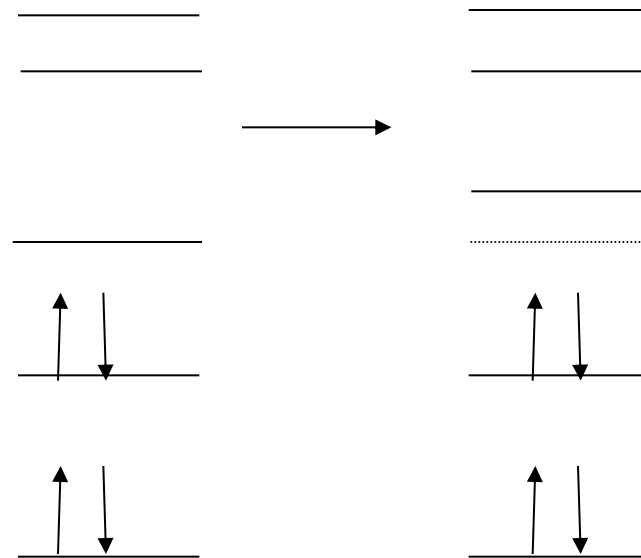
PSB in **Green** Rhodopsin : ~ 530 nm

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

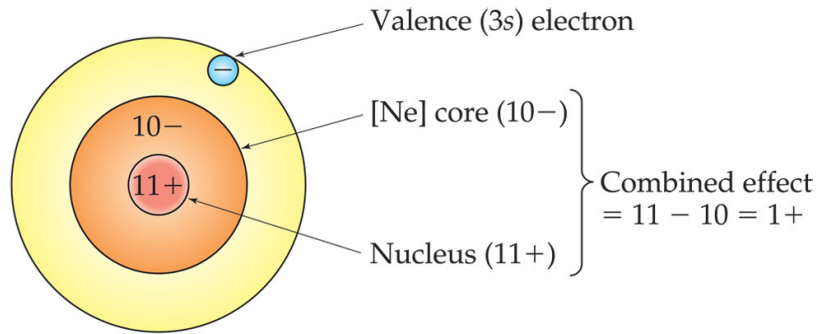
- Not covered:
 - Molecular Orbital Theory

Chapter 7

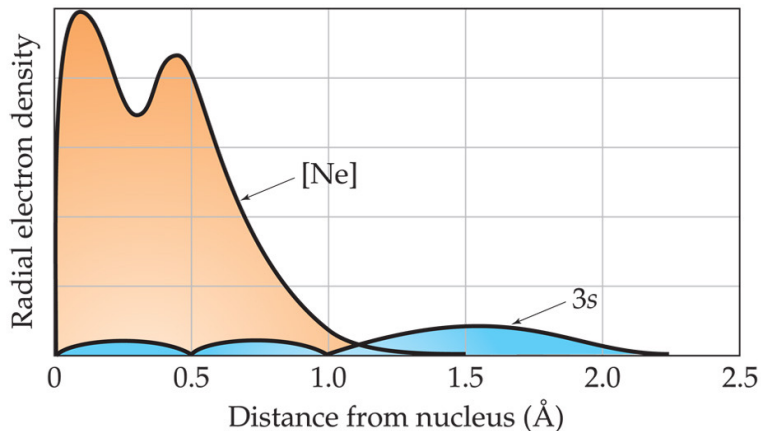
- Periodic trends
- Effective nuclear charge
- Ionization energy, trends
- electron affinity, trends.

Effective Nuclear Charge

Na



(a)



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

$$Z_{\text{eff}} = Z - S$$

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

O²⁻

Co

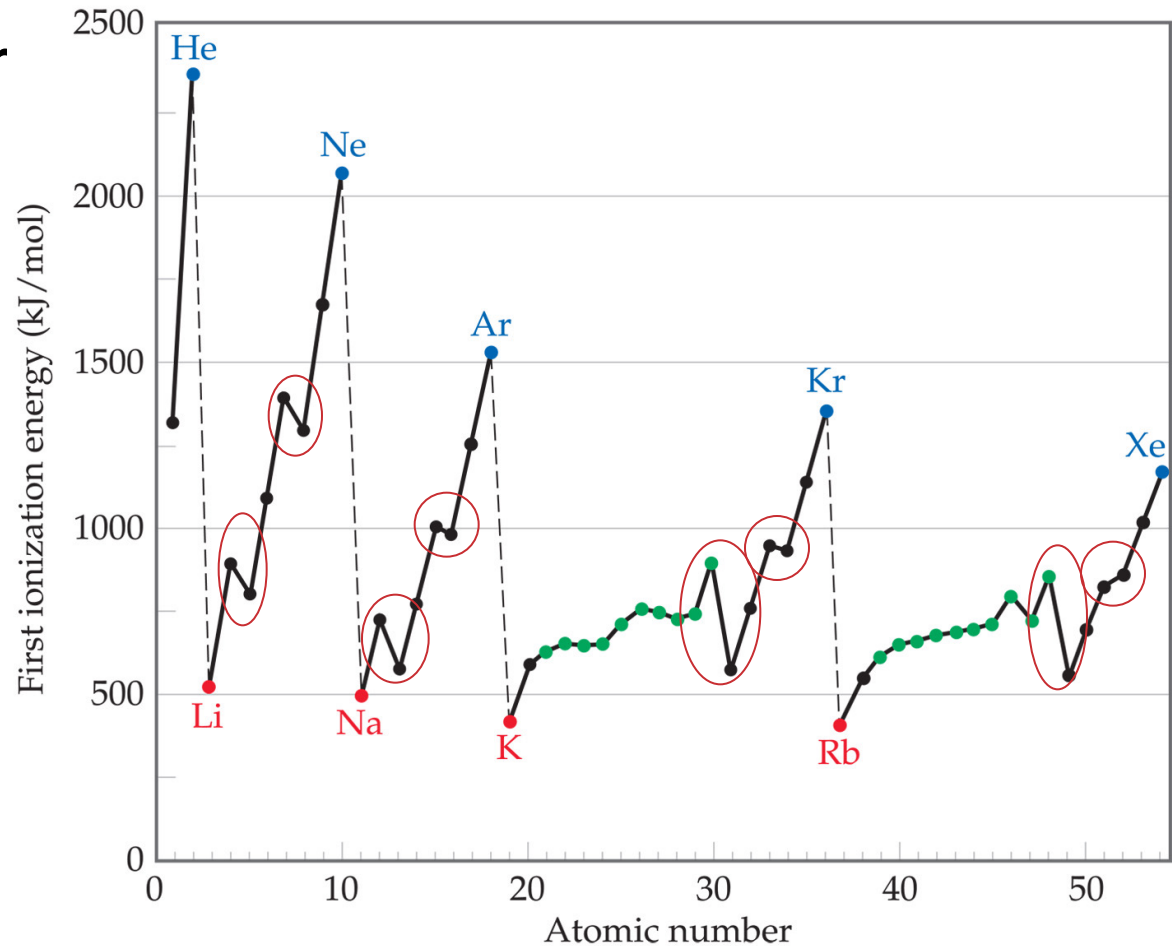
Co²⁺

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

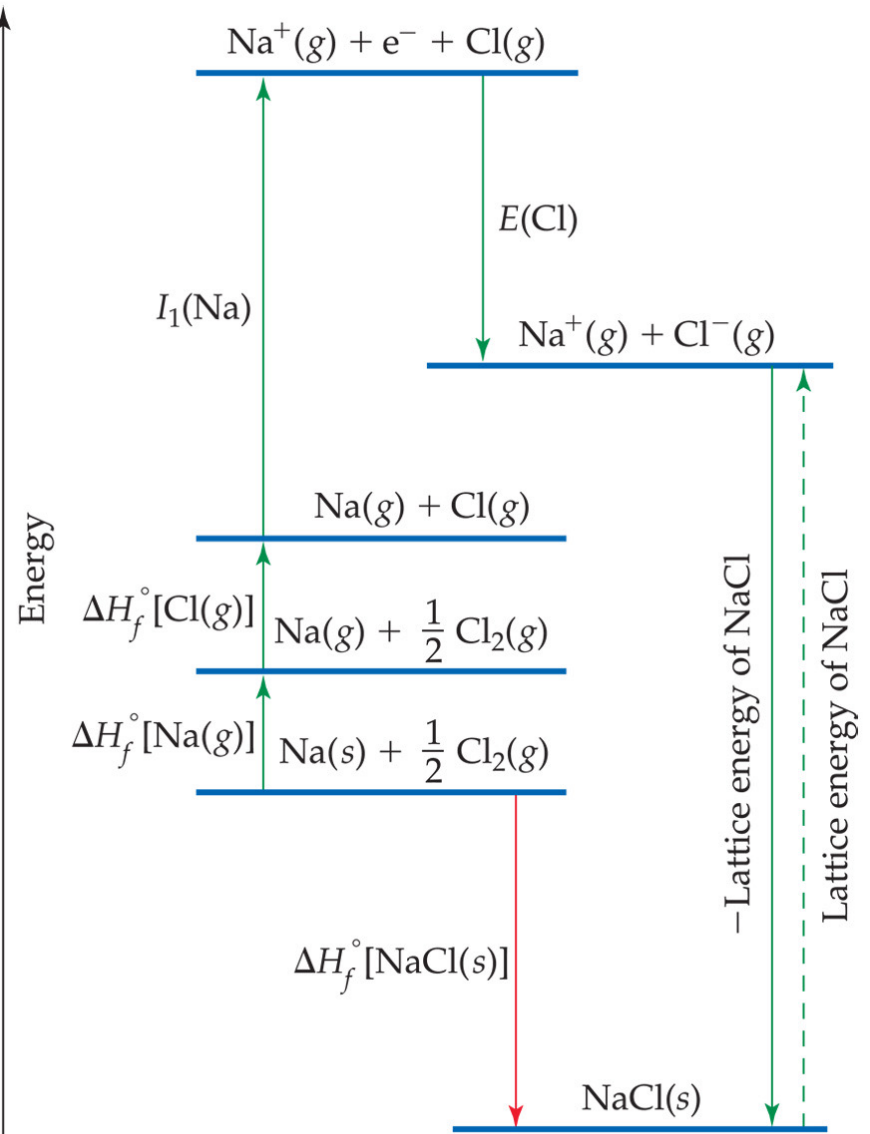
H -73							He > 0
Li -60	Be > 0	B -27	C -122	N > 0	O -141	F -328	Ne > 0
Na -53	Mg > 0	Al -43	Si -134	P -72	S -200	Cl -349	Ar > 0
K -48	Ca -2	Ga -30	Ge -119	As -78	Se -195	Br -325	Kr > 0
Rb -47	Sr -5	In -30	Sn -107	Sb -103	Te -190	I -295	Xe > 0
1A	2A	3A	4A	5A	6A	7A	8A

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



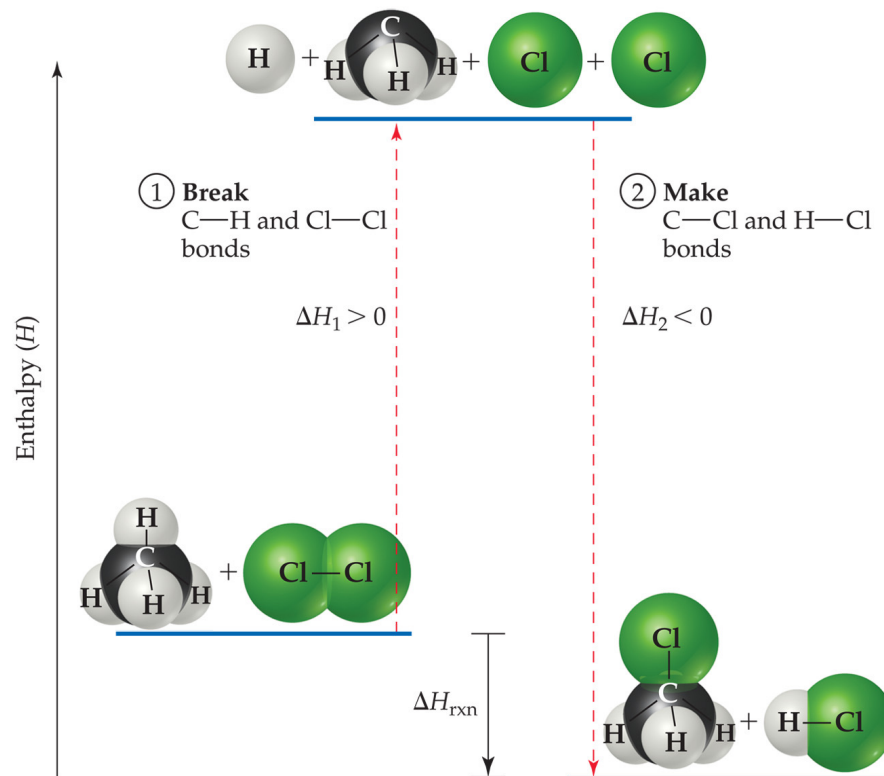
Exam 3 topics

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



Exam 3 topics

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



<i>Bin</i>	<i>Frequency</i>
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

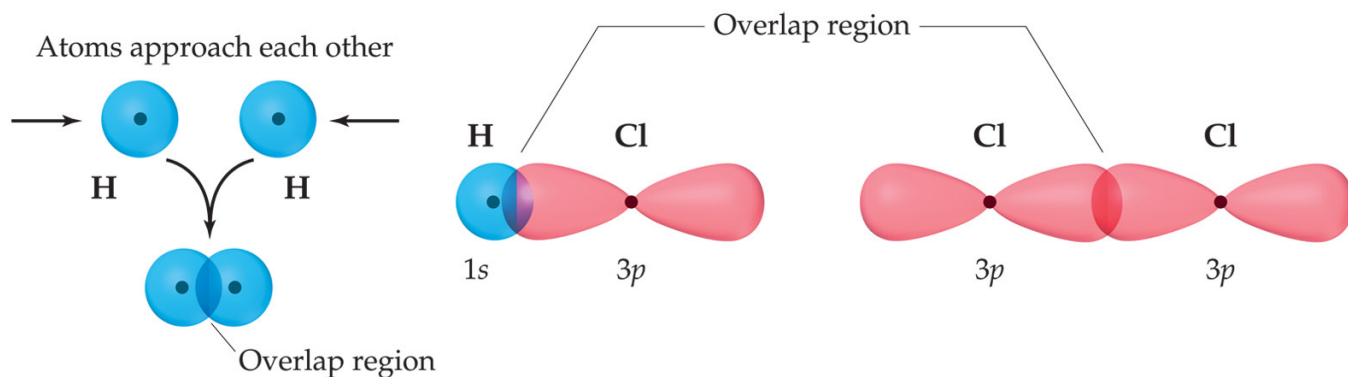
Exam 3 topics

Chapter 9, introduction to covalent bonding, diatomics

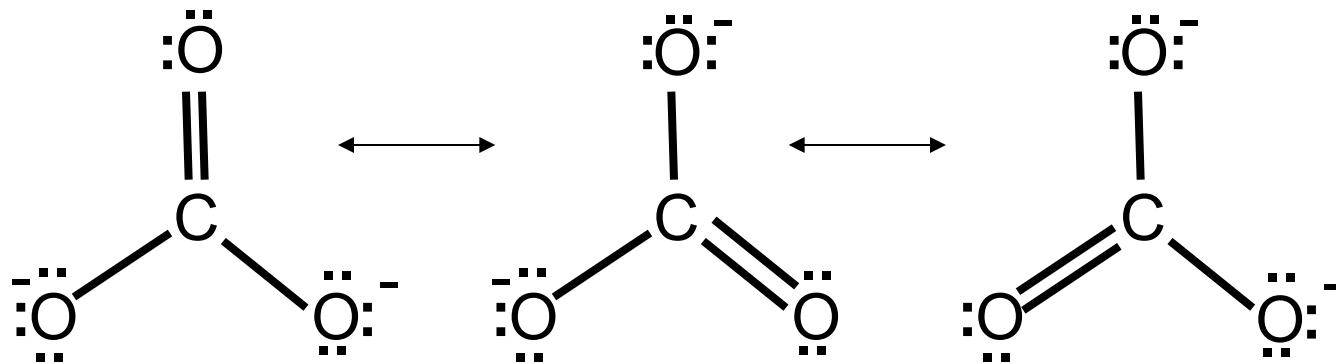
covalent bonds form when electrons are “shared.”

But how, when the electrons are in these atomic orbitals? Do atomic orbitals overlap?

Yes.



15.



trigonal planar, trigonal planar, nonpolar

