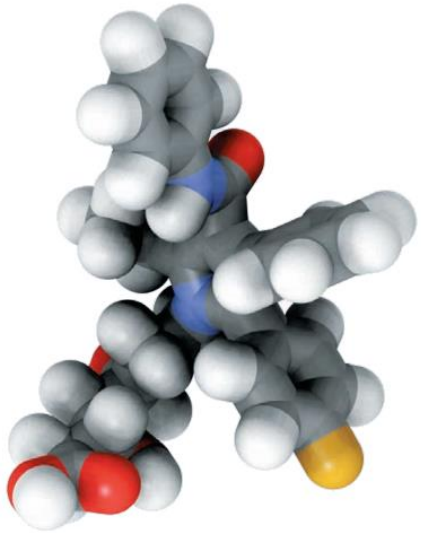
GENERAL CHEMISTRY I



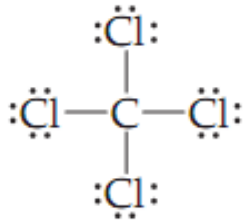
Chapter 9
Molecular Geometry and Bonding Theories

Contents

9-1 Molecular Shapes

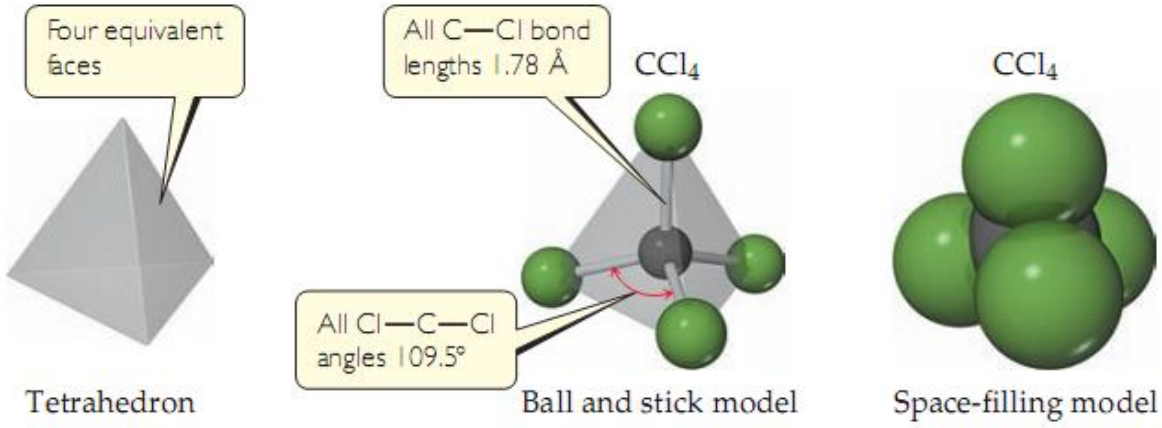
- The Lewis structures are two dimensional

Example: CCl_4



- The actual geometry of a molecule might be three dimensional.

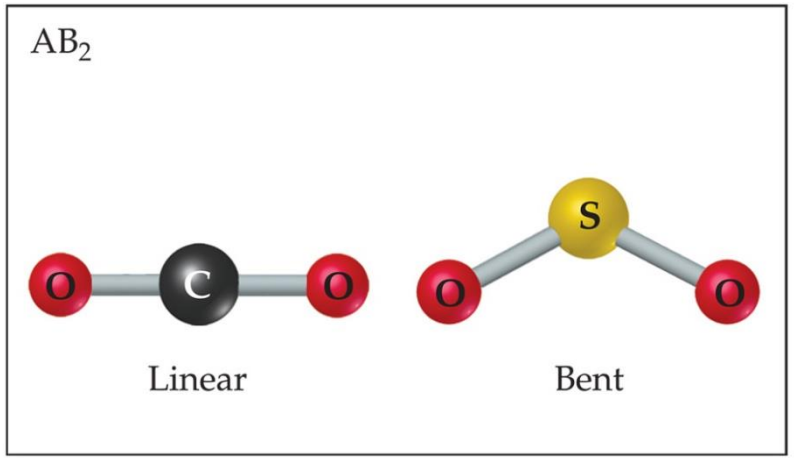
Example: CCl_4

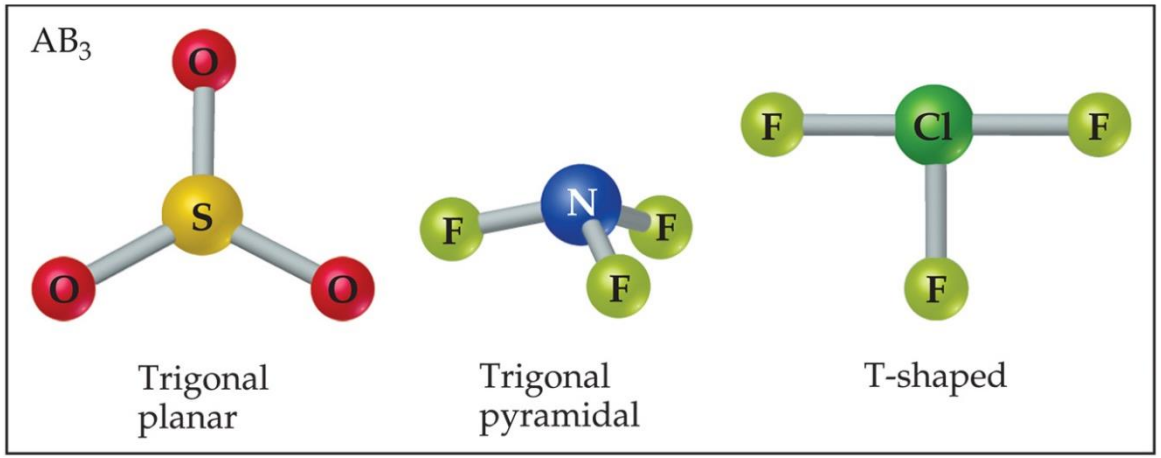


The shape of a molecule is determined by its bond angles

The size of a molecule is defined by its bond angles and bond lengths

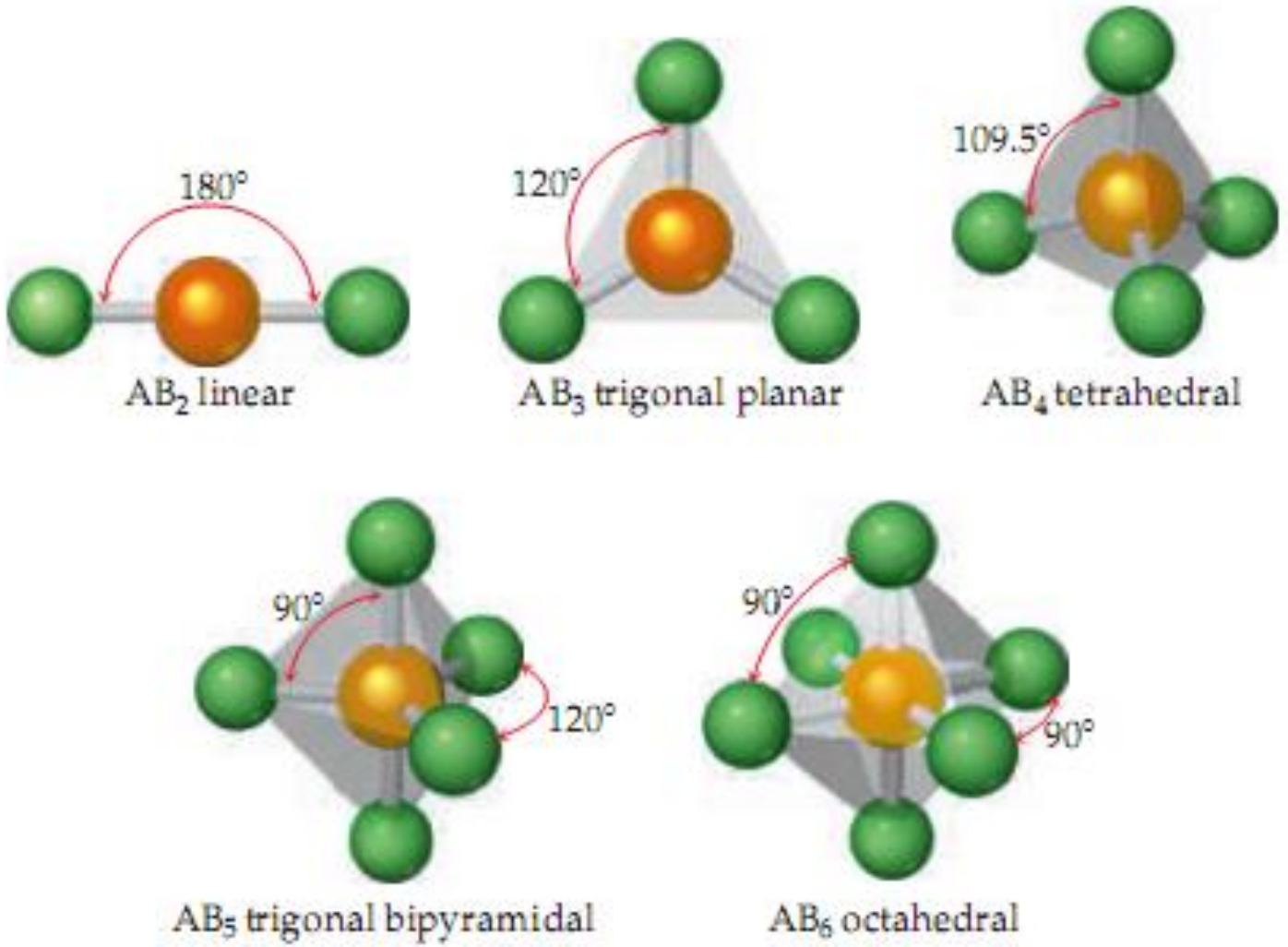
The number of shapes possible for AB_n molecules depends on the value of n





We can easily predict the 3D structure of a molecule just by **adding up bound atoms & lone pairs**

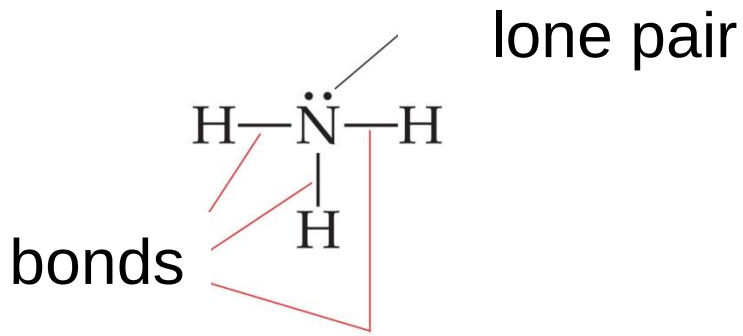
The shapes of most AB_n molecules can be derived from just five basic geometric arrangement:



9-2 The VSEPR Model (Valence Shell Electron Pair Repulsion)

A region in which the electrons are most likely to be found is referred to as an **electron domain**

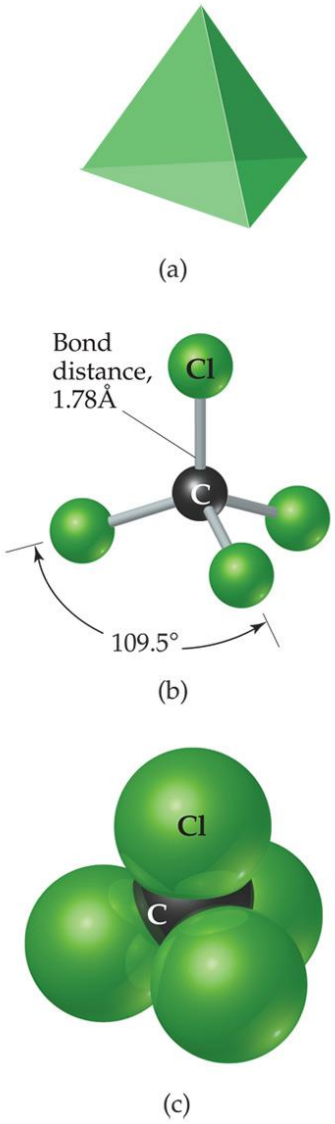
The central atom has four **electron domain** around it.

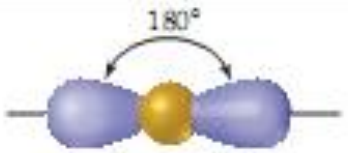
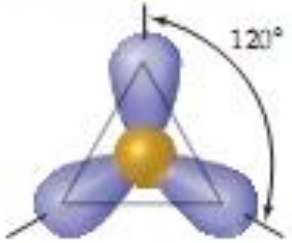
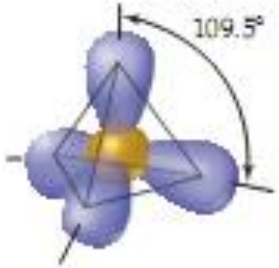
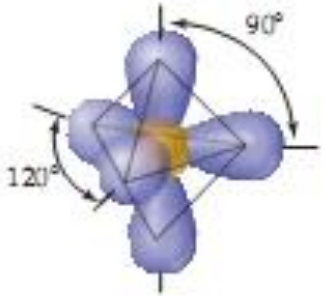
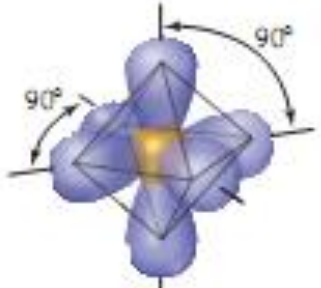


- **atoms and lone pairs take up space and prefer to be as far from each other as possible**
- **shape can be predicted from simple geometry**

"The best arrangement of a given number of electron domains is the one that minimizes the repulsions among them."

"The shapes of different ABn molecules or ions depend on the number of electron domains surrounding the central atom"



Number of Electron Domains	Arrangement of Electron Domains	Electron-Domain Geometry	Predicted 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.

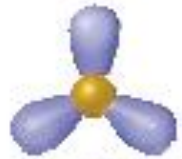
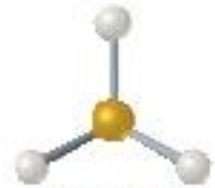
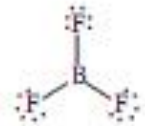
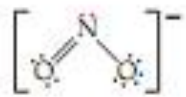
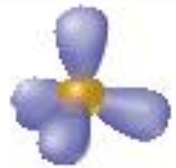
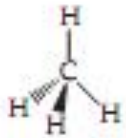
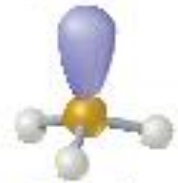
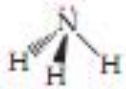
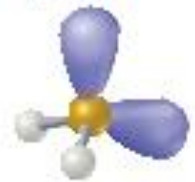
You must learn these!

How to Predict the Shapes of Molecules and Ions Using the VSEPR Model

1. Draw the Lewis structure of the molecule or ion, and count the number of electron domains around the central atom. Each nonbonding electron pair, each single bond, each double bond, and each triple bond counts as one electron domain.

2. Determine the electron-domain geometry by arranging the electron domains about the central atom so that the repulsions among them are minimized, as shown in Table 9.1.

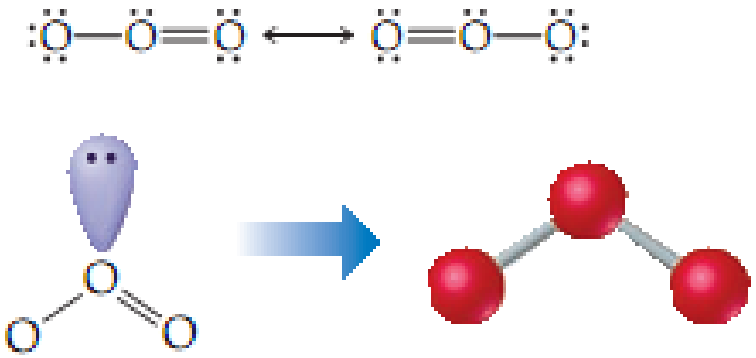
3. Use the arrangement of the bonded atoms to determine the molecular geometry.

Number of Electron Domains	Electron-Domain Geometry	Bonding Domains	Nonbonding Domains	Molecular Geometry	Example
2	 Linear	2	0	 Linear	
3	 Trigonal planar	3	0	 Trigonal planar	
		2	1	 Bent	
4	 Tetrahedral	4	0	 Tetrahedral	
		3	1	 Trigonal pyramidal	
		2	2	 Bent	

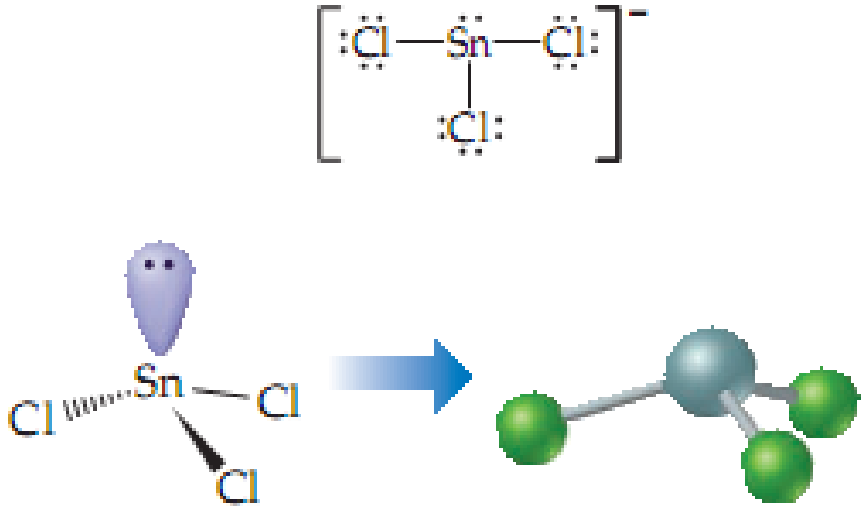
EXAMPLE

Use the VSEPR model to predict the molecular geometry of

(a) O_3,



(b) $SnCl_3^-$



PRACTICE 1

Consider the following AB_3 molecules and ions: PCl_3, SO_3, $AlCl_3$, SO_3^{2-}, and CH_3^+. How many of these molecules and ions do you predict to have a trigonal-planar molecular geometry?

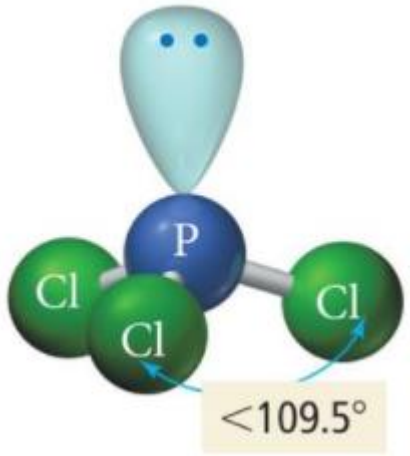
(a) 1

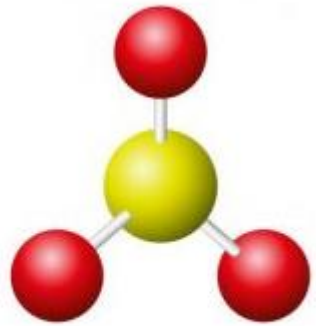
(b) 2

(c) 3

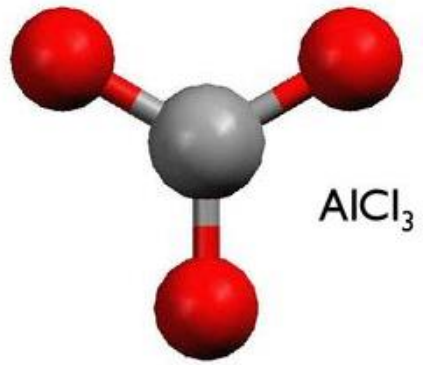
(d) 4

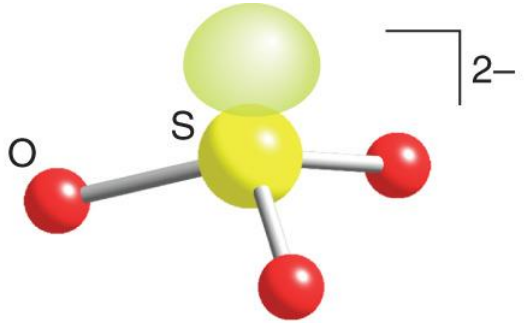
(e) 5





SO_3



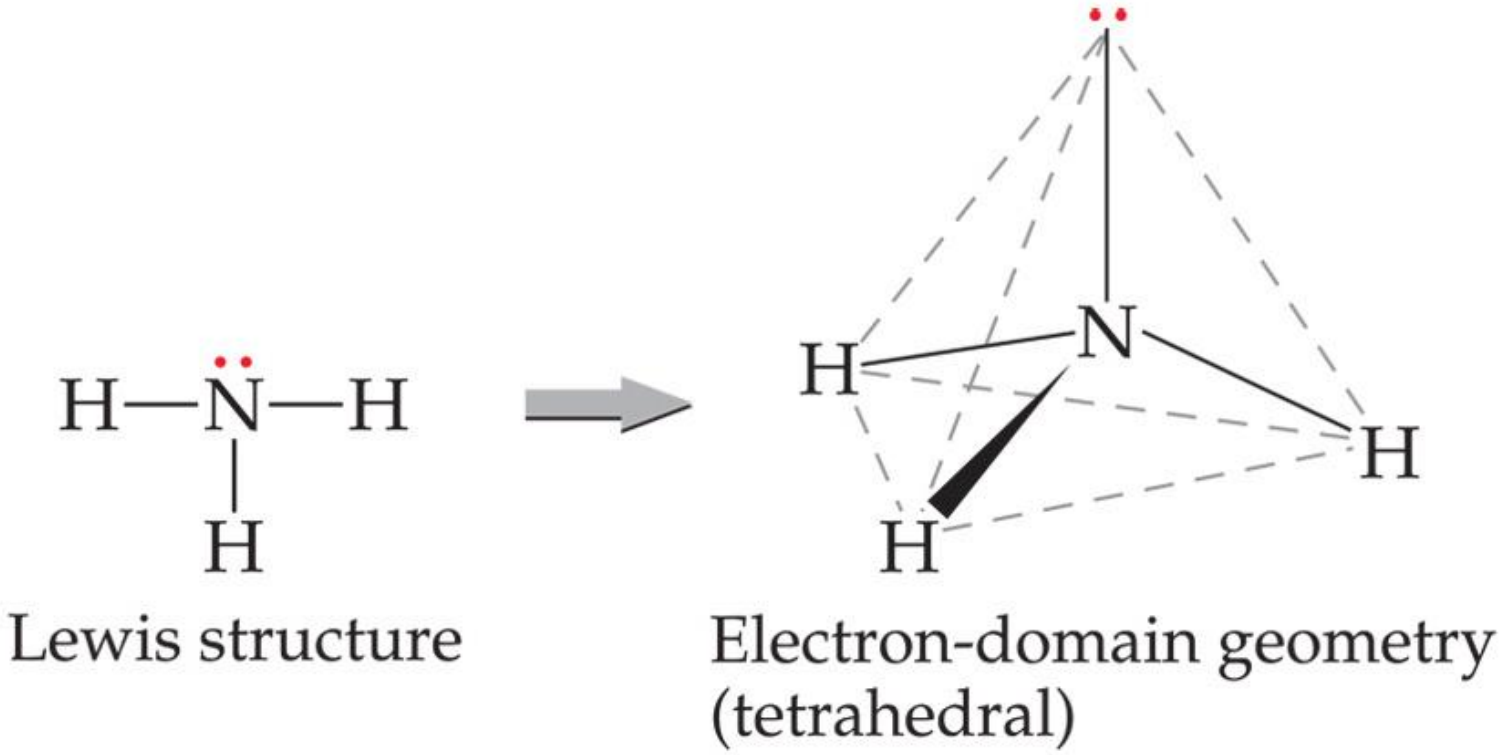


PRACTICE 2

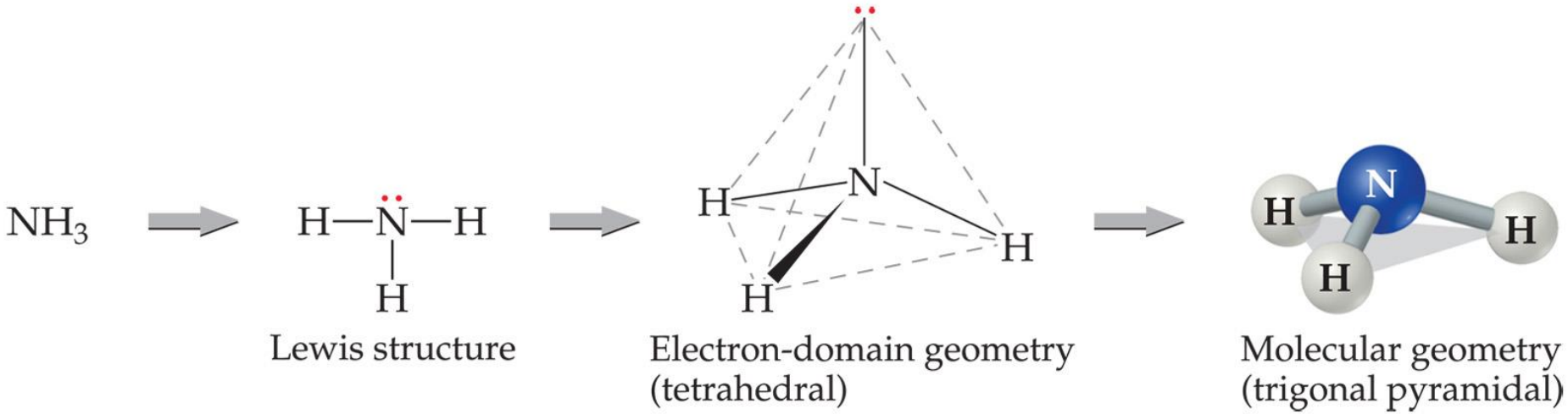
Predict the electron-domain and molecular geometries for

(a) $SeCl_2$,

(b) CO_3^{2-} .



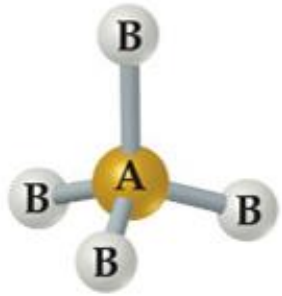
- All one must do is count the number of electron domains in the Lewis structure.
- The geometry will be that which corresponds to that number of electron domains



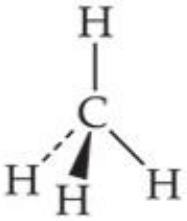
- The geometry is often *not* the shape of the molecule, however.
- The **"shape"** is defined by the positions of ***only*** **the atoms in the molecules, not the lone pairs.**

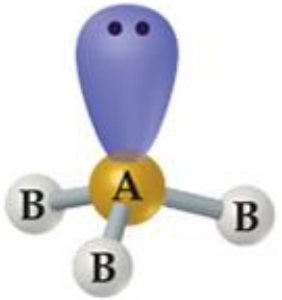
Geometries vs. shape

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

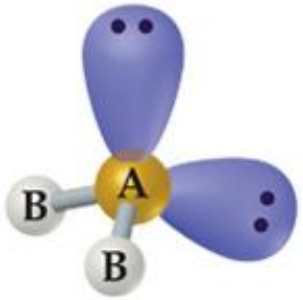


Tetrahedral



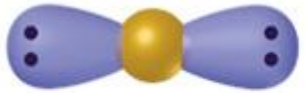
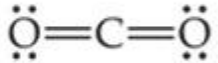


Trigonal pyramidal



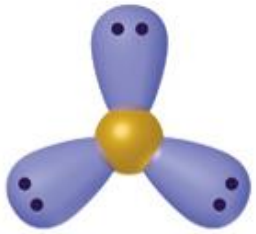
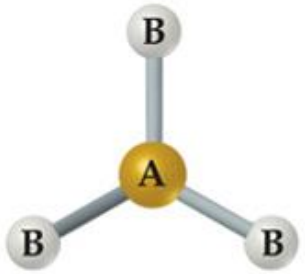
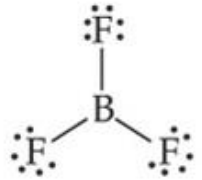
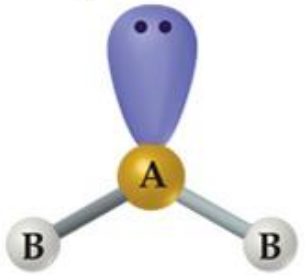
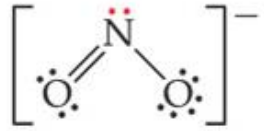
Bent

Linear geometry

Number of Electron Domains	Electron-Domain Geometry	Bonding Domains	Nonbonding Domains	Molecular Geometry	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.

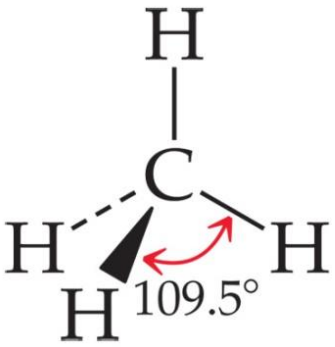
Trigonal Planar geometry

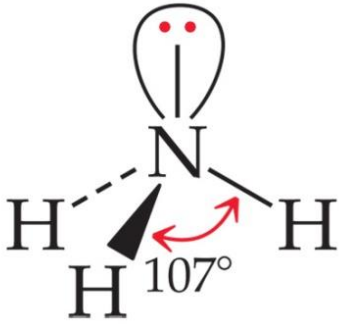
Number of Electron Domains	Electron-Domain Geometry	Bonding Domains	Nonbonding Domains	Molecular Geometry	Example
3	 Trigonal planar	3	0	 Trigonal planar	
		2	1	 Bent	

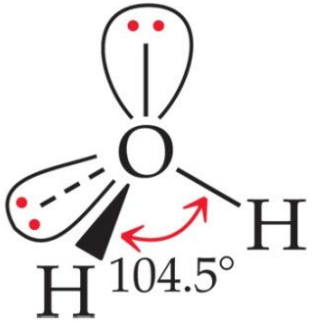
- There are two molecular geometries:
  - Trigonal planar, if there are no lone pairs
  - Bent, if there is a lone pair.

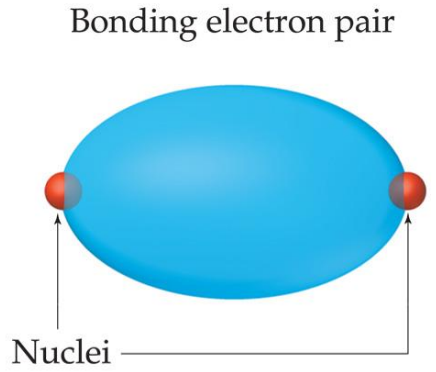
Lone pairs and Bond Angle

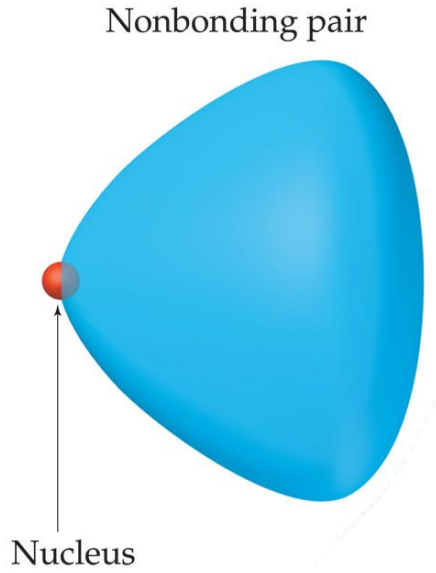
- Lone pairs are physically larger than atoms.
- Therefore, their repulsions are greater; this tends to decrease bond angles in a molecule.



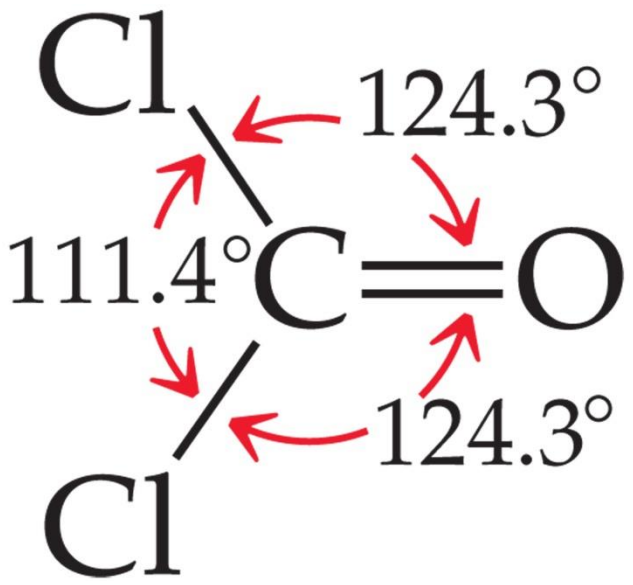






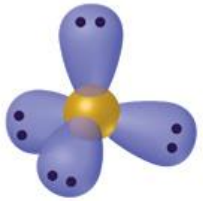
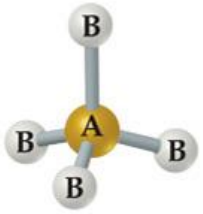
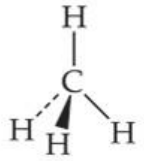
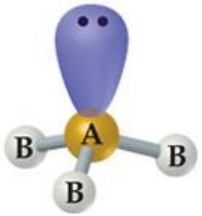
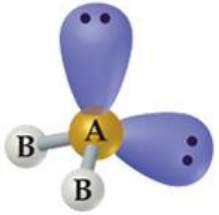


Multiple Bonds and Bond Angles



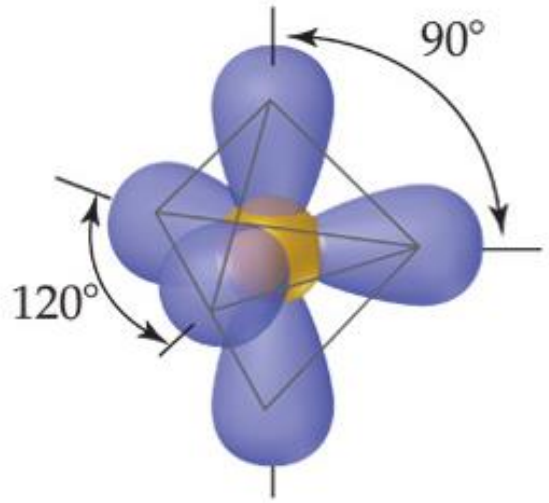
- Double and triple bonds place greater electron density on one side of the central atom than do single bonds.
- Therefore, they also affect bond angles.

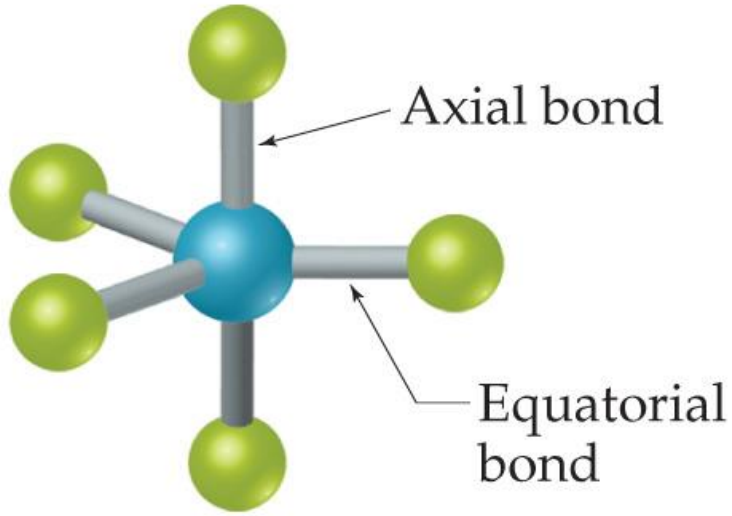
Tetrahedral geometry

Number of Electron Domains	Electron-Domain Geometry	Bonding Domains	Nonbonding Domains	Molecular Geometry	Example
4	 Tetrahedral	4	0	 Tetrahedral	
		3	1	 Trigonal pyramidal	
		2	2	 Bent	

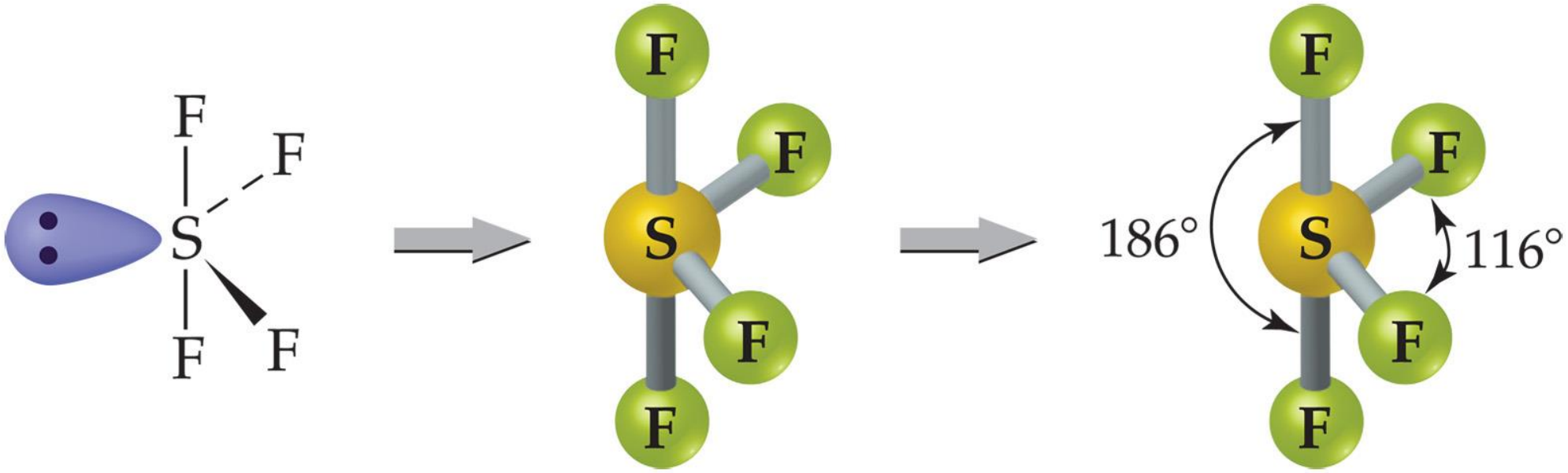
- There are three molecular geometries:
  - Tetrahedral, if no lone pairs
  - Trigonal pyramidal if one is a lone pair
  - Bent if there are two lone pairs

Trigonal Bipyramidal geometry



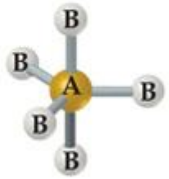
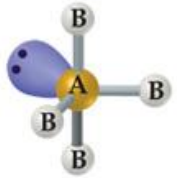
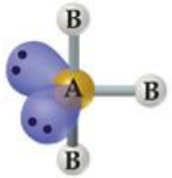
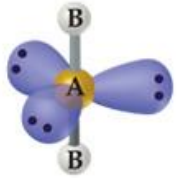


- There are two distinct positions in this geometry:
  - Axial
  - Equatorial



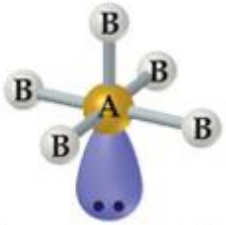
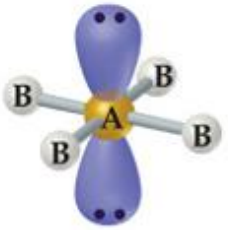
Lower-energy conformations result from having lone pairs in equatorial, rather than axial, positions in this geometry.

Trigonal Bipyramidal geometry

Total Electron Domains	Electron-Domain Geometry	Bonding Domains	Nonbonding Domains	Molecular Geometry	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

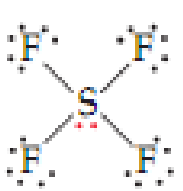
Total Electron Domains	Electron-Domain Geometry	Bonding Domains	Nonbonding Domains	Molecular Geometry	Example
6	 Octahedral	6	0	 Octahedral	SF_6
		5	1	 Square pyramidal	BrF_5
		4	2	 Square planar	XeF_4

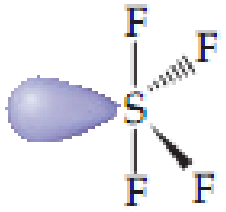
- All positions are equivalent in the octahedral domain.
- There are three molecular geometries:

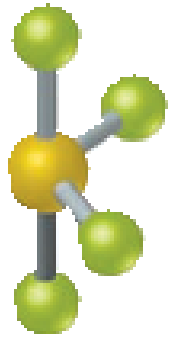
EXAMPLE

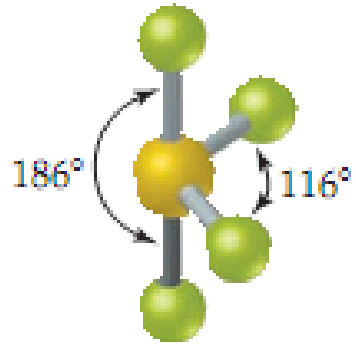
Use the VSEPR model to predict the molecular geometry of

(a) SF_4,

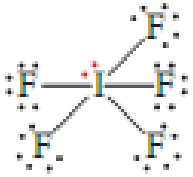


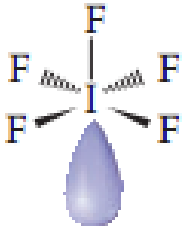


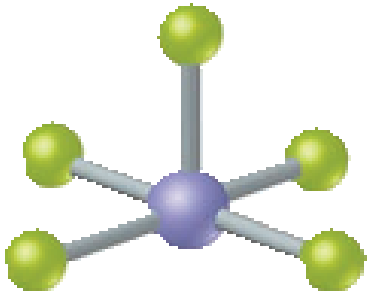




(b) IF_5.







PRACTICE 1

A certain AB_4 molecule has a square-planar molecular geometry. Which of the following statements about the molecule is or are true?:

(i) The molecule has four electron domains about the central atom A.

(ii) The B-A-B angles between neighboring B atoms is 90°.

(iii) The molecule has two nonbonding pairs of electrons on atom A.

(a) Only one of the statements is true.

(b) Statements (i) and (ii) are true.

(c) Statements (i) and (iii) are true.

(d) Statements (ii) and (iii) are true.

(e) All three statements are true.

PRACTICE 2

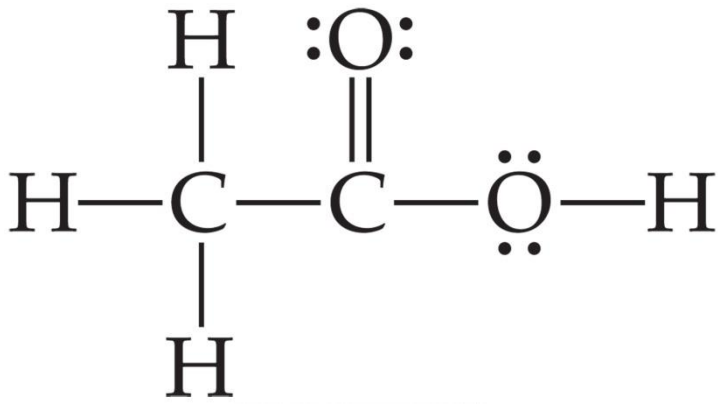
Predict the electron-domain and molecular geometries of

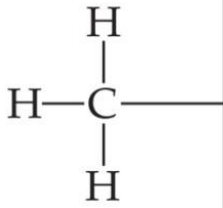
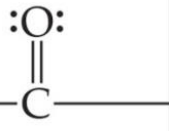
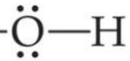
(a) BrF_3,

(b) SF_5^+.

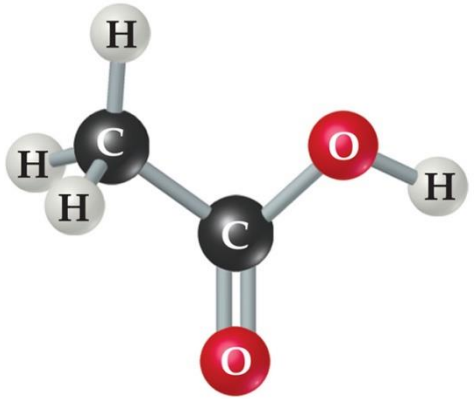
Larger Molecules

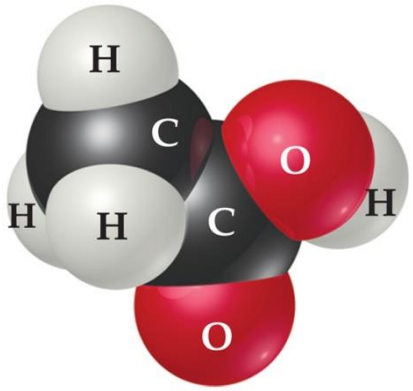
In larger molecules, we talk about the geometry about a particular atom rather than the geometry of the molecule as a whole.



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

Larger Molecules

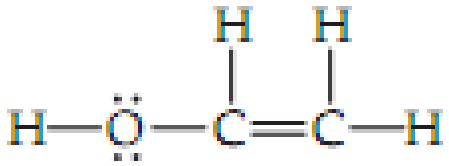




The structure of the whole molecule is only clear when we look at the whole molecule. But the geometry about each atom still follows the same rules!

EXAMPLE

Eyedrops for dry eyes usually contain a water-soluble polymer called poly(vinyl alcohol), which is based on the unstable organic molecule vinyl alcohol. Predict the approximate values for the H – O – C and O – C – C bond angles in vinyl alcohol.



4 electron domains
(2 bonding, 2 nonbonding)

Tetrahedral (109.5°)

compressed somewhat by the nonbonding pairs

➔ this angle to be slightly less than 109.5°

3 electron domains

Trigonal planar (120°)

larger size of the C – C domain

➔ This angle should be slightly greater than 120°.

PRACTICE 1

The atoms of the compound methylhydrazine, CH_6N_2, which is used as a rocket propellant, are connected as follows (note that lone pairs are not shown). What do you predict for the ideal values of the C–N–N and H–N–H angles, respectively?

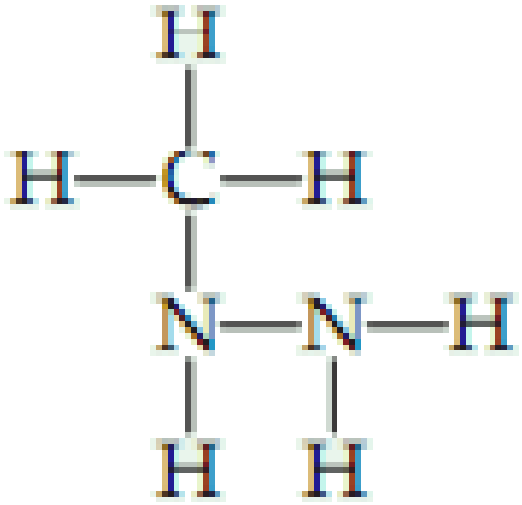
(a) 109.5° and 109.5°

(b) 109.5° and 120°

(c) 120° and 109.5°

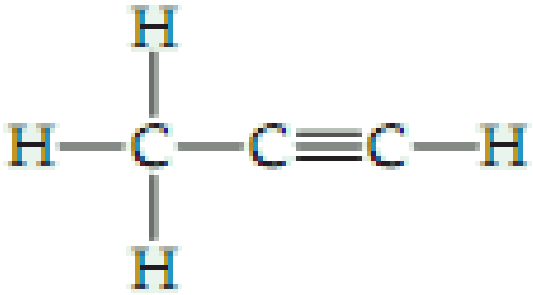
(d) 120° and 120°

(e) None of the above



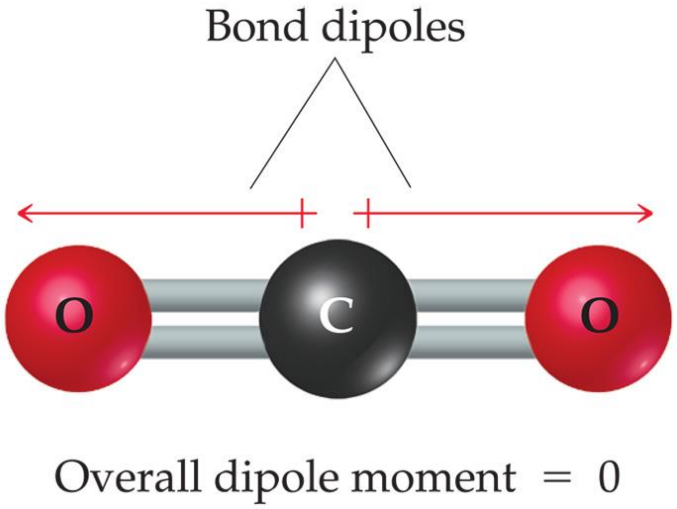
PRACTICE 2

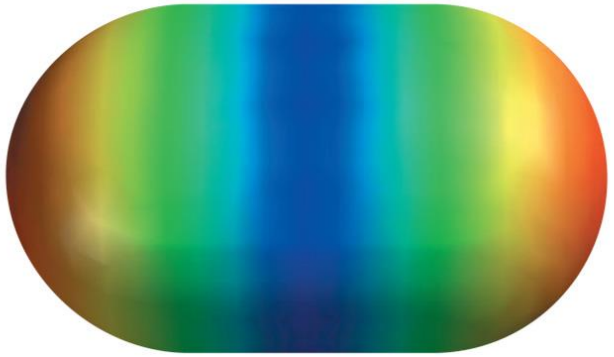
Predict the H–C–H and C–C–C bond angles in propyne:



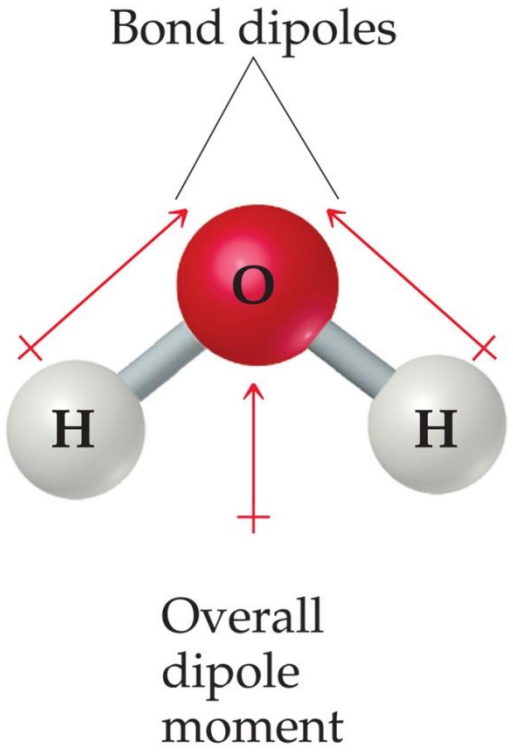
9-3 Molecular Shape and Molecular Polarity

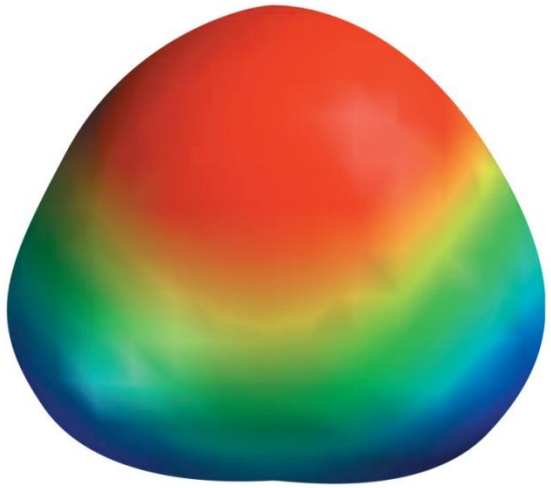
- In Chapter 8 we discussed bond dipoles.
- Regarding polar bonds versus polar molecules, we must think about the molecule as a whole.





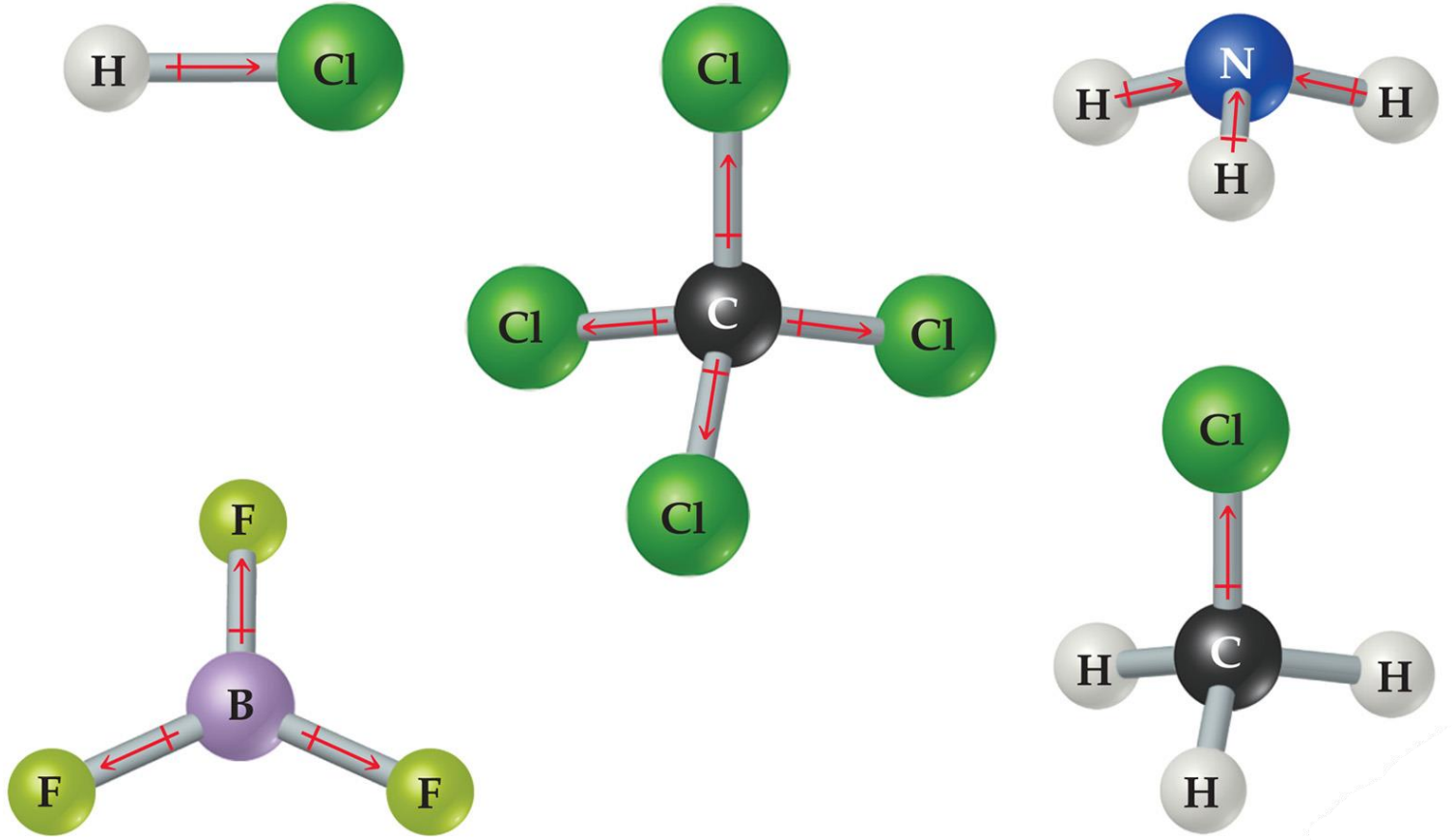
Polarity





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

Polarity
“The tractor pull”



EXAMPLE

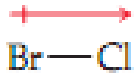
Predict whether these molecules are polar or nonpolar:

(a) BrCl,

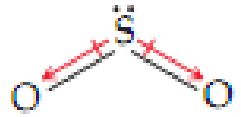
(b) SO_2,

(c) SF_6.

(a) Chlorine is more electronegative than bromine. All diatomic molecules with polar bonds are polar molecules. Consequently, BrCl is polar, with chlorine carrying the partial negative charge:

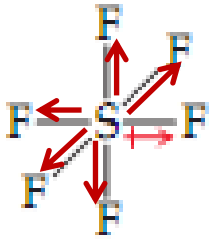


(b) Because oxygen is more electronegative than sulfur, SO_2 has polar bonds. Three resonance forms can be written:



(c) Fluorine is more electronegative than sulfur, so the bond dipoles point toward fluorine.

Because the octahedral molecular geometry is symmetrical, the bond dipoles cancel, and the molecule is nonpolar



PRACTICE 1

Consider an AB3 molecule in which A and B differ in electronegativity. You are told that the molecule has an overall dipole moment of zero. Which of the following could be the molecular geometry of the molecule?

(a) Trigonal pyramidal

(b) Trigonal planar

(c) T-shaped

(d) Tetrahedral

(e) More than one of the above

PRACTICE 2

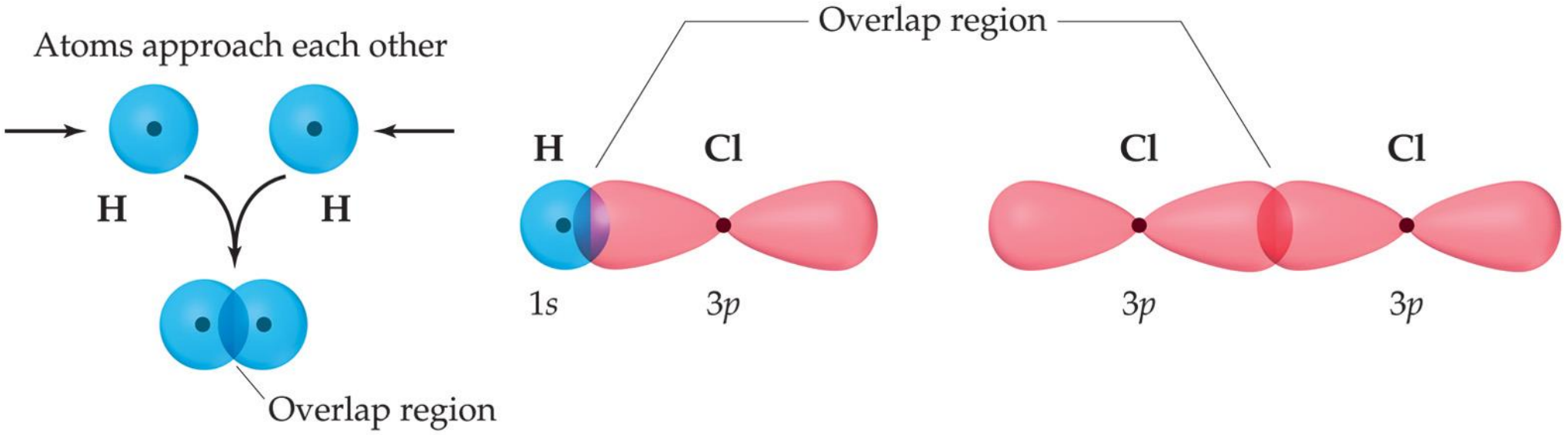
Determine whether the following molecules are polar or nonpolar:

(a) SF_4,

(b) $SiCl_4$

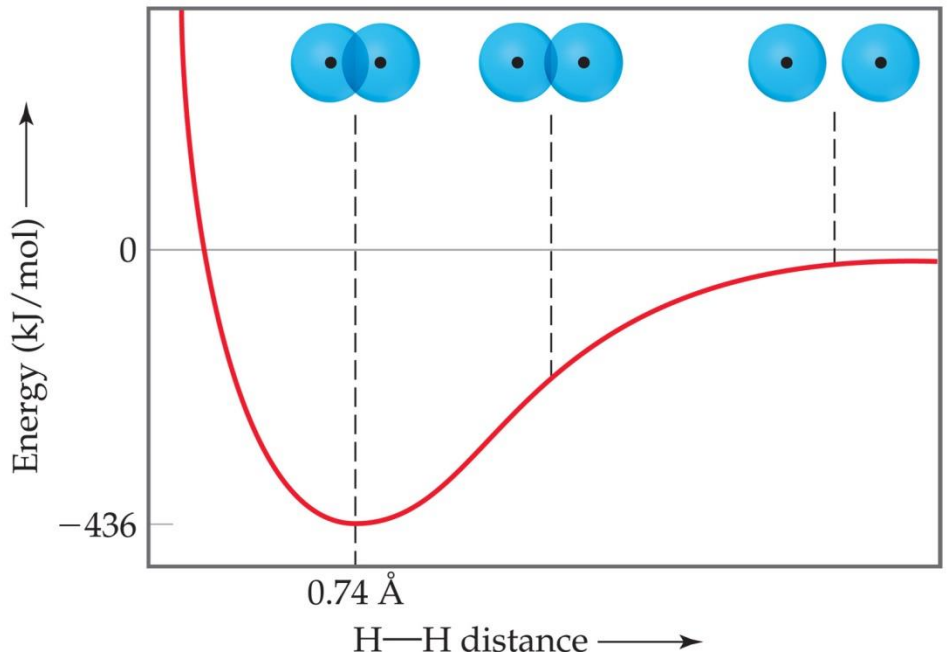
9-4 Covalent Bonding and Orbital Overlap

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

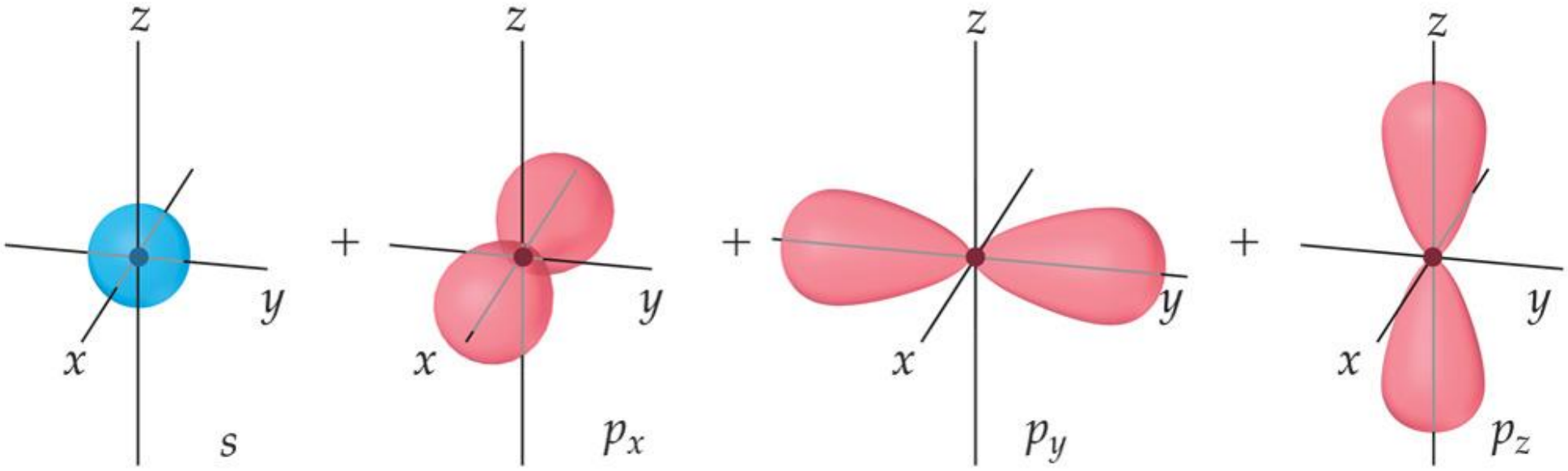


Overlap and Bonding

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



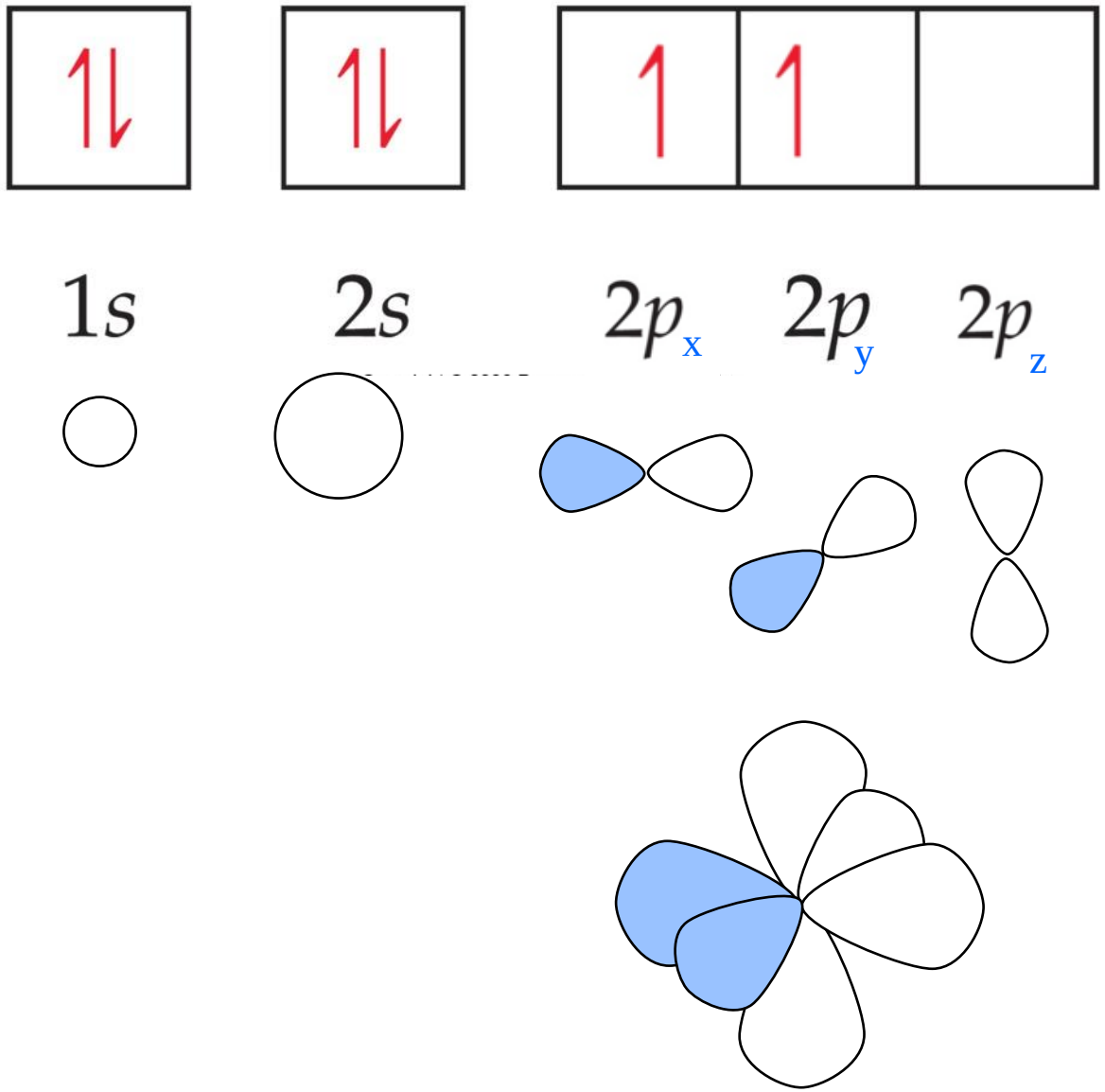
9-5 Hybrid Orbitals



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

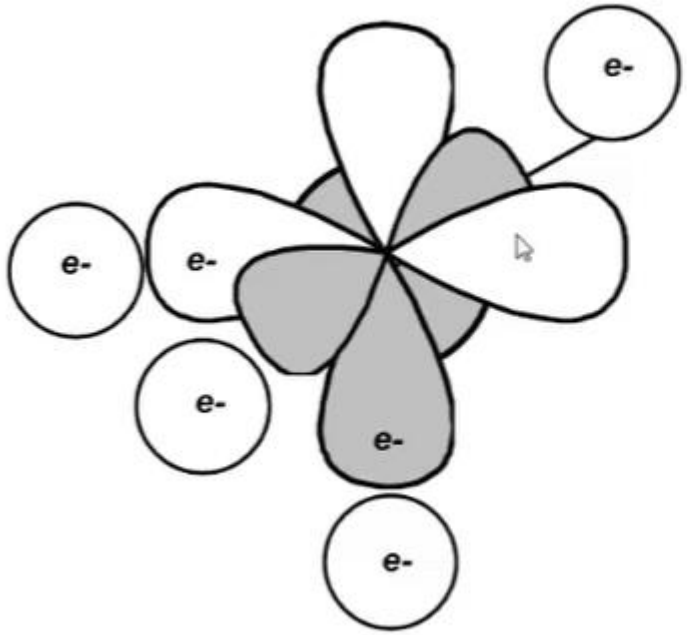
Hybrid Orbitals

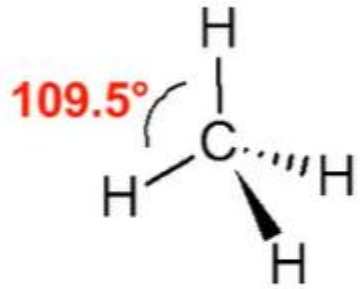
- Consider carbon: $1s^2\ 2s^2\ 2p^2$



Hybrid Orbitals

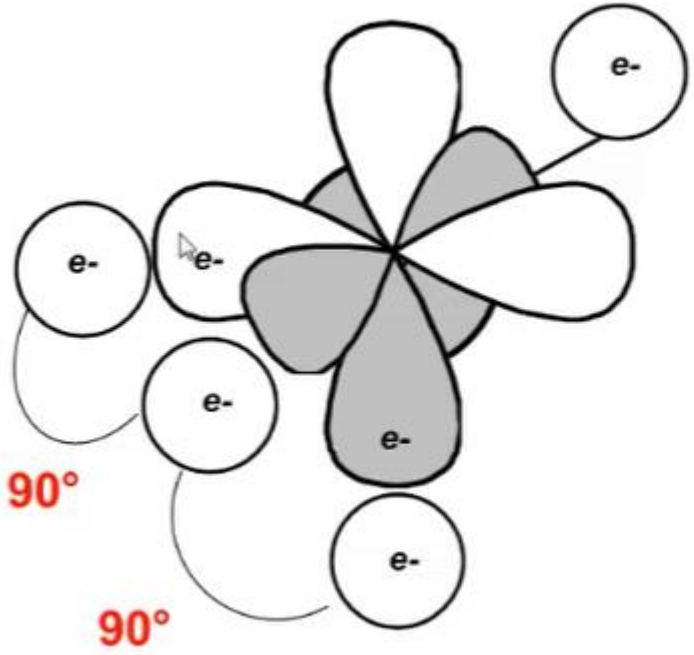
- Consider CH_4

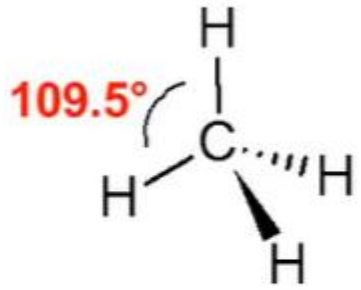




Hybrid Orbitals

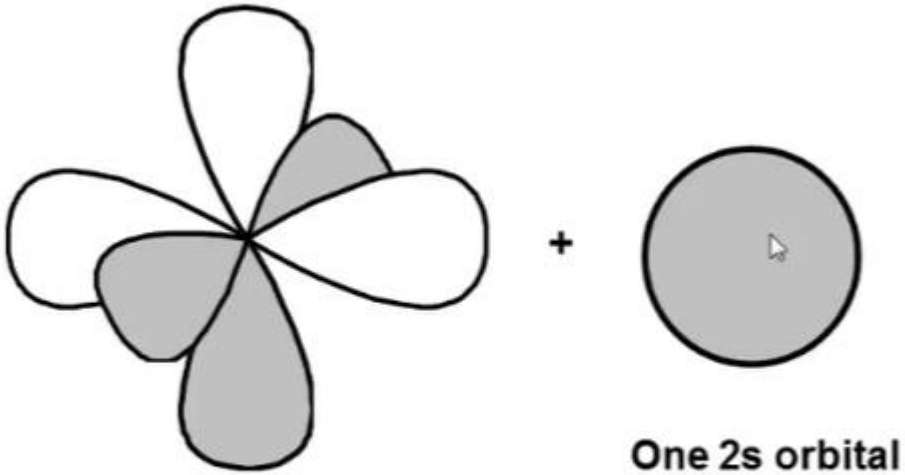
- Consider CH_4

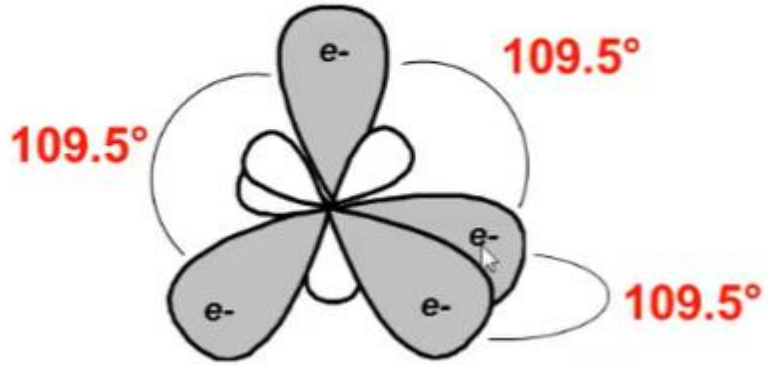




Hybrid Orbitals

- Consider CH_4

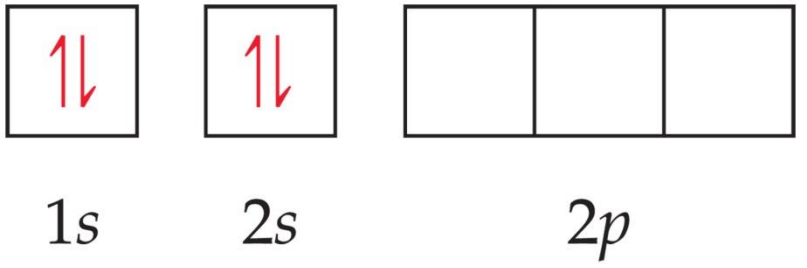




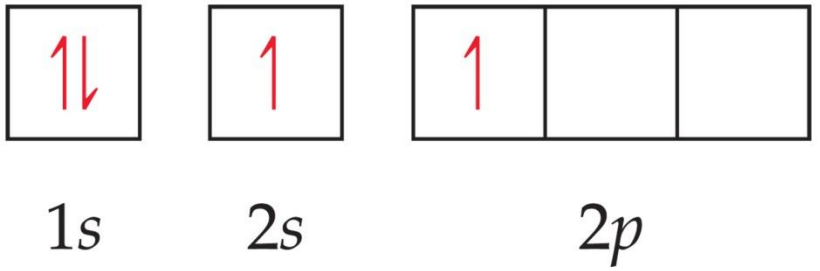
Four sp^3 orbitals

Hybrid Orbitals

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

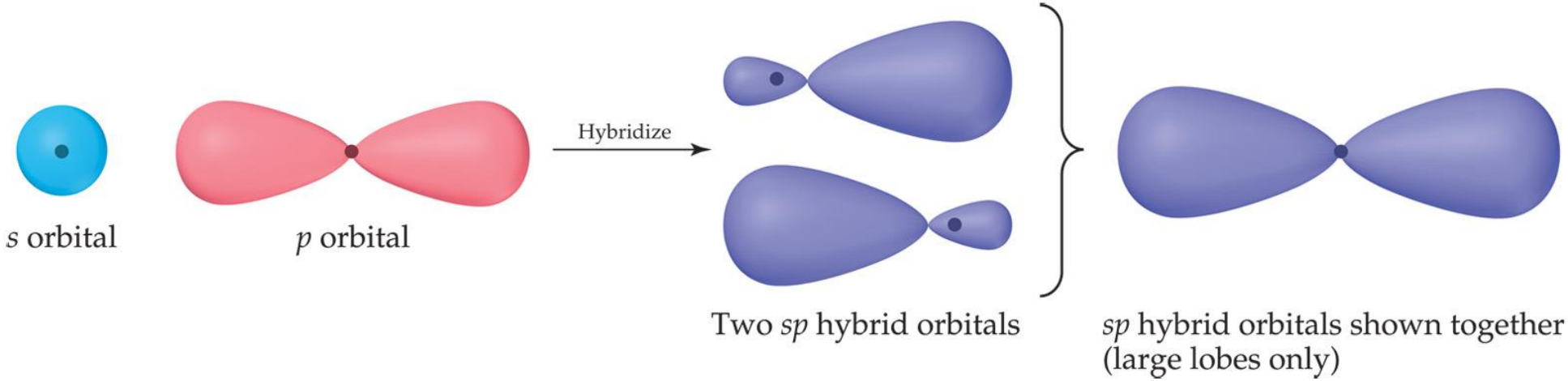


  - But if it absorbs the small amount of energy needed to promote an electron from the 2*s* to the 2*p* orbital, it can form two bonds.



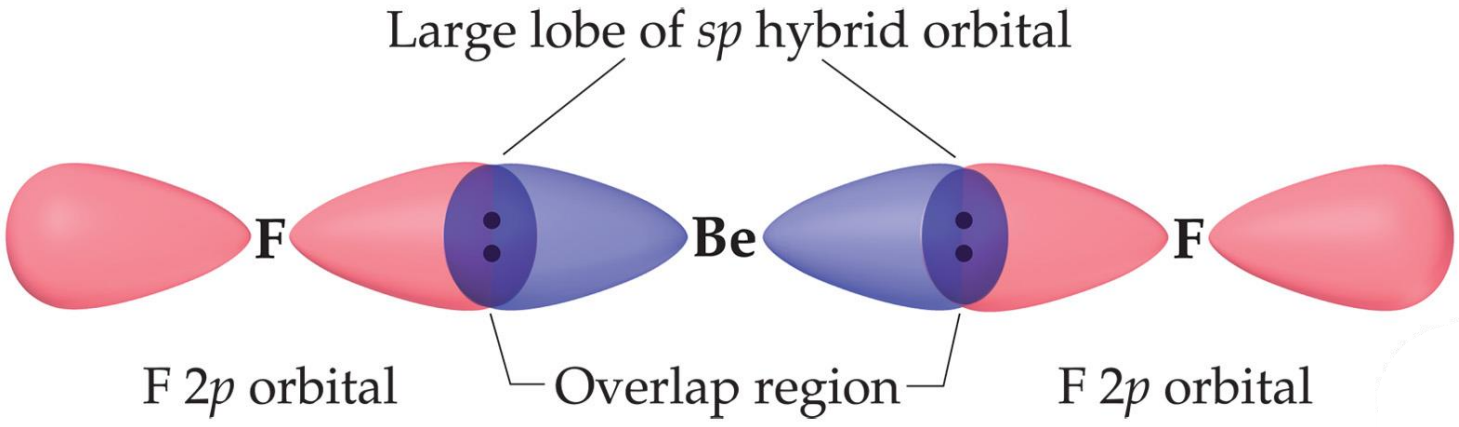
Hybrid Orbitals

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

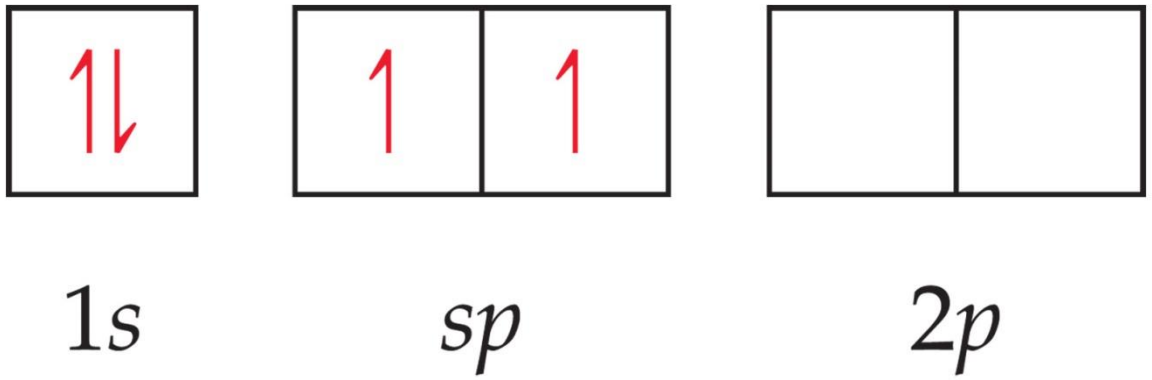


Hybrid Orbitals

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



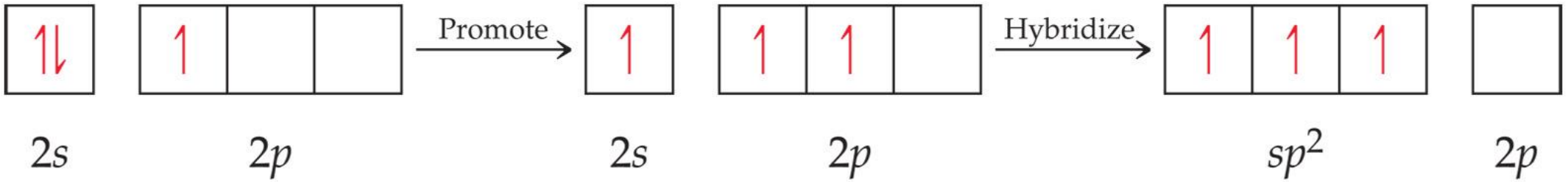
Hybrid Orbitals



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

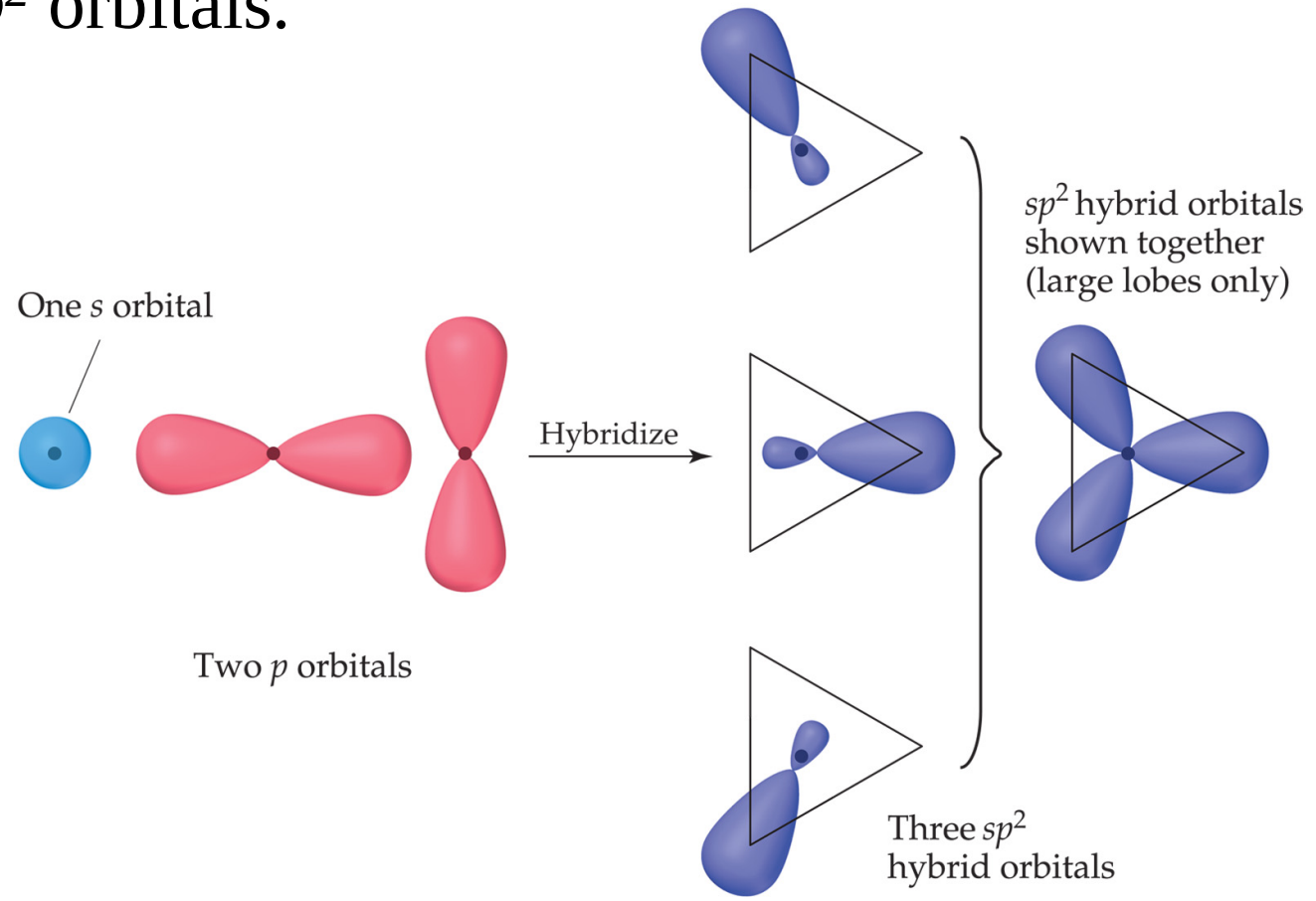
Hybrid Orbitals

Using a similar model for boron leads to…



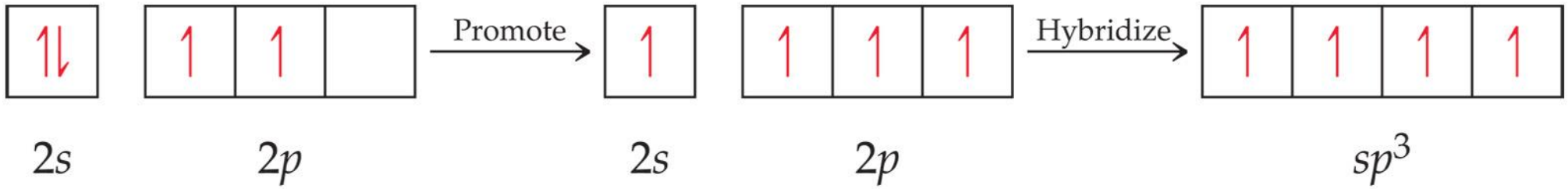
Hybrid Orbitals

…three degenerate sp^2 orbitals.



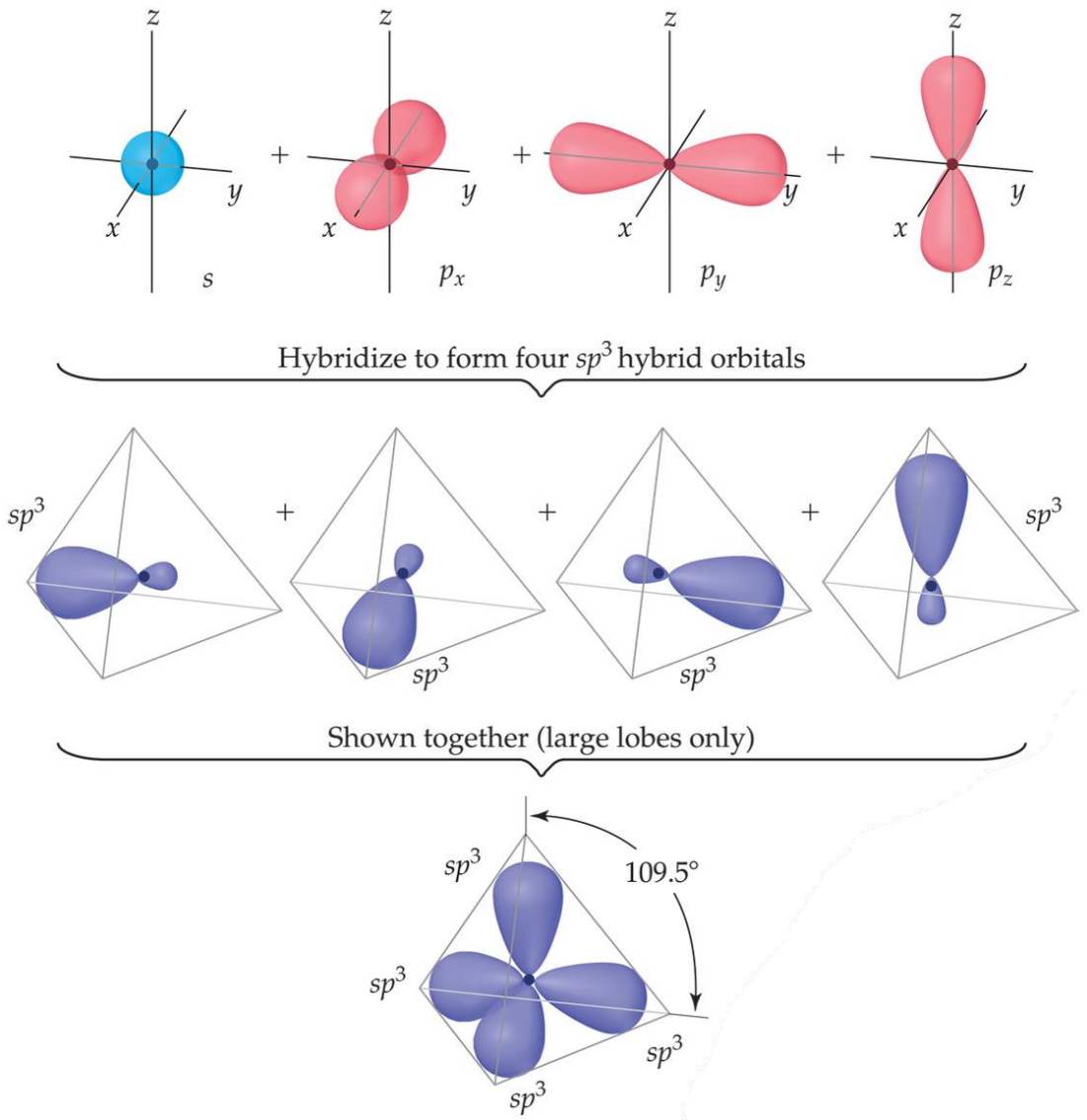
Hybrid Orbitals

With carbon we get…



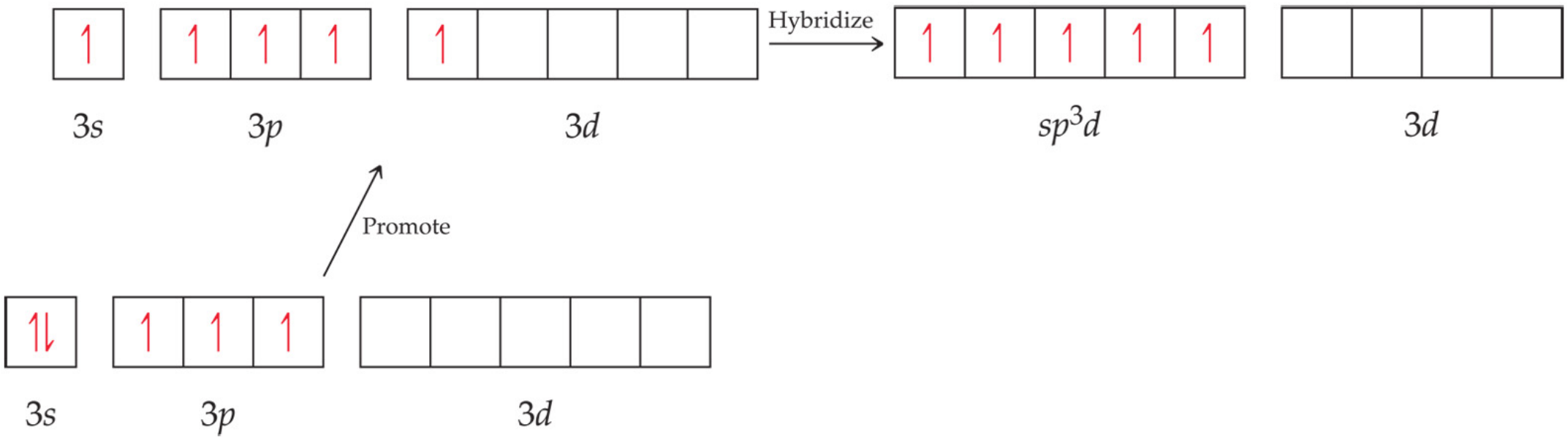
Hybrid Orbitals

…four degenerate sp^3 orbitals.

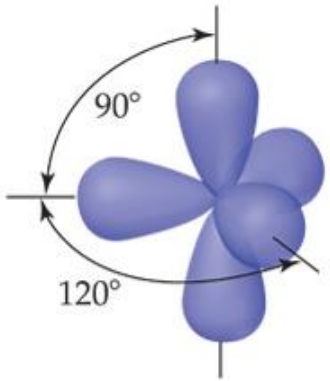


Hybrid Orbitals

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



Hybrid Orbitals

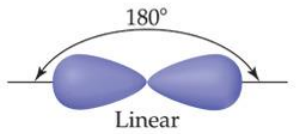
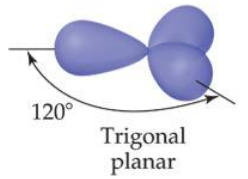
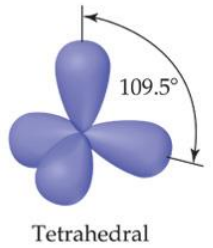
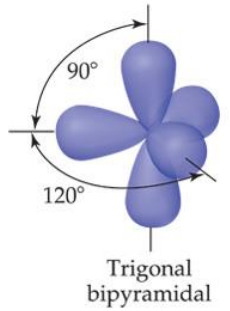
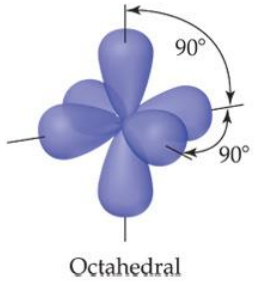


This leads to five degenerate sp^3d orbitals…

…or six degenerate sp^3d^2 orbitals.

Hybrid Orbitals

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

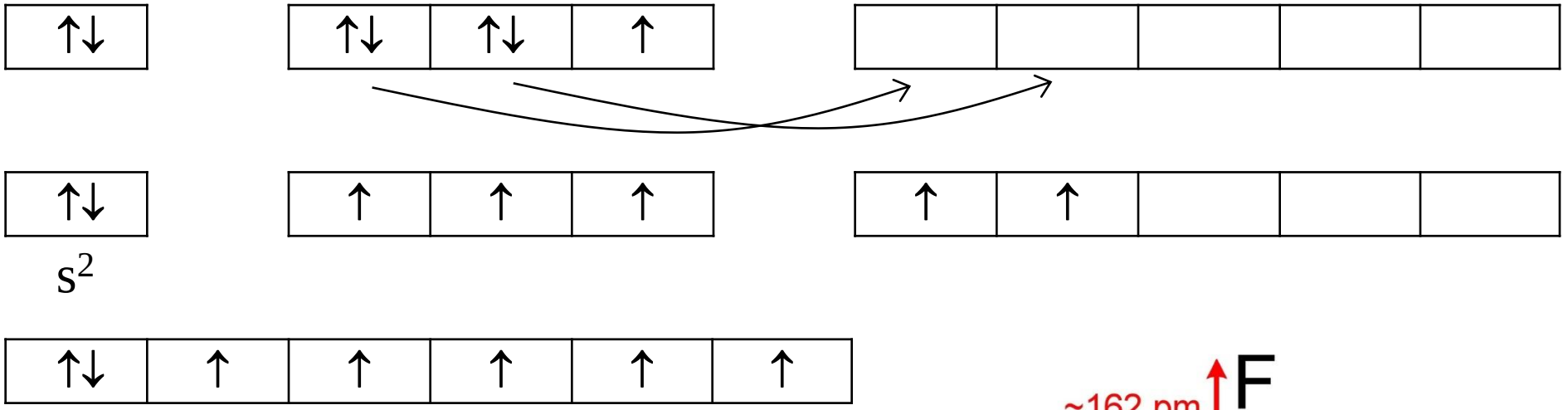
Atomic Orbital Set	Hybrid Orbital Set	Geometry	Examples
s,p	Two *sp*		BeF_2, $HgCl_2$
s,p,p	Three sp^2		BF_3, SO_3
s,p,p,p	Four sp^3		CH_4, NH_3, H_2O, NH_4^+
s,p,p,p,d	Five sp^3d		PF_5, SF_4, BrF_3
s,p,p,p,d,d	Six sp^3d^2		SF_6, ClF_5, XeF_4, PF_6^-

EXAMPLE 3

Use boxes to present the hybrid orbital of Cl in ClF_5 and state the molecular geometry of ClF_5

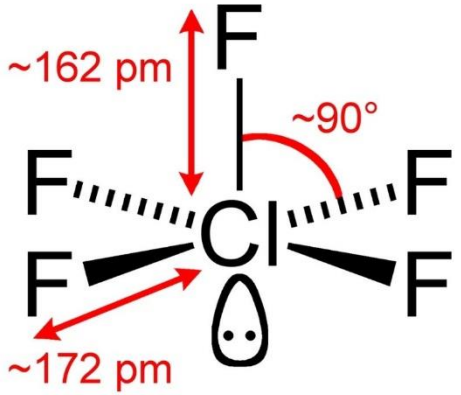
Cl: group 7A, period 3 => 7 valence e and 3 shells

Cl: $3s^2 3p^5$



s^2

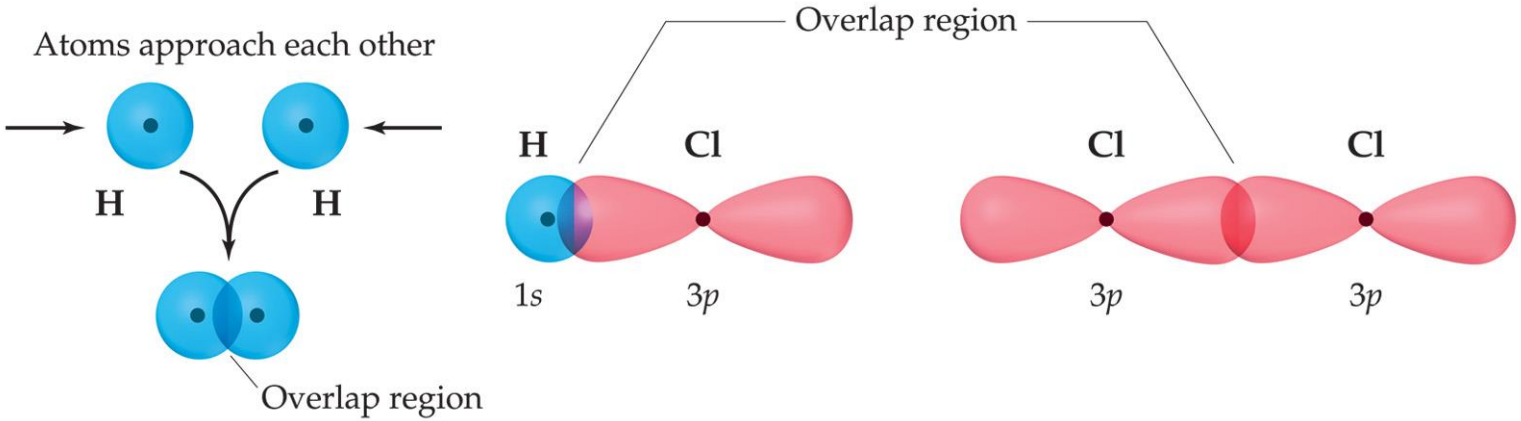
sp^3d^2



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.

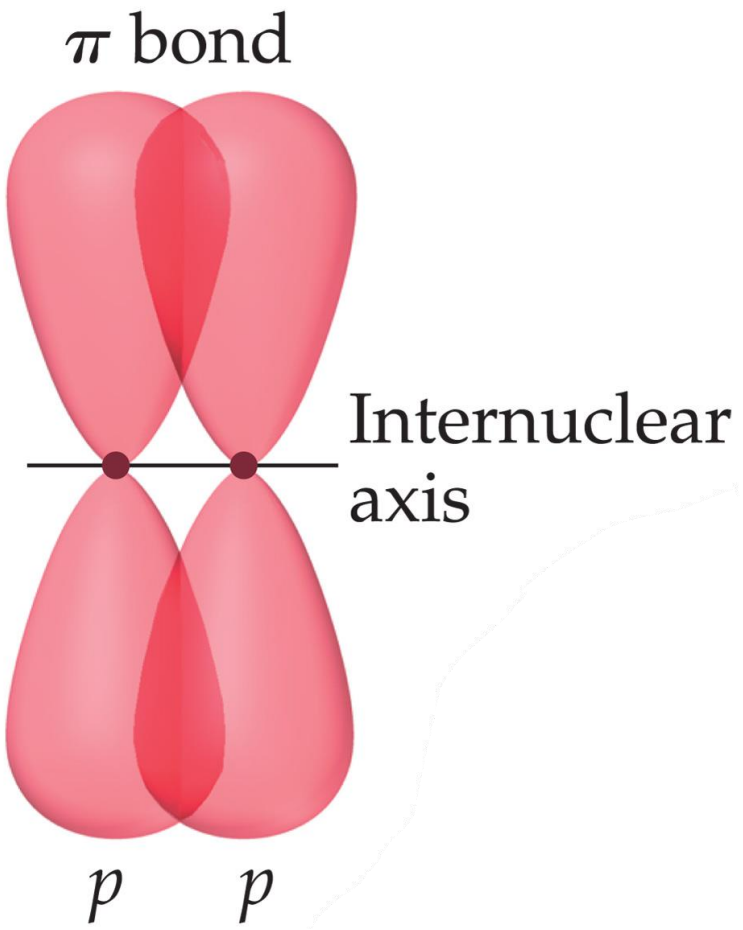
Sigma (σ) Bonds



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

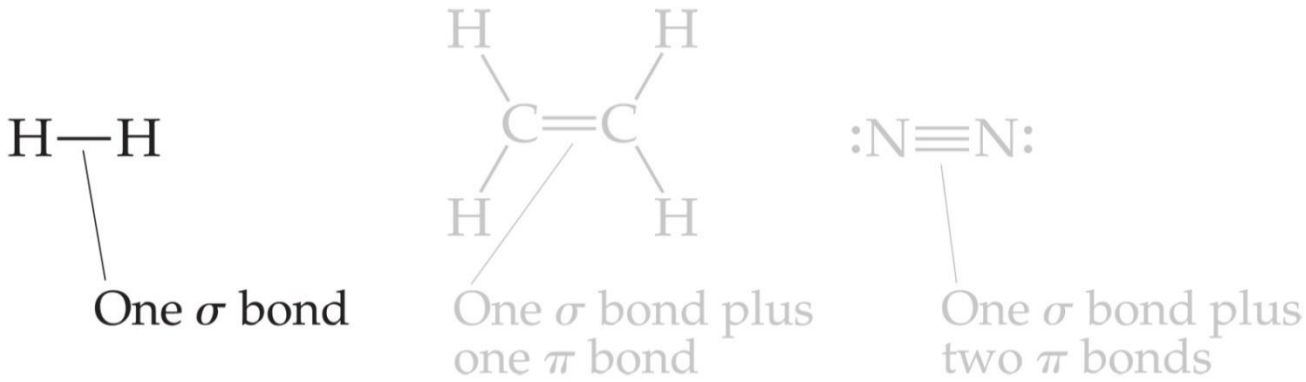
Pi (π) Bonds

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



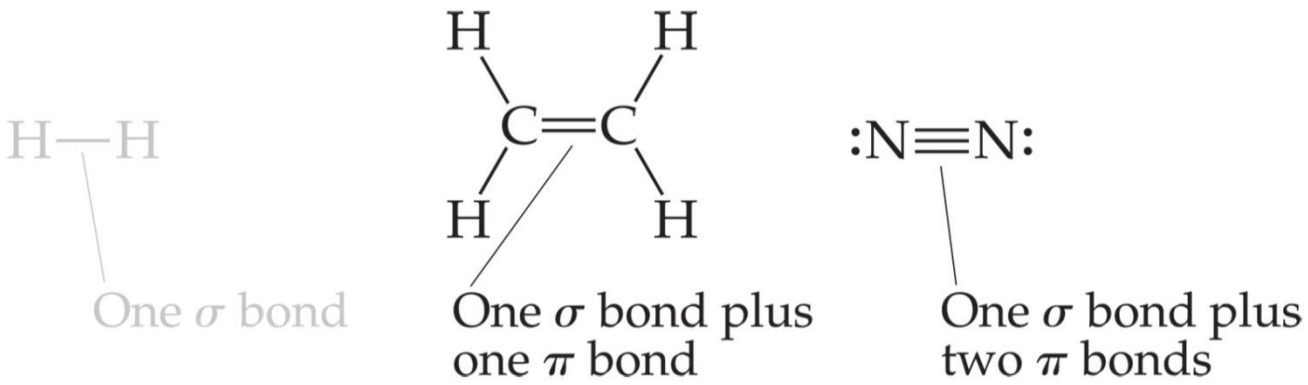
Single Bonds

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

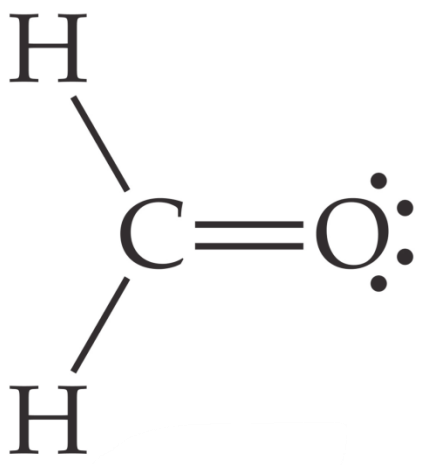


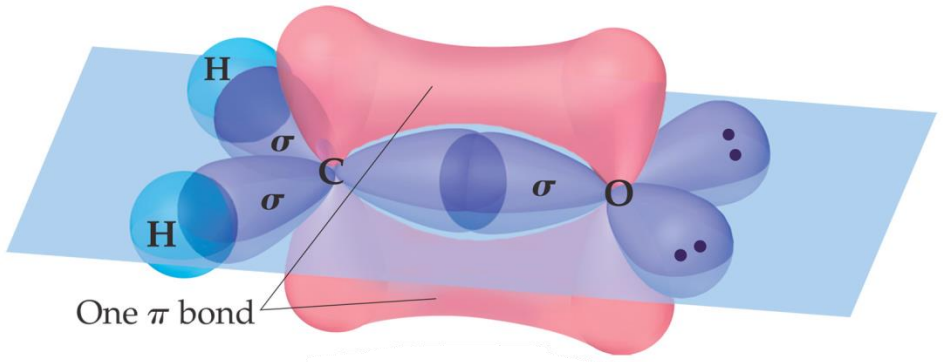
9-6 Multiple Bonds

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



Multiple Bonds

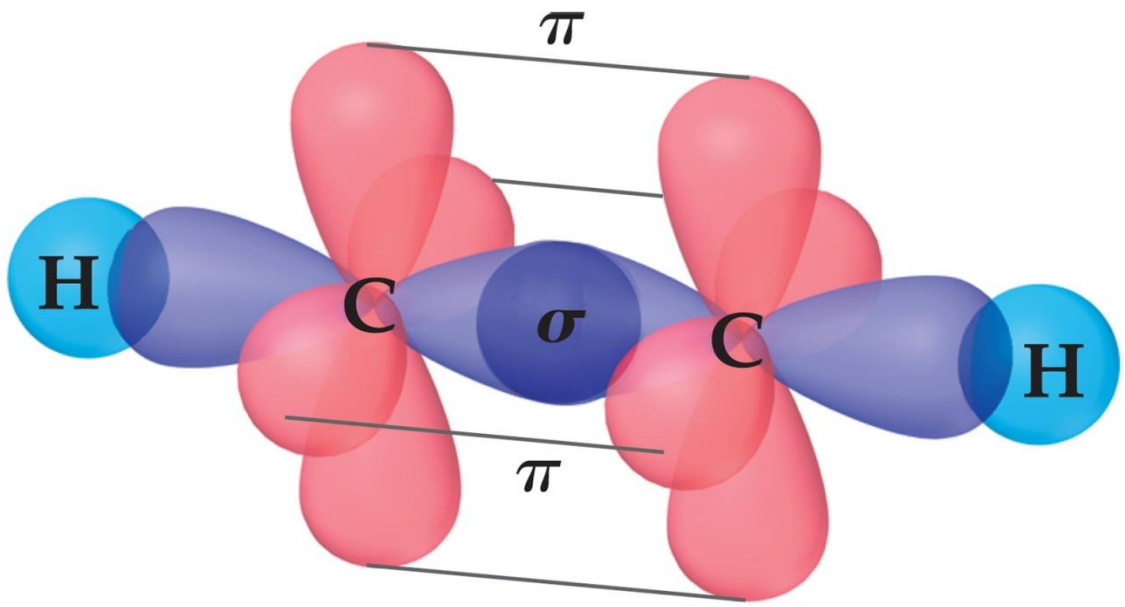




- Example: formaldehyde an sp^2 orbital on carbon overlaps in σ fashion with the corresponding orbital on the oxygen.
- The unhybridized *p* orbitals overlap in π fashion.

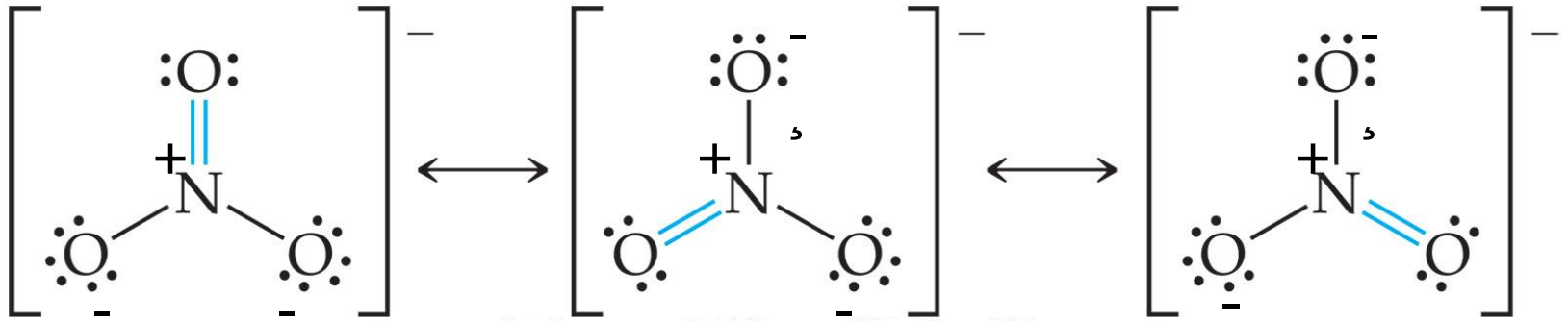
Multiple Bonds

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.

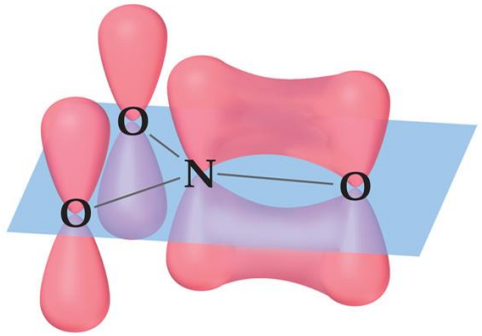


Delocalized Electrons: Resonance

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.



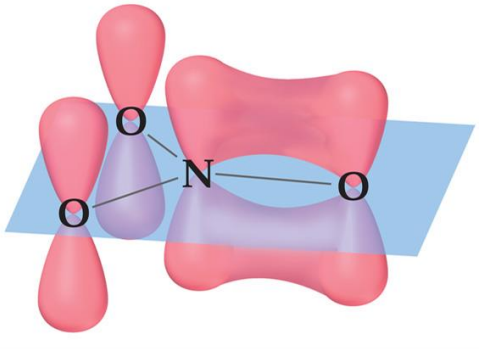
Delocalized Electrons: Resonance

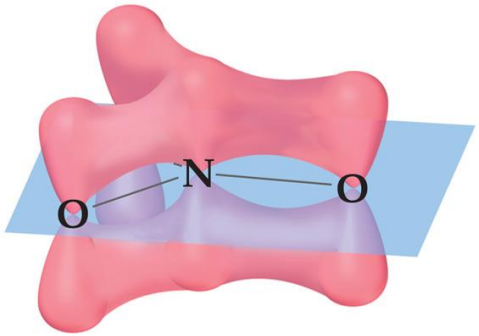


- each of the four atoms in the nitrate ion has a *p* orbital.

- The *p* orbitals on all three oxygens overlap with the *p* orbital on the central nitrogen.

Delocalized Electrons: Resonance

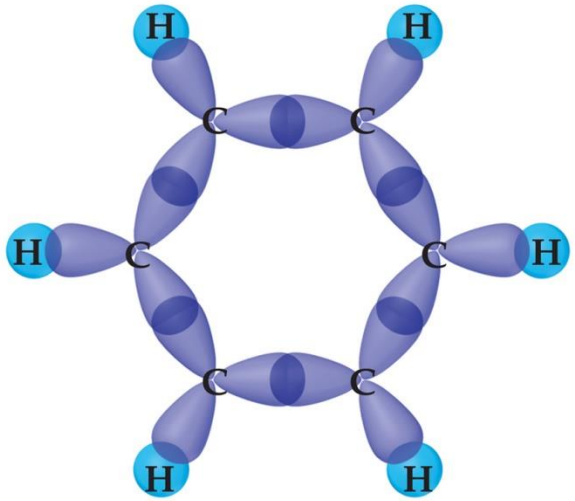


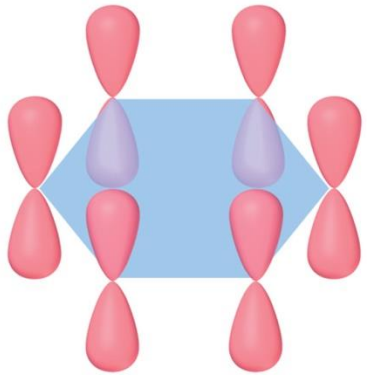


This means the π electrons are not localized between the nitrogen and one of the oxygens, but rather are delocalized throughout the ion.

Resonance

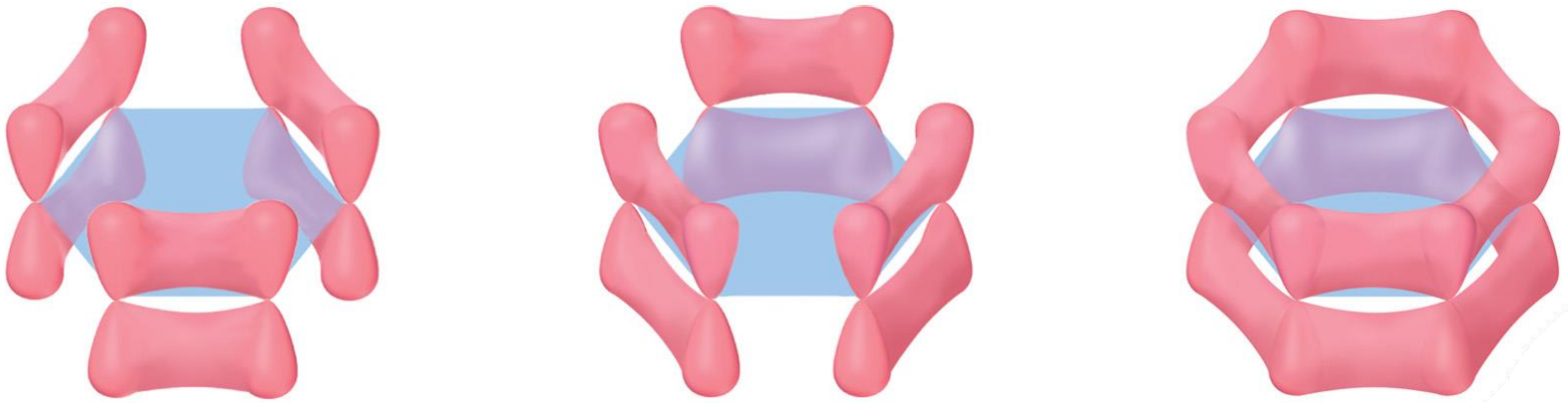
The organic molecule benzene has six σ bonds and a *p* orbital on each carbon atom.



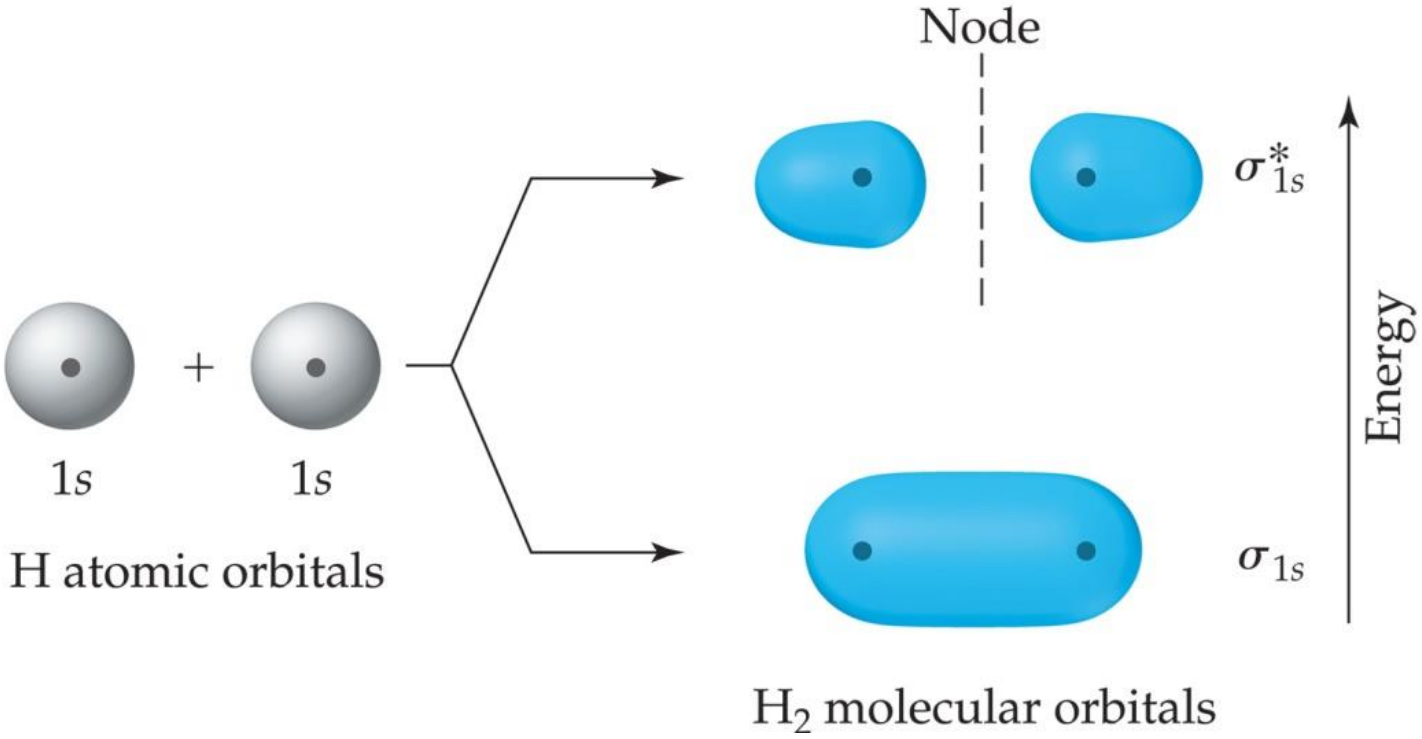


Resonance

- 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.

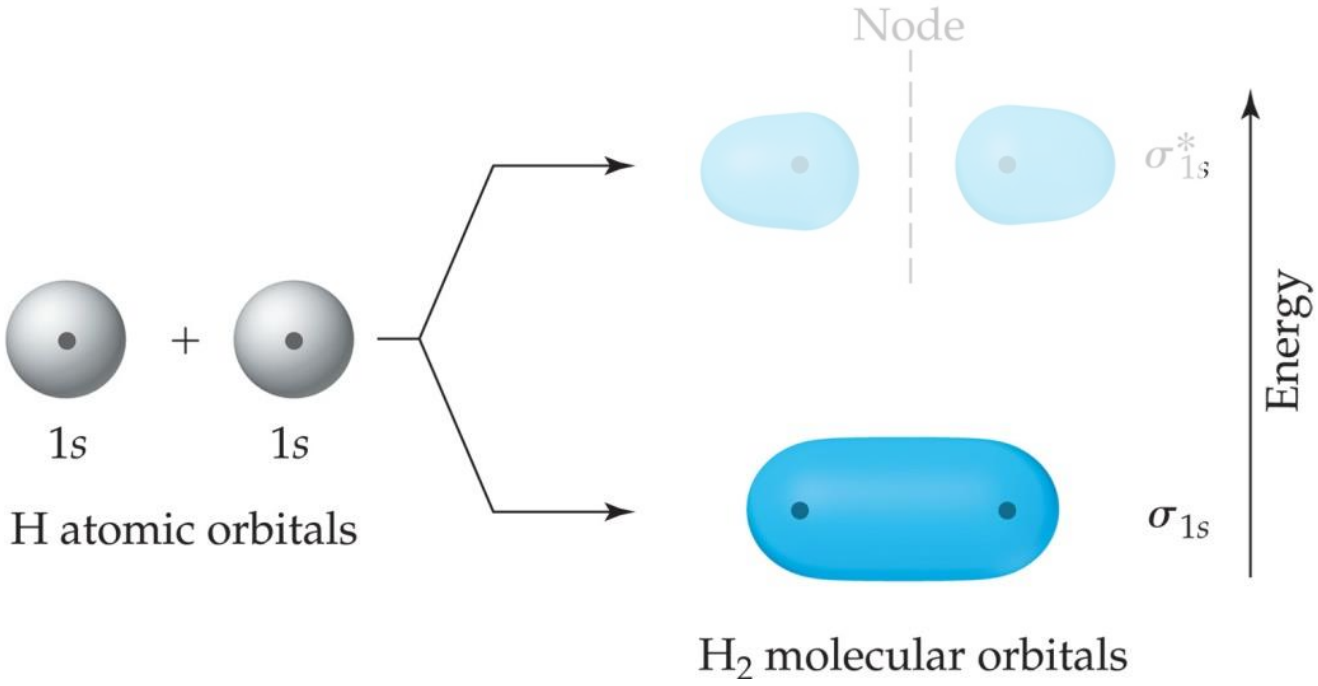


9-7 Molecular Orbitals



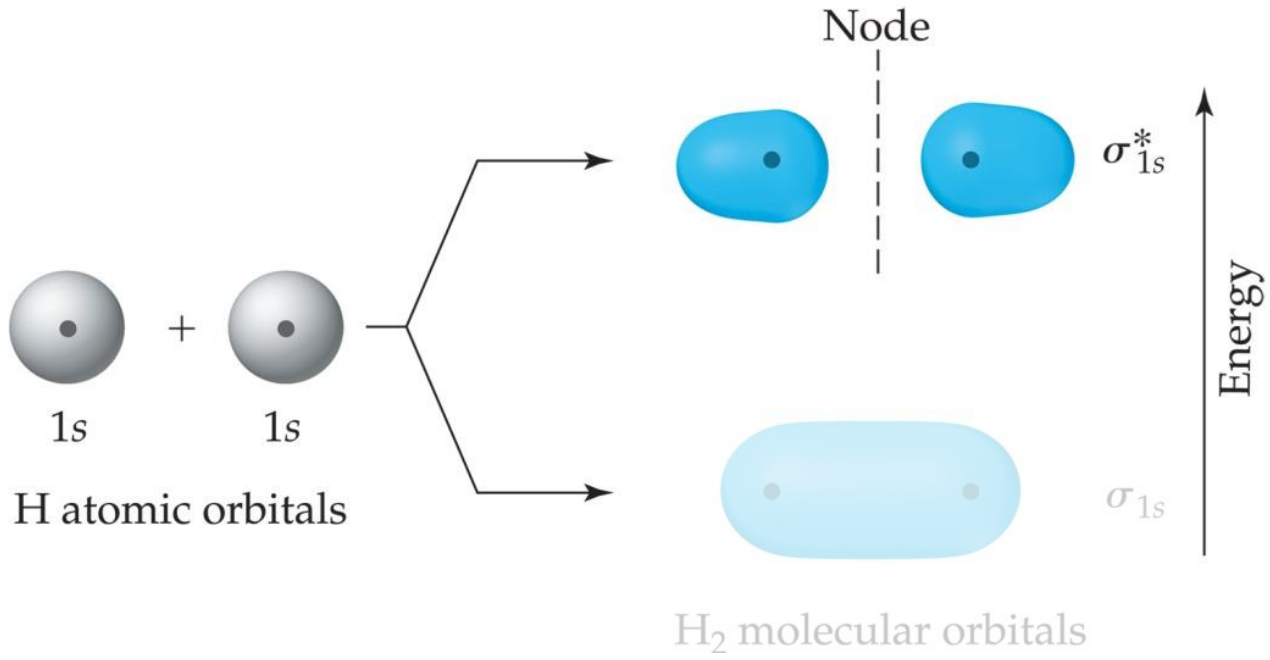
Valence bond theory works very well for most observed properties of ions and molecules, but there are some concepts better represented by molecular orbital theory.

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.

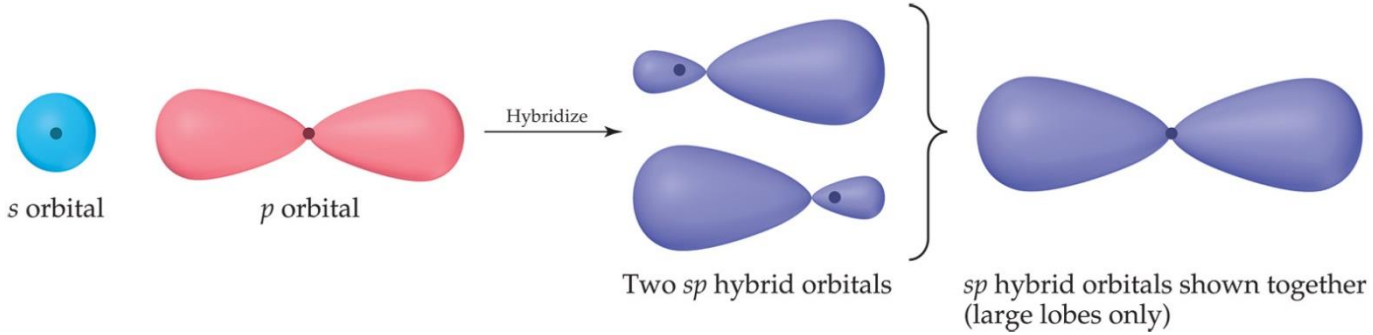
Molecular Orbital (MO) Theory



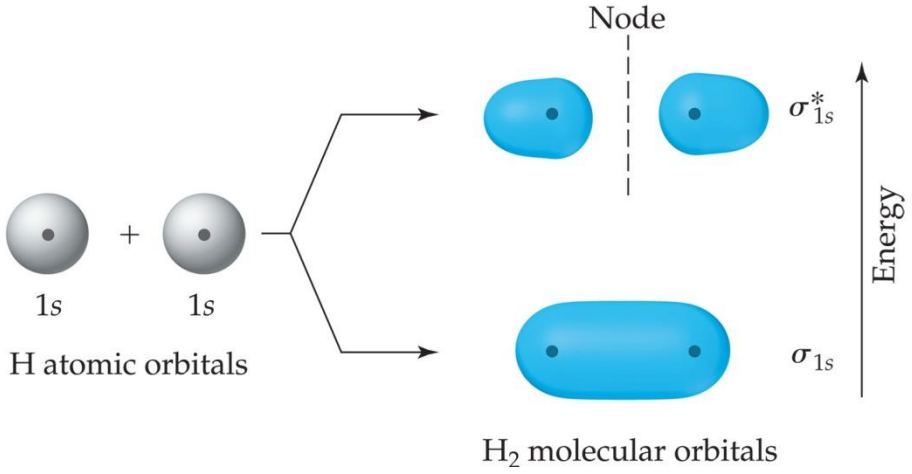
If waves interact destructively, the resulting orbital is higher in energy: an antibonding molecular orbital.

Molecular Orbital (MO) Theory

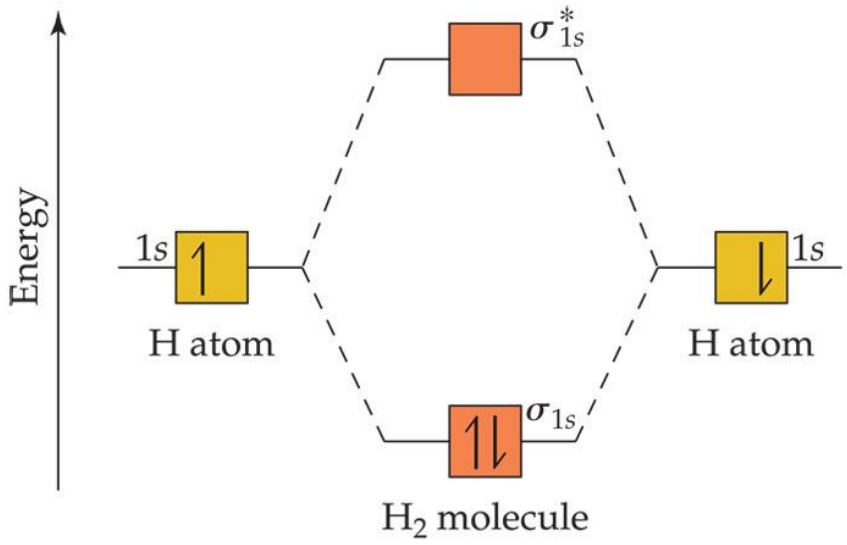
- Valence bond theory: atomic orbitals are mixed in each individual atom *before* bonding.



- Molecular orbital theory: no prebonding mixing. Molecular orbitals are computed *after* bonding.



MO Theory



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

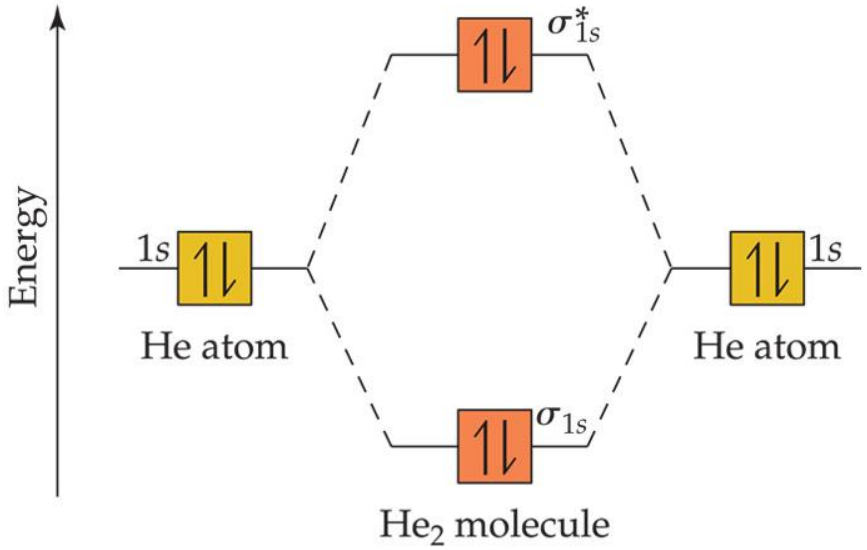
$$\frac{1}{2}(2 - 0) = 1$$

MO Theory

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

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

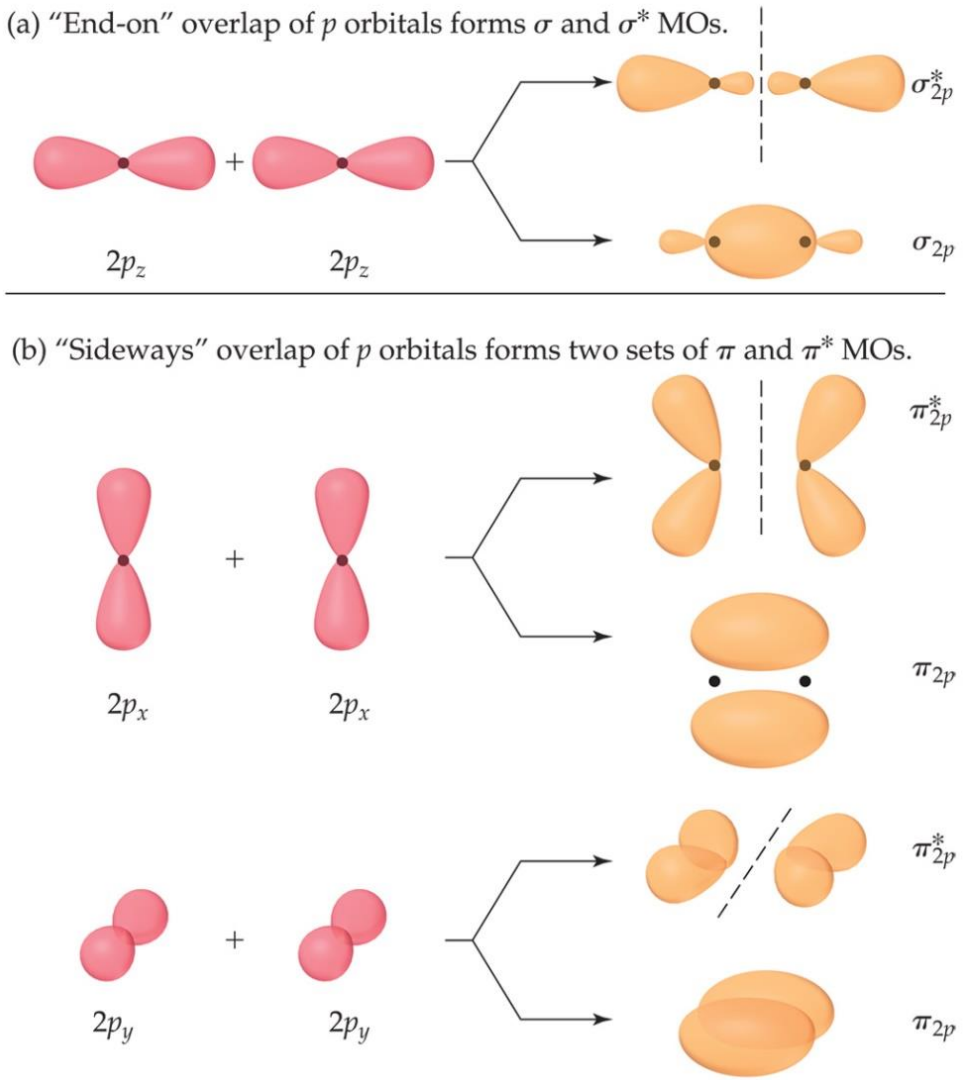
- Therefore, He_2 does not exist.



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, one 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.

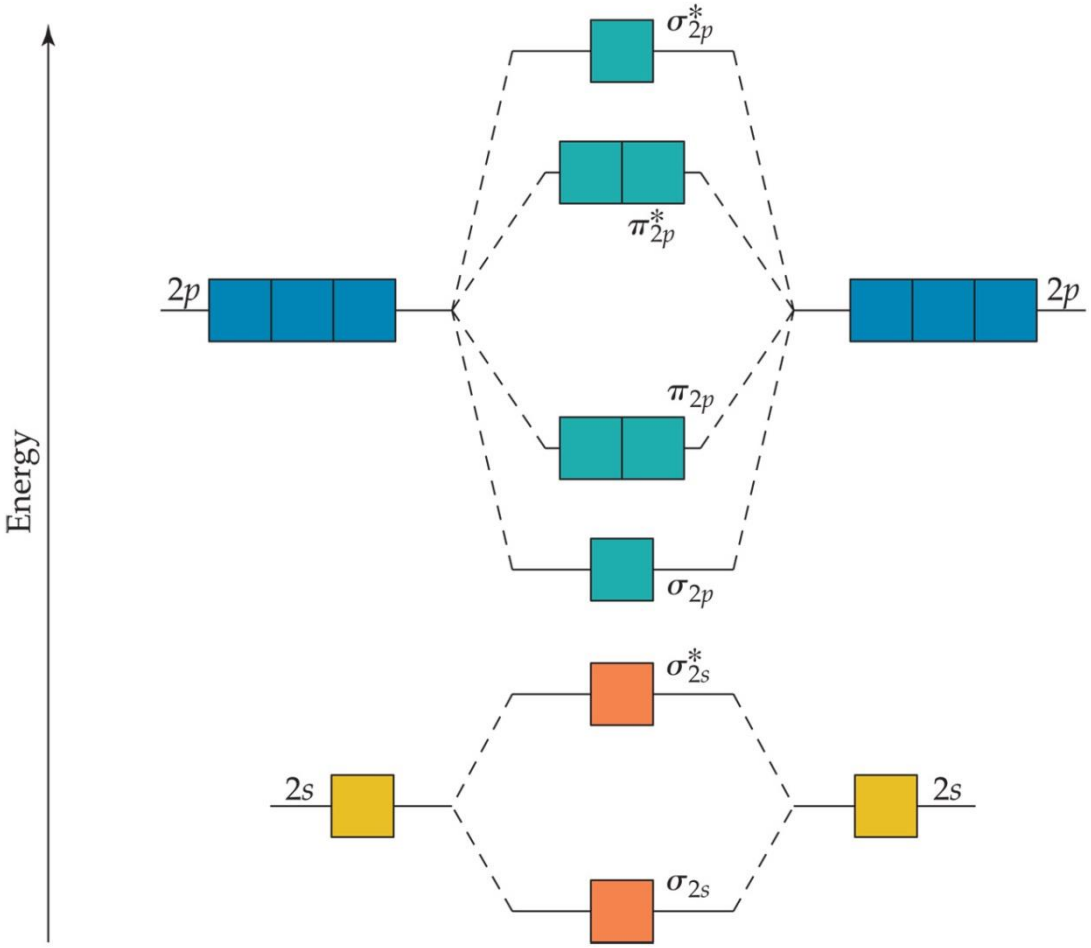
MO Theory



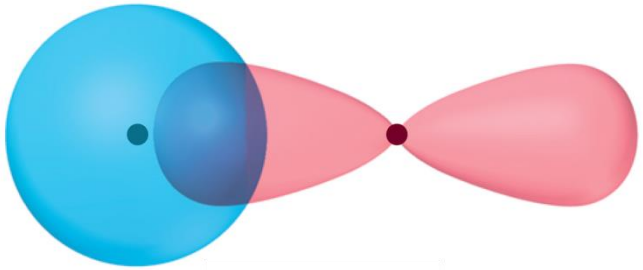
- For atoms with both *s* and *p* orbitals, there are two types of interactions:
  - The *s* and the *p* orbitals that face each other overlap in σ fashion.
  - The other two sets of *p* orbitals overlap in π fashion.

MO Theory

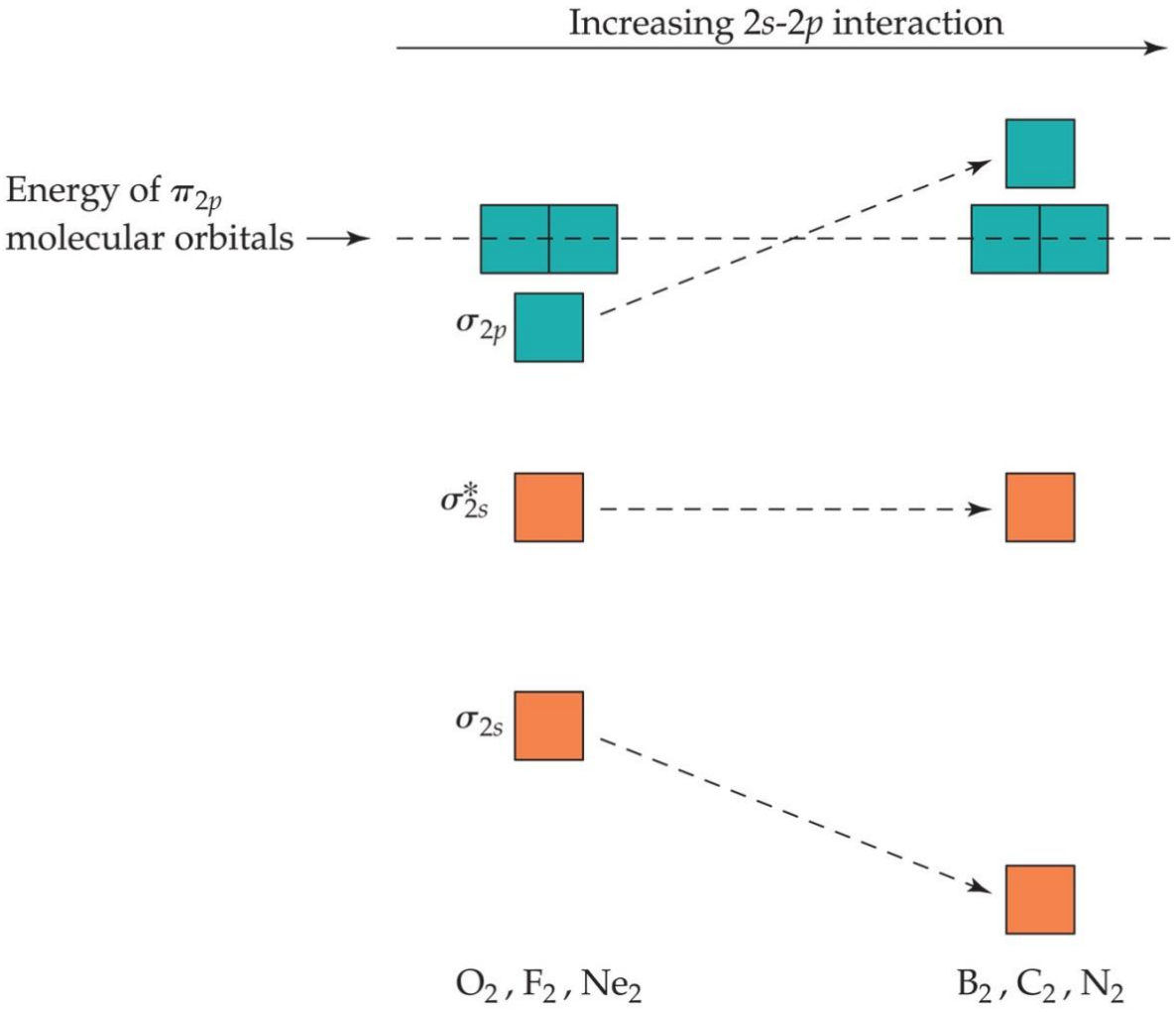
- The resulting MO diagram looks like this.
- There are both σ and π bonding molecular orbitals and σ* and π* antibonding molecular orbitals.



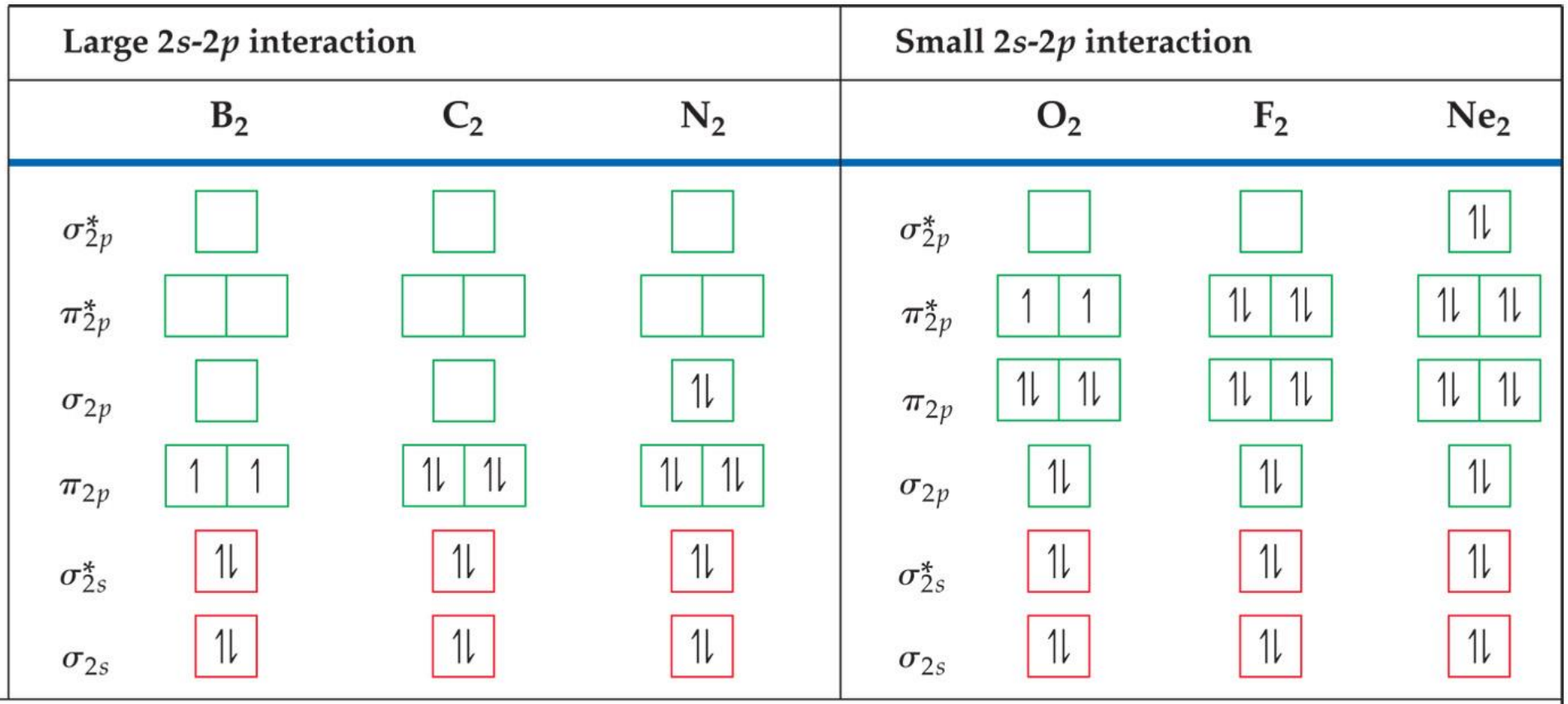
MO Theory



- 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.

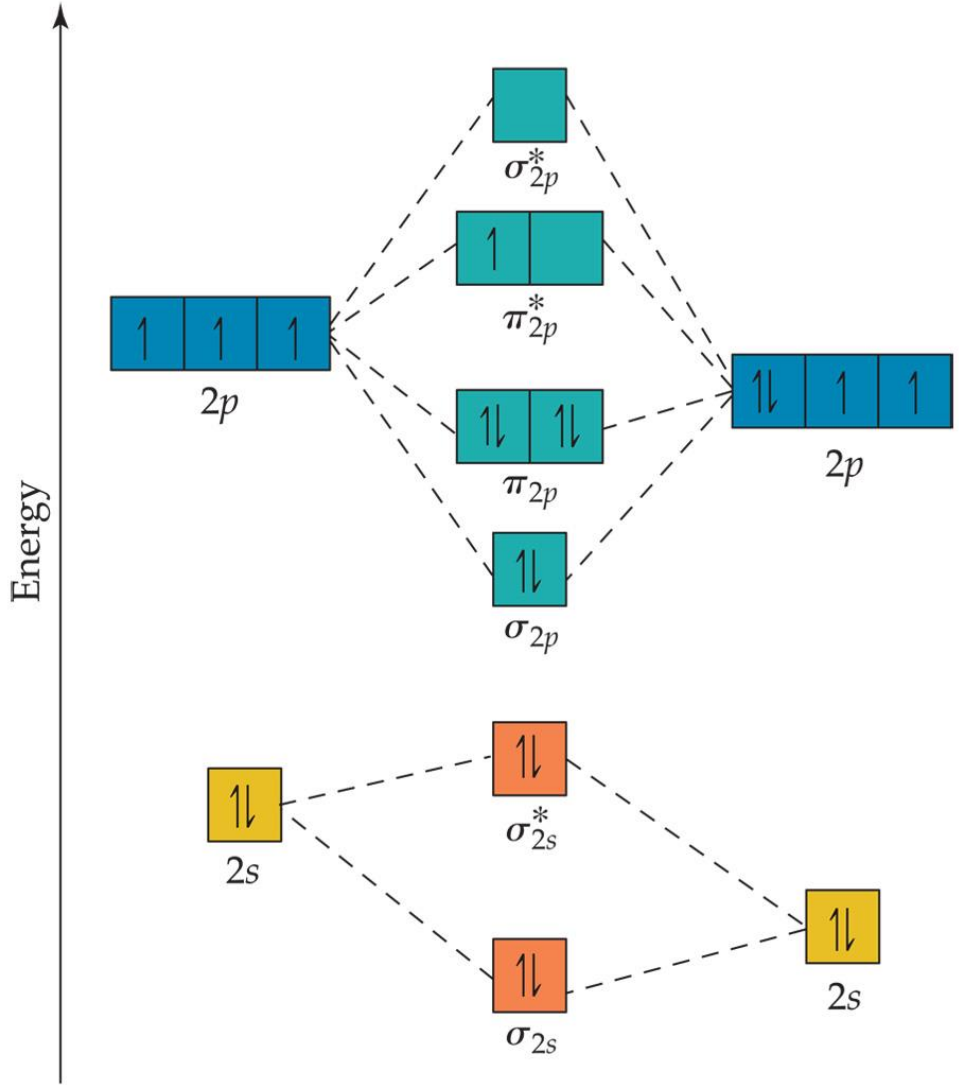


Second-Row MO Diagrams



	B_2	C_2	N_2	O_2	F_2	Ne_2
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	—

Heterodiatomic molecules



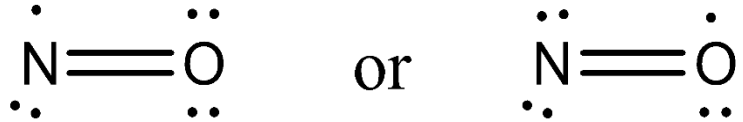
NO has

7 incomplete π* bonds

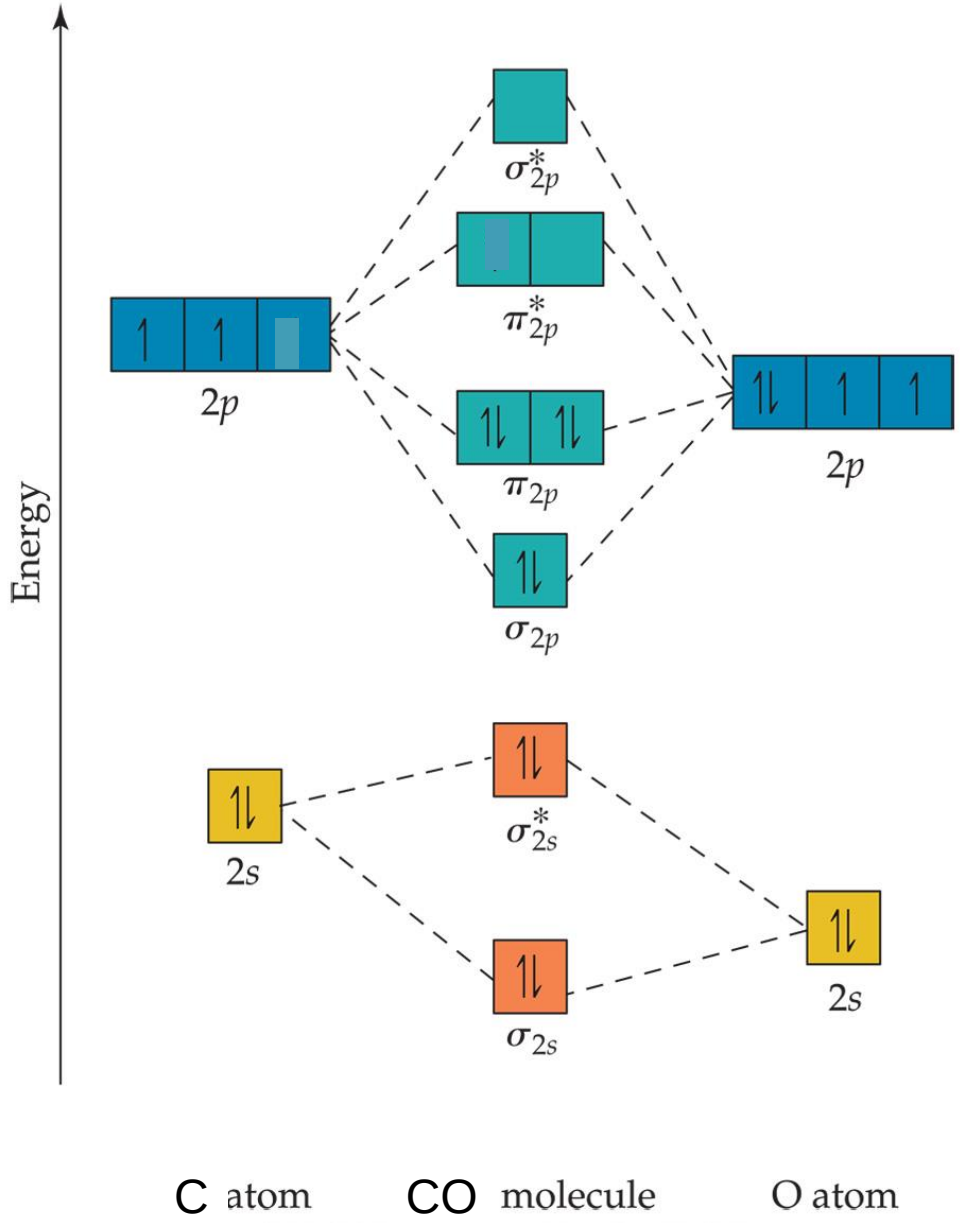
1 π bonds

1 σ bond

NO is paramagnetic radical with a double bond and 7 non-bonding electron

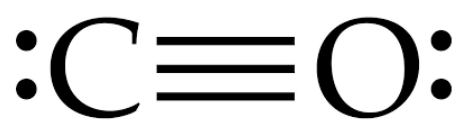


Heterodiatomic molecules

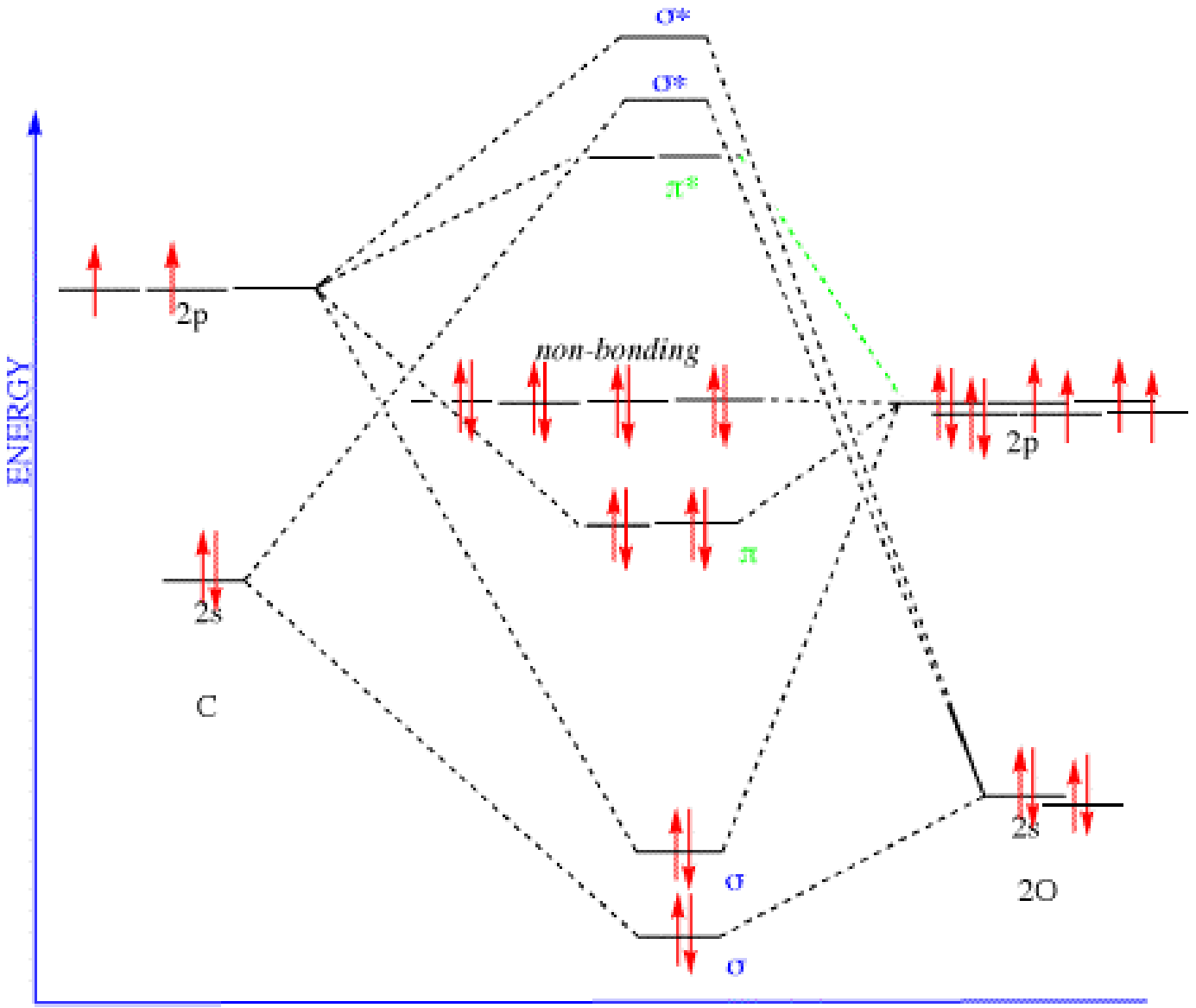


CO has a triple bond

1 σ bond and 2 π bonds



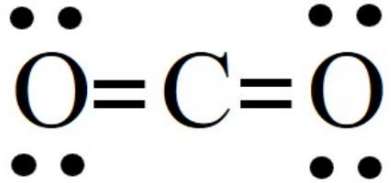
Polyatomic molecules



CO_2 has 2 double bonds

4 lone pairs

2 σ bond and 2 π bonds



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.

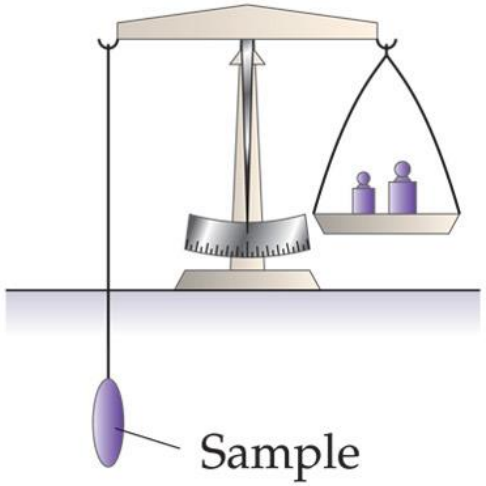
Electrons cause magnetism.

Three kinds of magnetism:

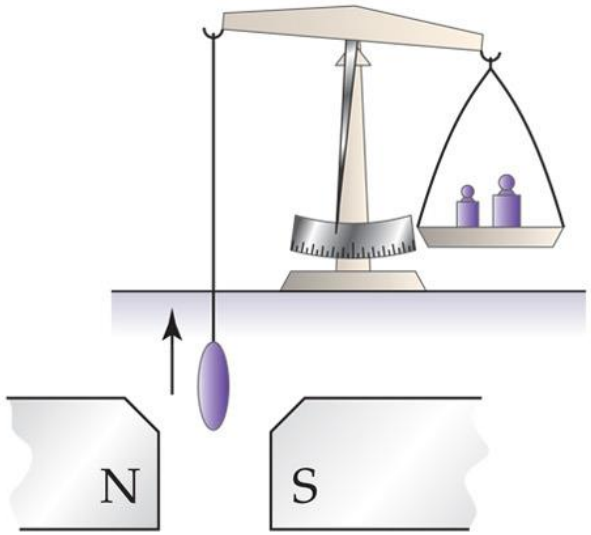
1. Diamagnetism
2. Paramagnetism
3. Ferromagnetism

Diamagnetic

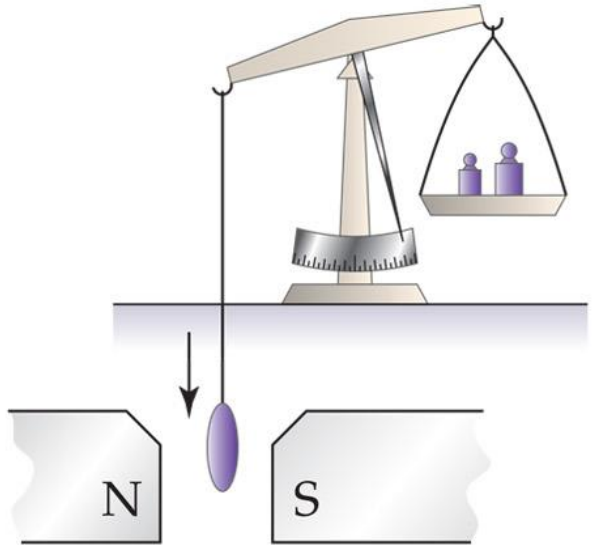
Paramagnetic



(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.

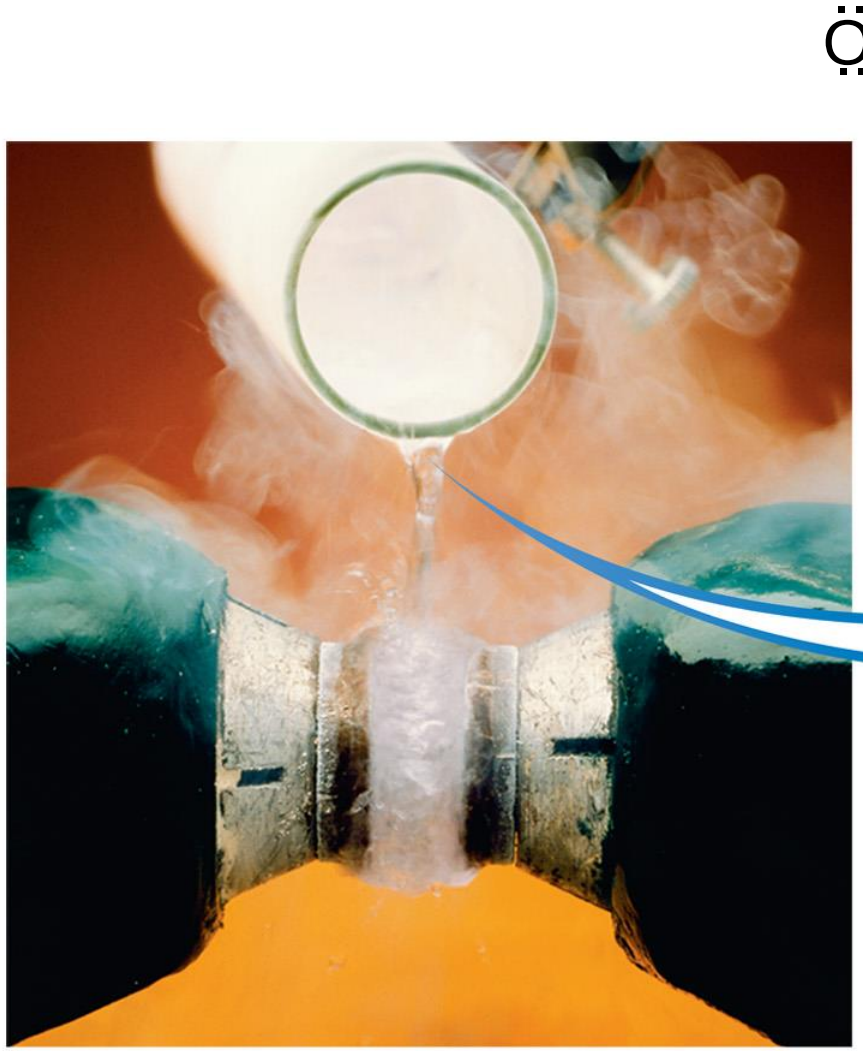


(c) A paramagnetic sample is drawn into the field and thus appears to gain mass.

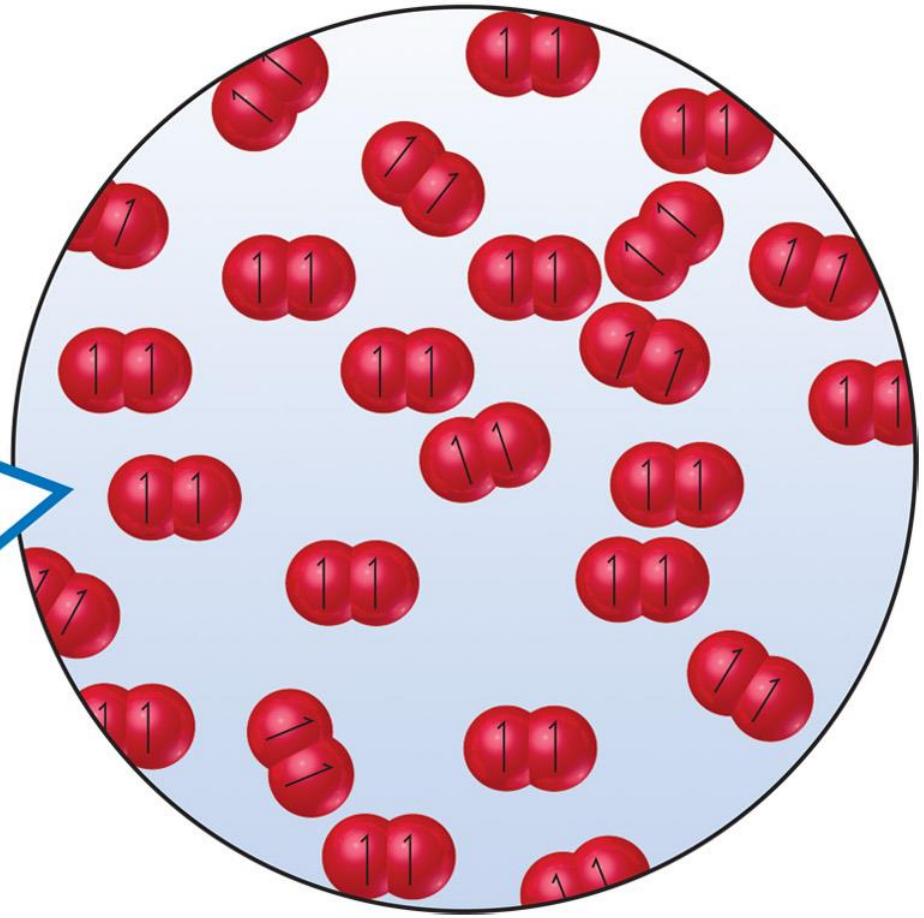
Electrons all paired

Unpaired electrons

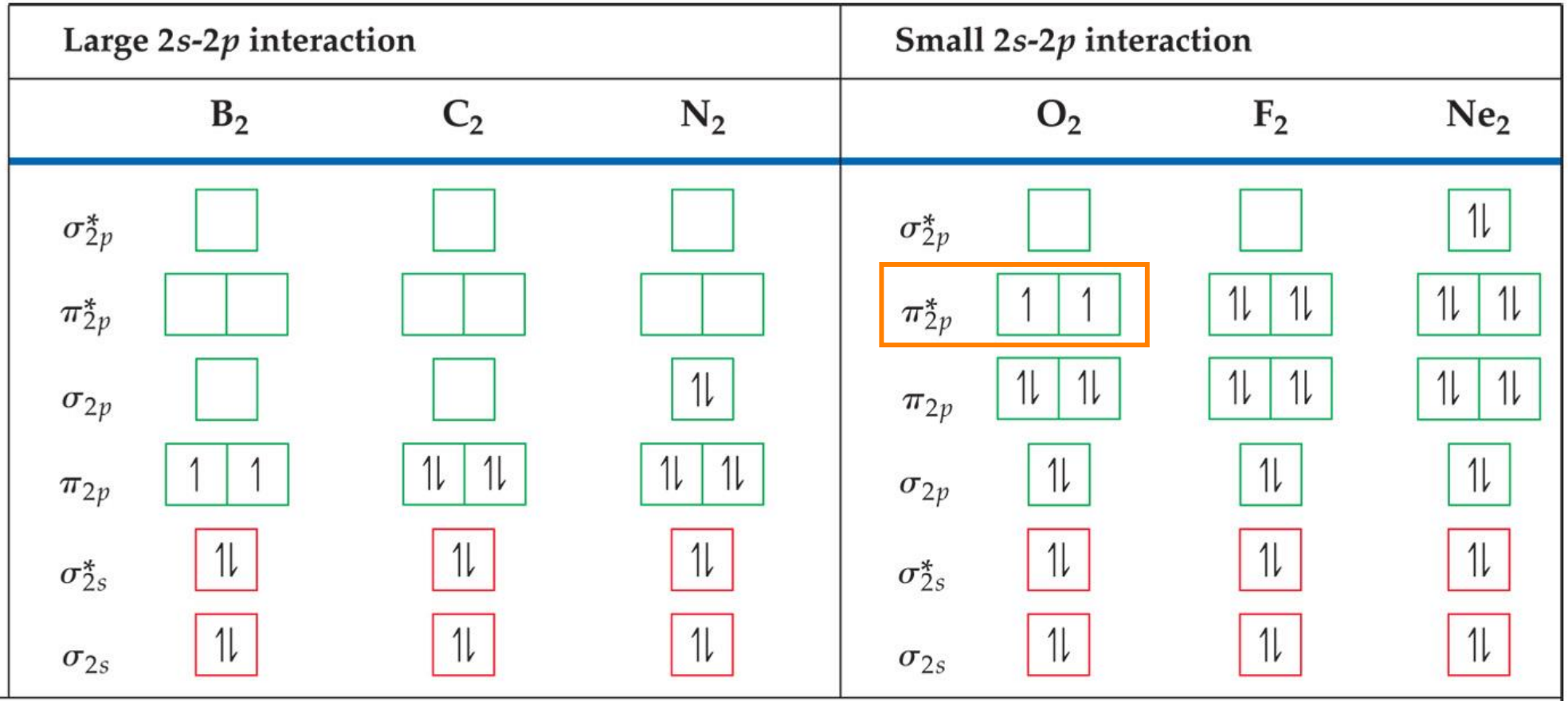
Oxygen O_2 is Paramagnetic!



Why?



MO to the rescue



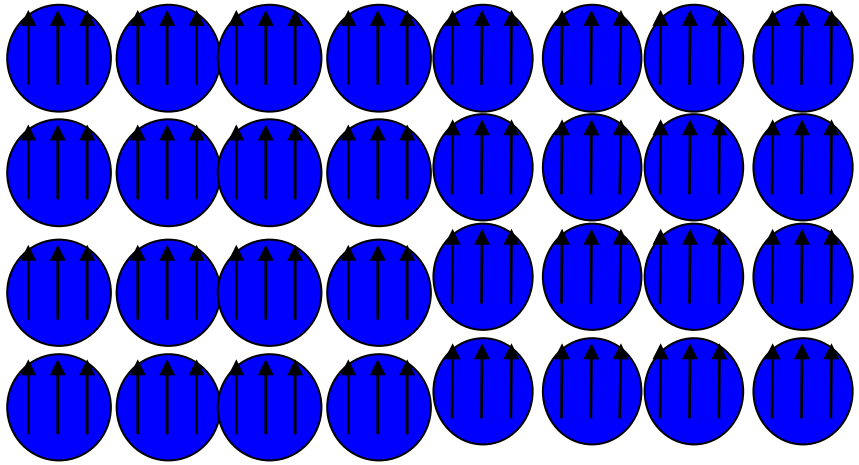
	B_2	C_2	N_2	O_2	F_2	Ne_2
Bond order	1	2	3	2	1	0
Bond enthalpy (kJ/mol)	290	620	941	495	155	—
Bond length (Å)	1.59	1.31	1.10	1.21	1.43	—
Magnetic behavior	Paramagnetic	Diamagnetic	Diamagnetic	Paramagnetic	Diamagnetic	—

Ferromagnetism

Like iron, pulled to a magnet.

Long range order of spins in material

S



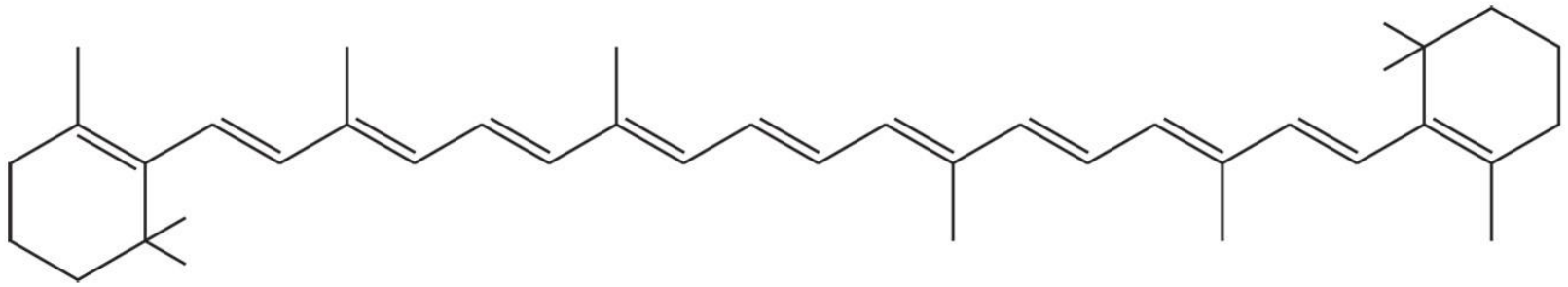
N

MO theory and color

Remember, elements produced color because of electrons moving from higher to lower energy levels.

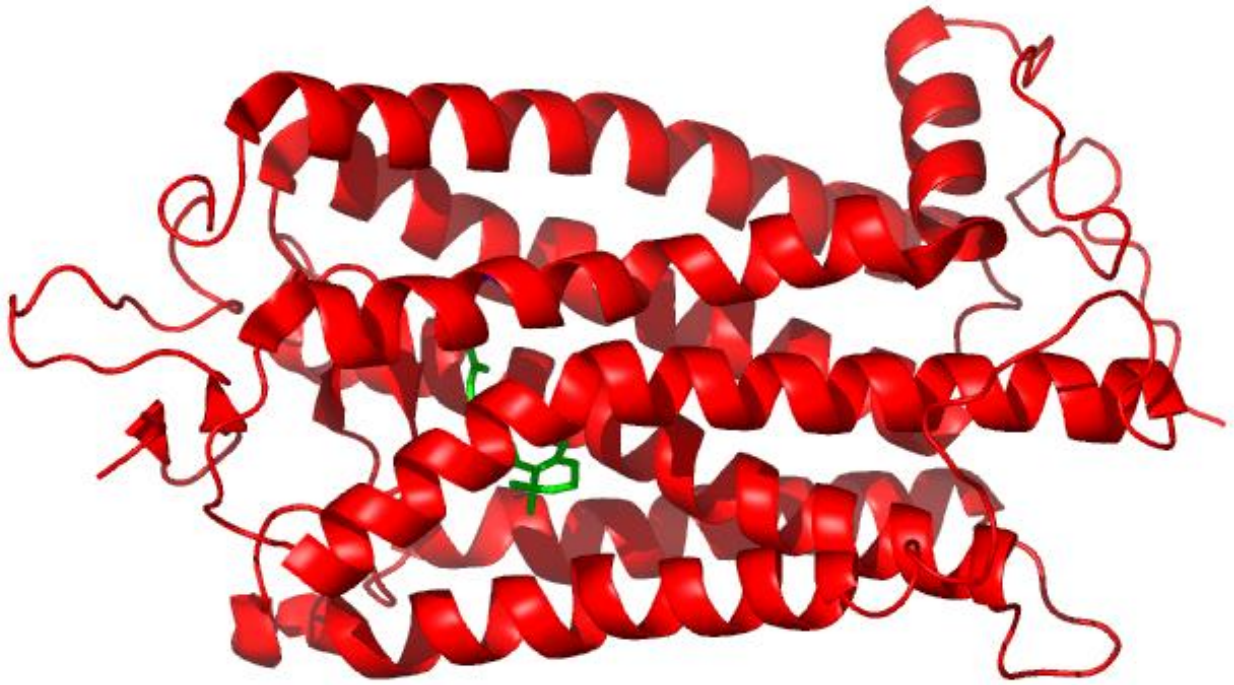
With MO theory, color of molecules is explained the same way

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



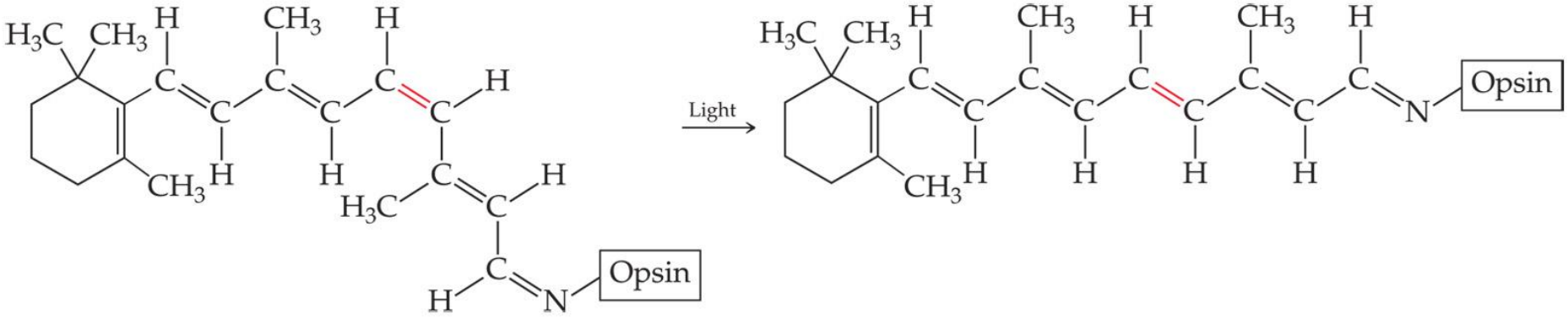
β-carotene

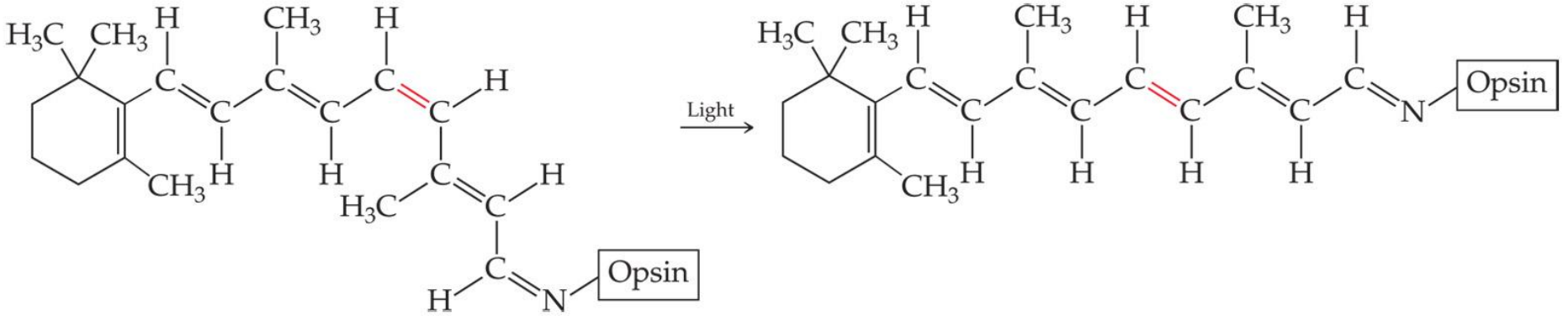
How do we see color?

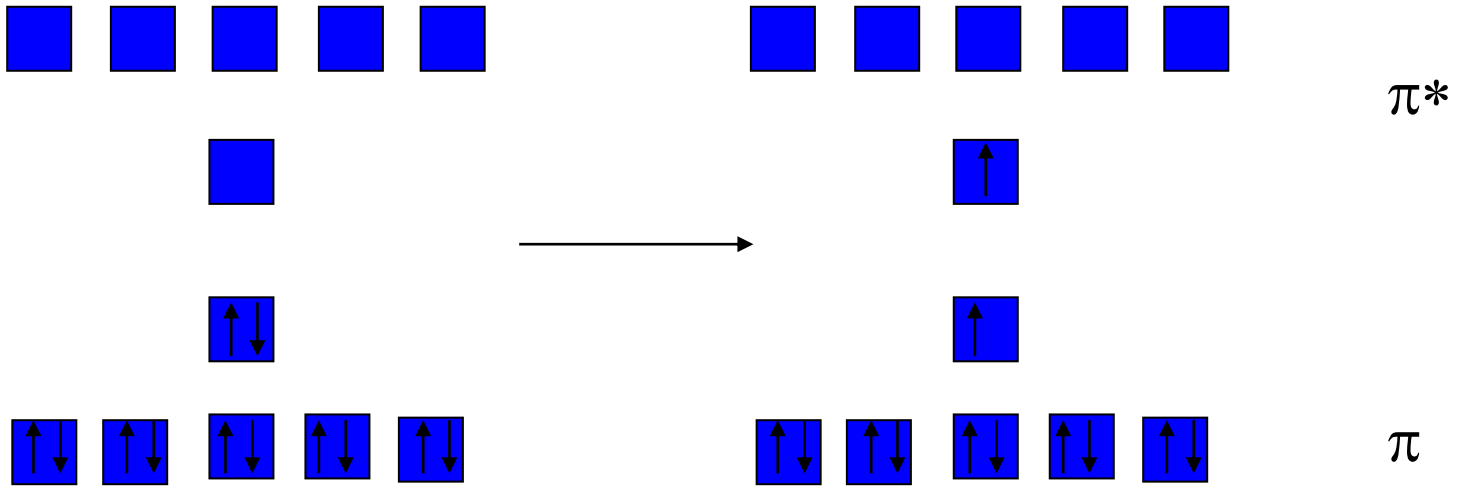


Rhodopsin

Isomerization wiggles the rest of the protein, sends nerve signal

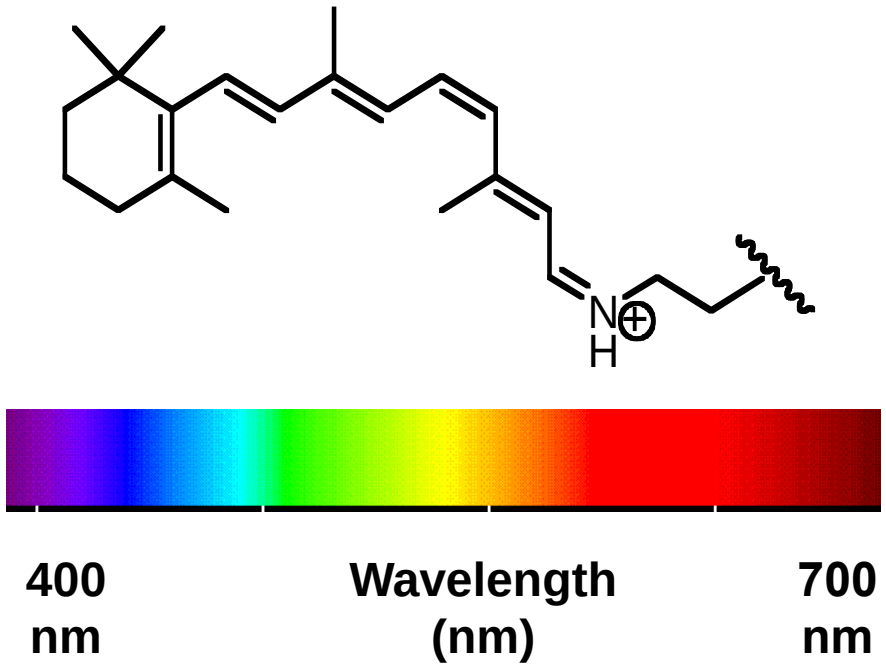






How does Color Vision work?

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

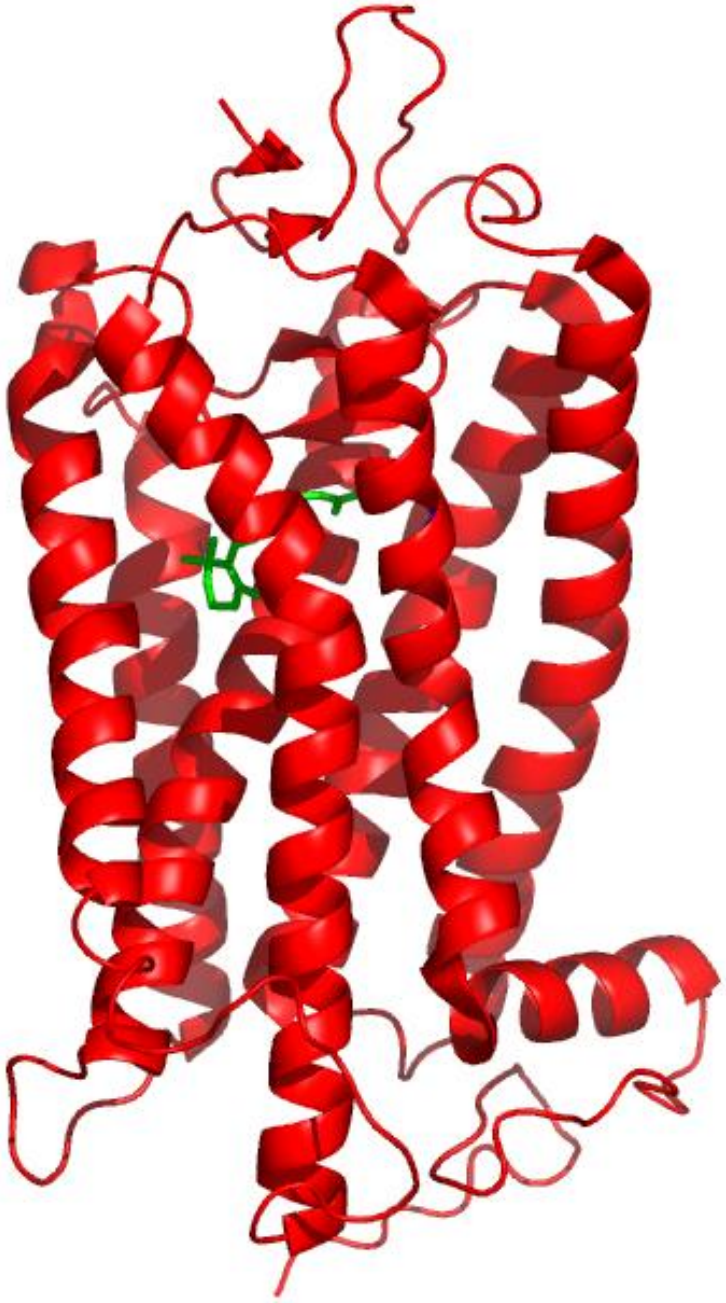
11-*cis*-retinal PSB : ~ 440 nm

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

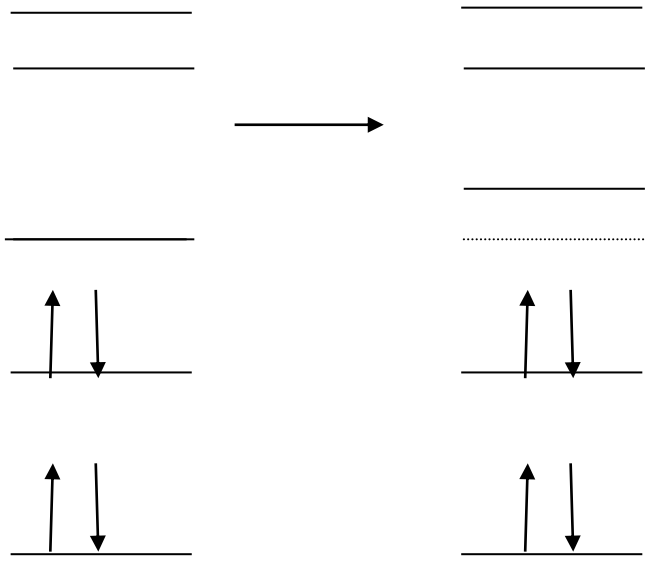
PSB in **Green** Rhodopsin : ~ 530 nm

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.



9-8 Bonding in Period 2 Diatomic Molecules

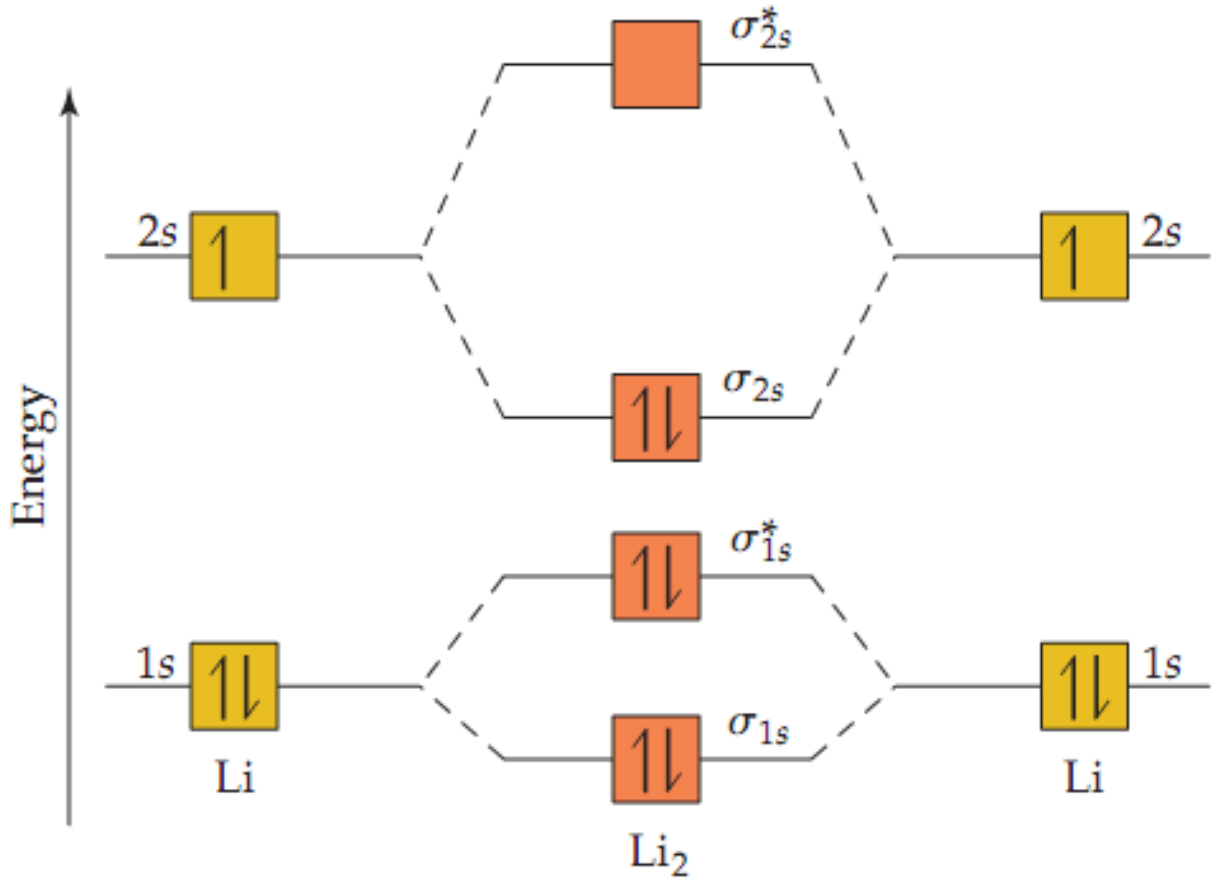
Guiding principles for the formation of MOs :

- The number of MOs formed equals the number of atomic orbitals combined.
- Atomic orbitals combine most effectively with other atomic orbitals of similar energy.
- As the overlap increases, the energy of the bonding MO is lowered and the energy of the antibonding MO is raised.
- Each MO can accommodate, at most, two electrons, with their spins paired (Pauli exclusion principle).
- When MOs of the same energy are populated, one electron enters each orbital (with the same spin) before spin pairing occurs (Hund’s rule)

Molecular Orbitals for Li_2 and Be_2

Li $1s^2 2s^1$

above its boiling point (1342°C), Li_2 is found in vapor phase



The 2s orbitals interact with one another producing bonding (σ_{2s}) and antibonding (σ_{2s}^*) MOs

The 1s orbitals combine to form bonding (σ_{1s}) and and antibonding (σ_{1s}^*) MOs

Molecular Orbitals for Li_2 and Be_2

Be $1s^2 2s^2$

eight electrons in molecular

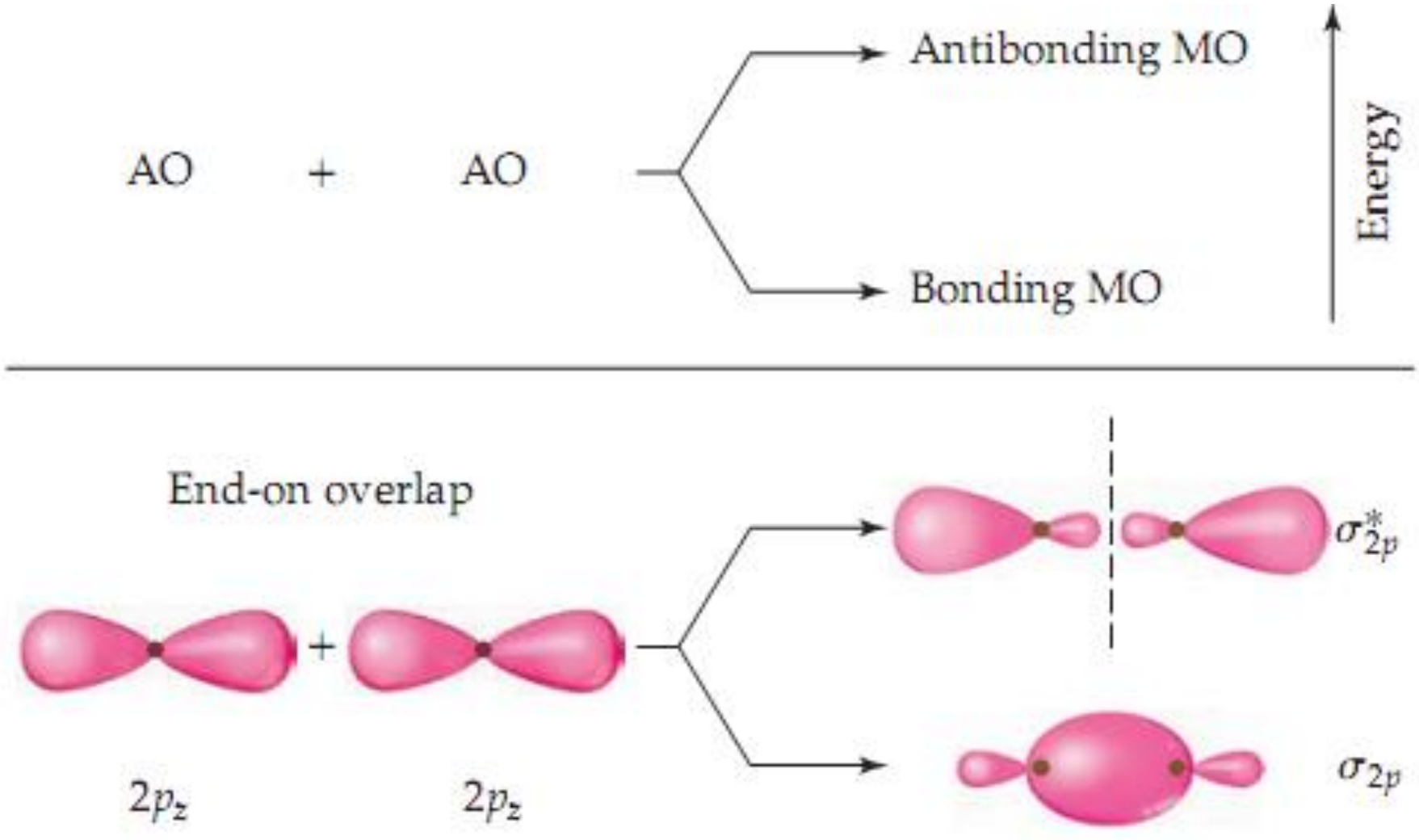
σ_{1s} , σ_{1s}^* , σ_{2s} and σ_{2s}^* MOs are completely filled

equal numbers of bonding and antibonding electrons

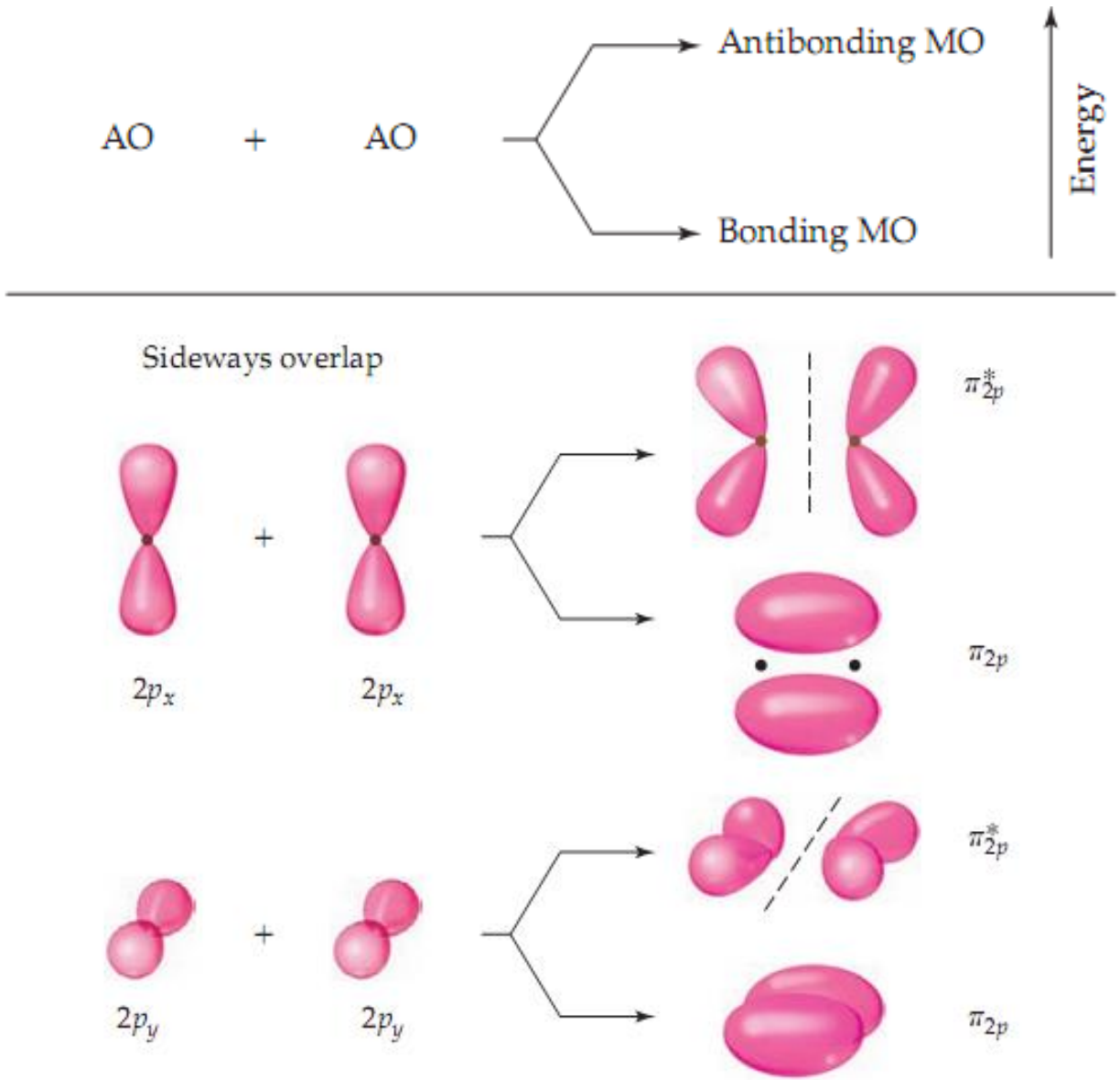
bond order is zero

➔ Be_2 does not exist

Molecular Orbitals from 2p Atomic Orbitals



Molecular Orbitals from 2p Atomic Orbitals



Quiz

- Predic the geometry of $SeCl_2$

A. Linear

B. Bent

- Predic the geometry of CO_3^{2-}

A. Trigonal planar

B. Trigonal paramidal

C. T-shape

Quiz

- Predict the approximate values for the O = Cl – O bond angle in $HClO_2$

A. Slightly larger than 120

B. Slightly greater than 109.5

C. Exactly 180

- Predict the approximate values for the Cl – O – H bond angle in $HClO_2$

A. Slightly larger than 120

B. Slightly smaller than 109.5

C. Exactly 120

Quiz

- What is the hybridization of H_2O, H_2O_2, SO_4^{2-}, ClF_5?