

# Chapter 9: Molecular Geometry and Bonding Theories

Problems: 9.1-9.67, 9.69, 9.76-9.77, 9.80-9.94, 9.99, 9.102-9.103, 9.105, 9.107, 9.118, 9.120, 9.123

## 9.1 MOLECULAR SHAPE

### Molecular Geometry (or Shape)

- the three-dimensional arrangement of atoms in molecules
- responsible for many physical and chemical properties of molecules

## 9.2 Valence-Shell Electron-Pair Repulsion (VSEPR) Theory

### Valence-Shell Electron-Pair Repulsion (VSEPR)

Repulsion between electrons causes them to be as far apart as possible

- a molecule's shape results from the electrons on its central atom orienting themselves to be as far away from each other as possible

### Determining the shapes of molecules

- If there are **only two atoms**, the molecule must be **linear**.
- If there are **more than two atoms** in the molecule
  - **the shape depends on number of electrons around the central atom**
    - The electrons orient themselves to maximize the distance between them.



The **steric number (SN)** of the central atom allows us to determine the shape of the molecule.

$$\text{steric number} = \left( \begin{array}{l} \# \text{ of atoms bonded} \\ \text{to the central atom} \end{array} \right) + \left( \begin{array}{l} \# \text{ of lone pairs} \\ \text{on the central atom} \end{array} \right)$$

## CENTRAL ATOMS WITH NO LONE PAIRS

### Molecule #1: BeH<sub>2</sub>

- Draw the Lewis structure below.
- Draw each bonding pair of electrons as a stick, maximizing the distance between the electron pairs, then draw the outer atoms as balls.

Lewis structure



- The shape of the BeH<sub>2</sub> molecule is \_\_\_\_\_ and its bond angle is \_\_\_\_\_.

**Molecule #2: BH<sub>3</sub>**

- a. Draw the Lewis structure below.                      b. 3D shape showing approximate bond angles

Lewis structure



- c. Note that the three outer atoms make a triangle and all four atoms are in the same plane, so this shape is called **trigonal planar**, where the bond angles are \_\_\_\_\_.

**Molecule #3: CH<sub>4</sub>**

- a. Draw the Lewis structure below.                      b. 3D shape showing bond angles are **109.5°**.

Lewis structure



Thus, this shape is called **tetrahedral**, in which the bond angles are **109.5°**.

Note: In tetrahedral, connecting the four outer atoms make four sides or faces.  
(In Greek: “tetra” = four, “hedra” = face.)

**Molecule #4:  $\text{PCl}_5$**

a. Draw the Lewis structure below.

Lewis structure

b. To maximize the distance between  $e^-$  pairs, electrons are  $90^\circ$  or  $120^\circ$  away from each other.



Thus, this shape is called **trigonal bipyramidal**, where the bond angles are  **$120^\circ$**  for equatorial atoms and  **$90^\circ$**  for axial atoms.

3. Note: Three of the outer atoms make a triangle and sit in the same plane with the central atom while one atom sits above the plane and another sits below.

– Connecting the outer atoms makes two pyramids → the name **trigonal bipyramidal**.

In this shape, the four atoms in the center (in the equator or **equatorial positions**) have  **$120^\circ$  bond angles** while the atoms above (on each axis or **axial positions**) and below form  **$90^\circ$  bond angles** with the equatorial atoms.

**Molecule #5:  $\text{SF}_6$**

1. Draw the Lewis formula below.

Lewis structure

b. To maximize the distance between  $e^-$  pairs, electrons are  $90^\circ$  away from each other.



Thus, this shape is called **octahedral**, where the bond angles are all  **$90^\circ$** .

3. Note that four of the outer atoms make a square and all sit in the same plane with the central atom while one atom sits above the plane and another sits below. Connecting all the outer atoms makes 8 faces or sides, so this shape is called **octahedral**.

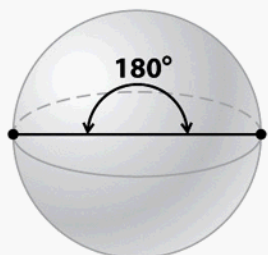
Note that all the atoms make right angles to one another, so all the bond angles are  **$90^\circ$** .

## Molecular Geometries with 2 to 6 Outer Atoms on the Central Atom (where the Central Atom Has No Lone Pairs)

Consider a molecule composed of only two types of atoms, A and B:

**A=central atom**      **B=outer atoms**

For **three or more atoms** in a molecule, general formula: **AB<sub>#</sub>** (where #=2 to 6)



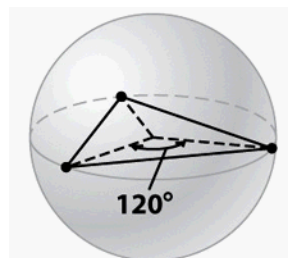
**Linear**

**AB<sub>2</sub>: linear**

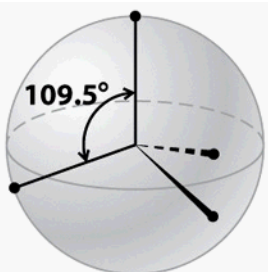
- the two outer atoms are **180°** from each other
- **steric number (SN) = 2**

**AB<sub>3</sub>: trigonal planar**

- three outer atoms at the corners of an equilateral triangle
- each outer atom is **120°** from the other two outer atoms
- **SN = 3**



**Trigonal planar**



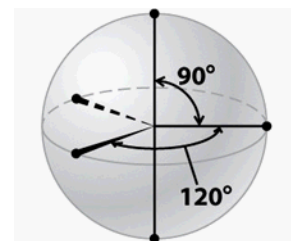
**Tetrahedral**

**AB<sub>4</sub>: tetrahedral** (*tetra* = four) since four-sided, or four faces

- maximum distance between electrons requires 3D structure with **109.5°** bond angles
- each outer atom is **109.5°** from the other outer atoms

**AB<sub>5</sub>: trigonal bipyramidal**

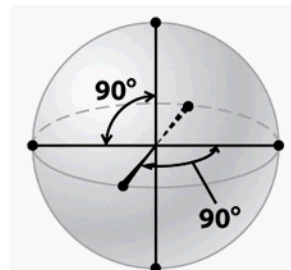
- trigonal = three outer atoms form a planar triangle around central atom
- bipyramidal = two outer atom directly above and below central atom, connecting outer atom forms two 3-sided pyramids
- 3 outer atoms are at **equatorial positions**, **120°** from one another at the ends of a planar triangle
- 2 outer atoms are at **axial positions**, above and below central atom and **90°** from the equatorial atoms



**Trigonal bipyramidal**

**AB<sub>6</sub>: octahedral** (*octa*=eight) connecting the B atoms → eight faces

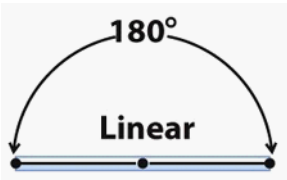
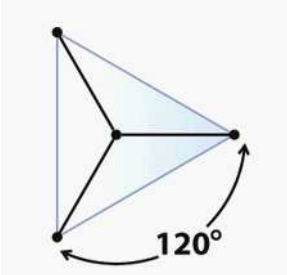
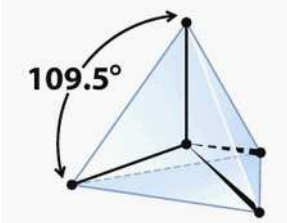
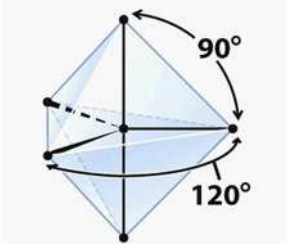
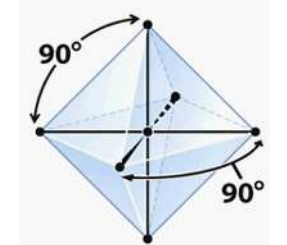
- all outer atoms are **90°** away from each other
- terms "axial" and "equatorial" do not apply because all six positions are identical



**Octahedral**

### Molecular Shapes Where Central Atoms Have No

## Lone Pairs

Steric Number	# of Outer Atoms	# of Lone Pairs on Central Atom	General Formula	MOLECULAR GEOMETRY and NAME
2	2	0	$AB_2$	 <p style="text-align: center;"><b>Linear</b></p>
3	3	0	$AB_3$	 <p style="text-align: center;"><b>Trigonal planar</b></p>
4	4	0	$AB_4$	 <p style="text-align: center;"><b>Tetrahedral</b></p>
5	5	0	$AB_5$	 <p style="text-align: center;"><b>Trigonal bipyramidal</b></p>
6	6	0	$AB_6$	 <p style="text-align: center;"><b>Octahedral</b></p>

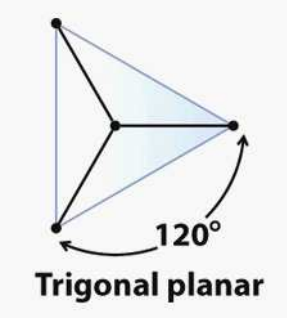
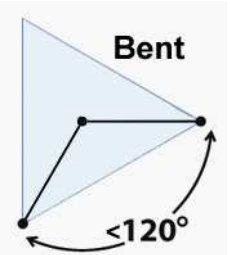
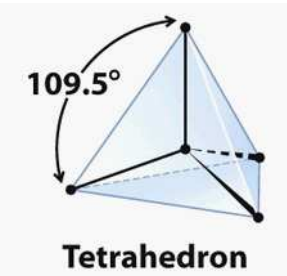
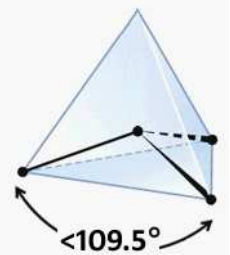
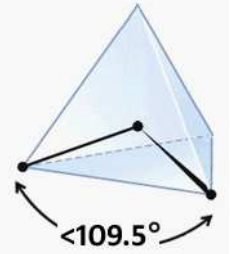
## Molecules Where Central Atom Has One Or More Lone Pairs

A central atom with lone pairs has three types of repulsive forces

$\text{lone - pair vs. lone - pair repulsion} > \text{lone - pair vs. bonding - pair repulsion} > \text{bonding - pair vs. bonding - pair repulsion}$

- **bonding pairs:** takes up less space than lone pairs since held by attractive forces exerted by nuclei of two bonded atoms
- **lone pairs:** take up more space than bonding-pair

## Molecules Where Central Atom Has Lone Pairs

Original Shape	General Formula	# of Outer Atoms	# of Lone Pairs on Central Atom	Molecular Shape and Name
 <p>Trigonal planar SN=3</p>	$AB_2E$	2	1	 <p>Bent bent or angular</p>
 <p>Tetrahedron SN=4</p>	$AB_3E$	3	1	 <p>trigonal pyramidal</p>
	$AB_2E_2$	2	2	 <p>bent or angular</p>

### From Trigonal Planar (SN=3)

#### **AB<sub>2</sub>E: bent**

- start with AB<sub>3</sub> molecule (trigonal planar) and **replace a B atom** with a **lone pair**
- bond angles are now **<120°**

### From Tetrahedral (SN=4)

#### **AB<sub>3</sub>E: trigonal pyramidal** (central atom + 3 outer atoms make a pyramid)

- start with AB<sub>4</sub> molecule (tetrahedral) and **replace a B atom** with **lone pair**
- bond angles are now **less than 109.5°**

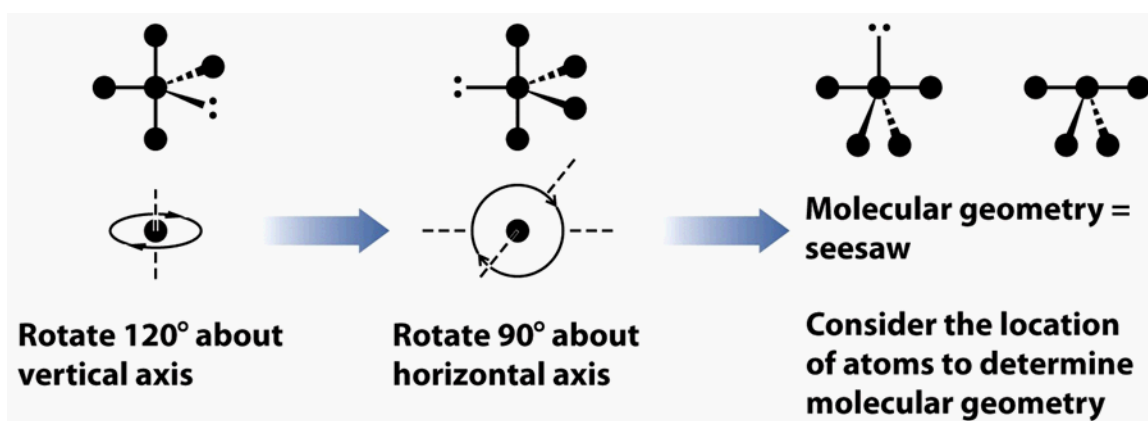
#### **AB<sub>2</sub>E<sub>2</sub>: bent**

- start with AB<sub>4</sub> molecule (tetrahedral) and replace **2 B atoms** with **2 lone pairs**

### From Trigonal Bipyramidal (SN=5)

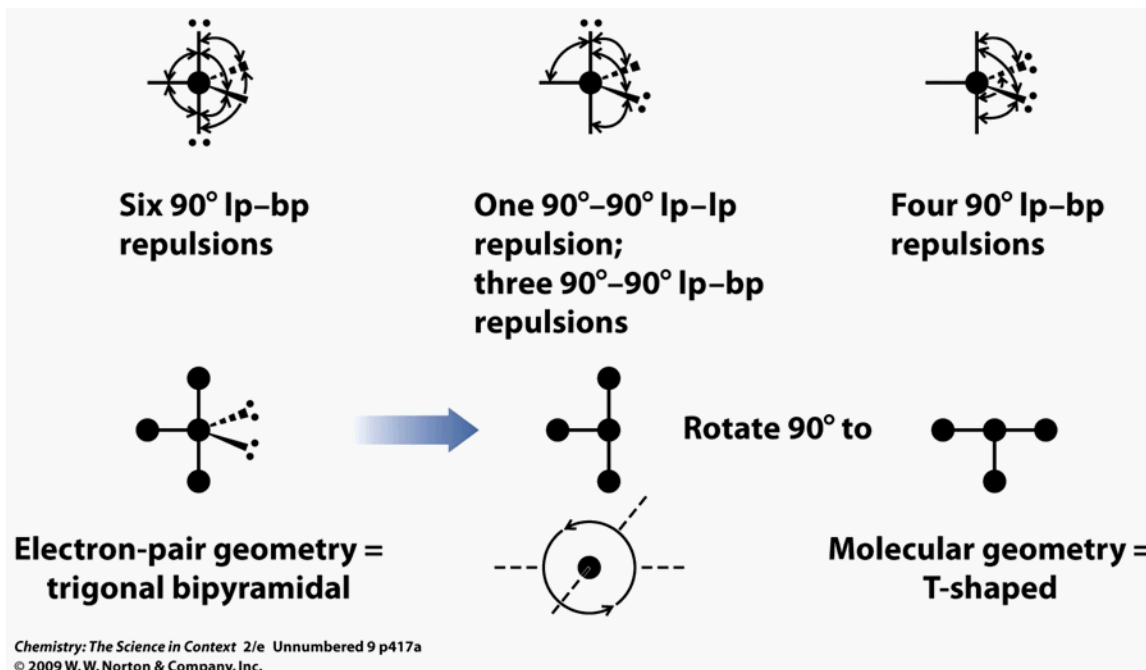
#### **AB<sub>4</sub>E: seesaw**

- start with AB<sub>5</sub> molecule and replace **one B atom** with **one lone pair**
  - an outer atom can be taken from an axial or an equatorial position
    - from **axial**: lone pair is 90° from equatorial atoms and 180° from other axial atom
    - from **equatorial**: lone pair is 90° from two axial and 120° from two other equatorial B atoms
  - taking the outer atom from the **equatorial position** maximizes the distance between the lone pair (lp) and bonding pairs (bp)
  - bond angles are now **<90° and <120°**



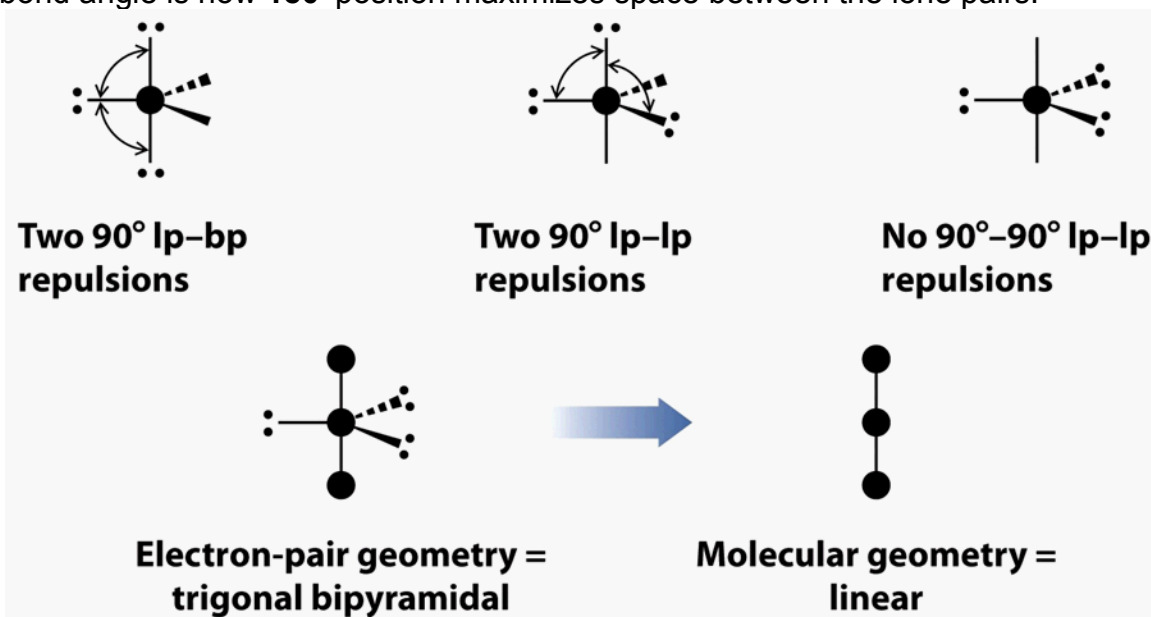
#### **AB<sub>3</sub>E<sub>2</sub>: T-shaped**

- start with  $AB_5$  molecule and replace **two B atoms** with **two lone pairs**
  - both B atoms are taken from equatorial positions to maximize distance between the lone pairs (lp) as well as between the lone pairs (lp) and bonding pairs (bp)
    - bond angles for remaining atoms are now  $<90^\circ$



### $AB_2E_3$ : linear

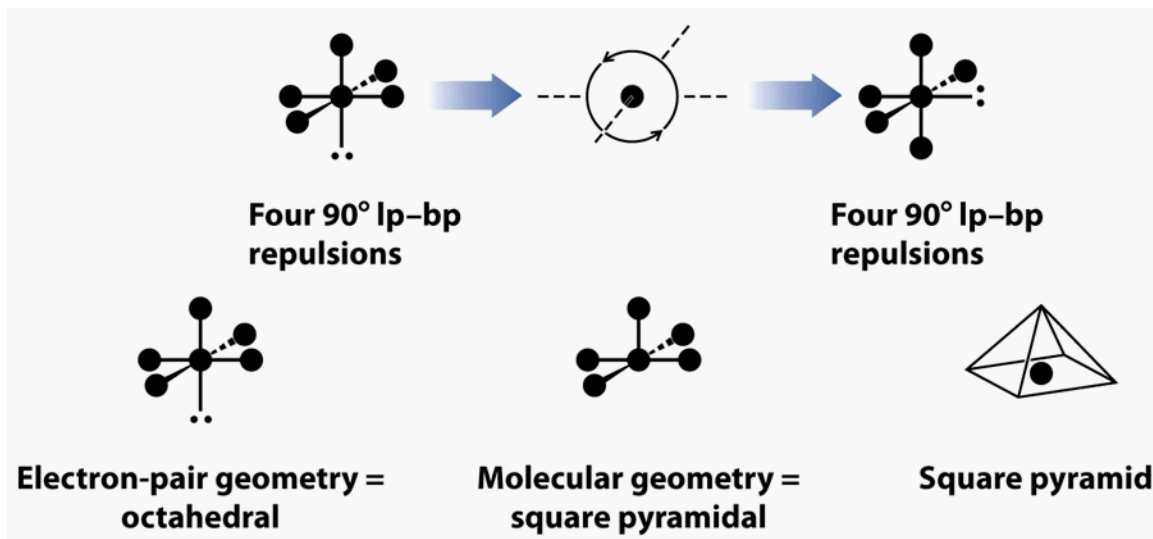
- start with  $AB_5$  molecule and replace **three B atoms** with **three lone pairs**
  - first two B atoms taken from equatorial positions; third B atom taken:
    - from **equatorial**:  $3^{\text{rd}}$  lone pair would be  $\sim 120^\circ$  from other lone pairs, so removing  $3^{\text{rd}}$  outer atom from equatorial
- bond angle is now  $180^\circ$  position maximizes space between the lone pairs.



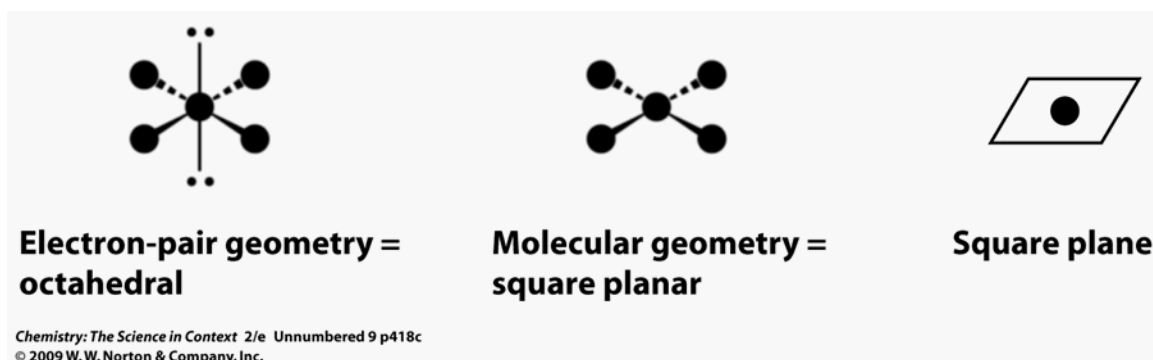
From Octahedral



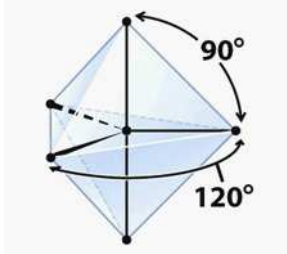
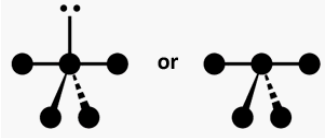
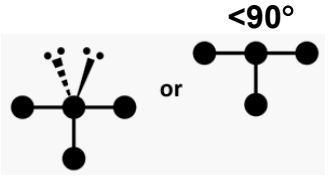
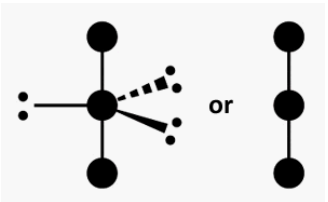
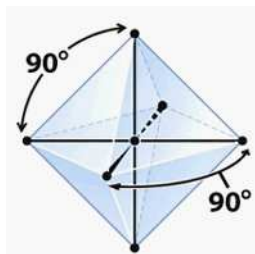
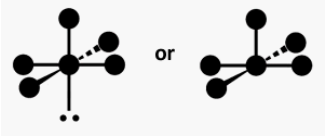
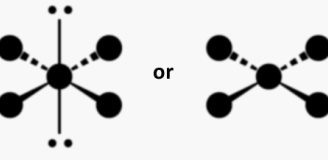
- AB<sub>5</sub>E:** **square pyramidal** (central atom + 5 B atoms make 4-faced pyramid)
- start with AB<sub>6</sub> (octahedral) and replace **one B atom** with **one lone pair**
  - since all six outer positions are identical, doesn't matter which outer atom you take  
→ **square pyramidal** shape
  - bond angles are now **less than 90°**



- AB<sub>4</sub>E<sub>2</sub>:** **square planar** (central atom + 4 B atoms form square all in 1 plane)
- start with AB<sub>6</sub> (octahedral) and replace **2 B atoms** with **2 lone pairs**
  - doesn't matter which B atom taken first, second B atom taken 180° away from it to maximize space between lone pairs  
→ **square planar** shape
  - bond angles are now **exactly 90°** since lone pairs balance each other



## Molecules Where Central Atom Has Lone Pairs (Continued)

Original Shape	General Formula	# of Outer Atoms	# of Lone Pairs on Central Atom	Molecular Geometry and Name
 <p>Trigonal bipyramid</p> <p>SN=5</p>	$AB_4E$	4	1	 <p>&lt;math&gt;&lt;120^\circ&lt;/math&gt; and &lt;math&gt;&lt;90^\circ&lt;/math&gt;</p> <p>See-saw</p>
	$AB_3E_2$	3	2	 <p>&lt;math&gt;&lt;90^\circ&lt;/math&gt;</p> <p>T-shaped</p>
	$AB_2E_3$	2	3	 <p>180°</p> <p>Linear</p>
 <p>Octahedron</p>	$AB_5E$	5	1	 <p>all &lt;math&gt;&lt;90^\circ&lt;/math&gt;</p> <p>Square Pyramid</p>
	$AB_4E_2$	4	2	 <p>all 90°</p> <p>Square Planar</p>

### Guidelines for Applying the VSEPR Model

1. Draw Lewis formula

2. Count number of outer atoms and lone pairs **around central atom** (treating double and triple bonds as single bonds) to get the General Formula
- Match the General Formula ( $AB_xE_y$ ) to get the Molecular Geometry.
  - Remember that lone pair electrons occupy more space than bonded pairs of electrons, so the bond angles are compressed when the central atom has lone pairs.

Ex: For each of the following,

- Draw the Lewis structure, including resonance structures if they apply, and minimize formal charges.
- Indicate the molecular geometry (shape) and the bond angles.

**PF<sub>3</sub>:**

**I<sub>3</sub><sup>-</sup>:**

shape = \_\_\_\_\_

shape = \_\_\_\_\_

bond angle(s) = \_\_\_\_\_

bond angle(s) = \_\_\_\_\_

**NH<sub>2</sub><sup>-</sup>:**

**SCN<sup>-</sup>:**

shape = \_\_\_\_\_

shape = \_\_\_\_\_

bond angles = \_\_\_\_\_

bond angles = \_\_\_\_\_

**SeF<sub>4</sub>:**

**IF<sub>4</sub><sup>-</sup>:**

shape = \_\_\_\_\_

shape = \_\_\_\_\_

bond angles = \_\_\_\_\_

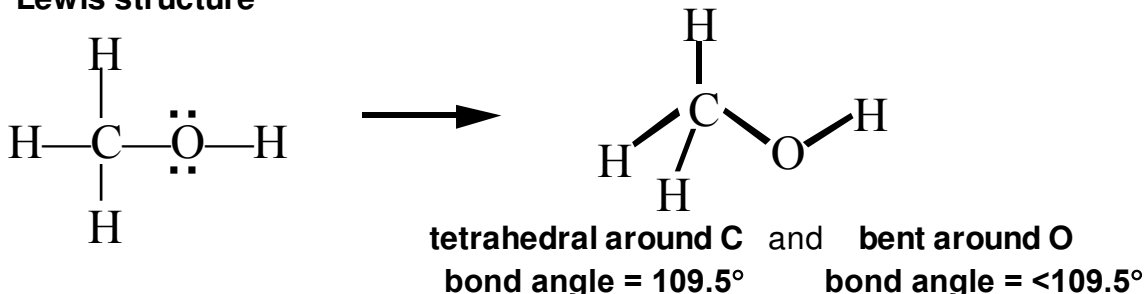
bond angles = \_\_\_\_\_

## 9.5 SHAPES AND BONDING IN LARGER MOLECULES

## Geometry of Molecules with More than One Central Atom

- Overall geometry of entire molecule cannot be described
  - instead describe the shape around **each** central atom in molecule
    - e.g.  $\text{CH}_3\text{OH}$

### Lewis structure

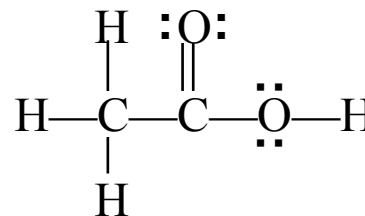


Ex. What is the geometry around each central atom in acetic acid,  $\text{CH}_3\text{COOH}$ ?

1<sup>st</sup> C: shape = \_\_\_\_\_, bond angle = \_\_\_\_\_

2<sup>nd</sup> C: shape = \_\_\_\_\_, bond angle = \_\_\_\_\_

O: shape = \_\_\_\_\_, bond angle = \_\_\_\_\_

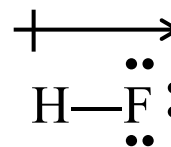


Sketch the 3D shape (with approximate bond angles) for acetic acid at the right:

## 9.3 POLAR BONDS AND POLAR MOLECULES

Bonding electrons are not always shared equally

- If two atoms bonded together have different electronegativity (EN) values
  - separation of charges = **dipole**
    - more EN atom gains a partial negative charge
    - other atom gains a partial positive charge
- molecules that have a dipole are **polar molecules**
  - A **dipole** is indicated with an arrow pointing to more EN atom.
  - The more polar the molecule, the greater its **dipole moment**, the *quantitative* measurement of the separation of positive and negative charges in the molecule.



### For diatomic molecules:

- nonpolar molecules:** when the 2 atoms have equal EN values → no dipole
- polar molecules:** when the 2 atoms have different EN values → dipole

### For molecules of three or more atoms:

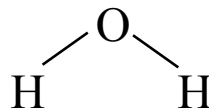
- polarity depend on individual bonds and geometry around central atom

Example: Determine whether the following have dipole moments:

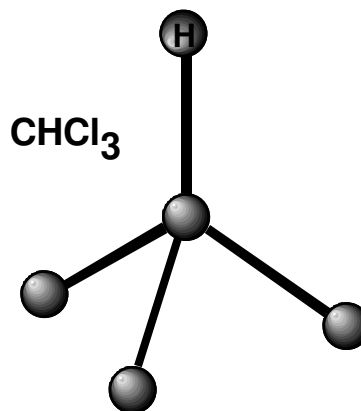
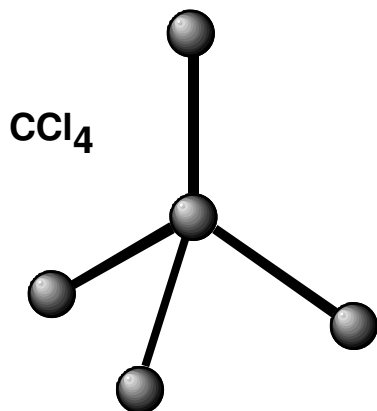
**BeCl<sub>2</sub>:**



**H<sub>2</sub>O:**



**CCl<sub>4</sub> versus CHCl<sub>3</sub>:**



Ex. 2: For each of the following molecules,

- Draw the Lewis structure (including resonance structures when necessary).
- Determine its molecular geometry and bond angle(s).
- Sketch the molecule's **3D shape**, draw a dipole arrow for each polar covalent bond.
- Indicate if the molecule is polar or nonpolar.

**a. SF<sub>4</sub>**

Lewis formula

sketch of 3D shape with dipoles

Molecular geometry: \_\_\_\_\_

SF<sub>4</sub> is \_\_\_\_\_.

Bond angles: \_\_\_\_\_

(Circle one) polar    nonpolar

**b. PF<sub>5</sub>**                      Lewis formula

sketch of 3D shape with dipoles

Molecular geometry: \_\_\_\_\_

Bond angles: \_\_\_\_\_

**PF<sub>5</sub>** is \_\_\_\_\_.

(Circle one) polar nonpolar

**c. SO<sub>2</sub>**

Lewis formula

sketch of 3D shape with dipoles

Molecular geometry: \_\_\_\_\_

Bond angles: \_\_\_\_\_

**SO<sub>2</sub>** is \_\_\_\_\_.

(Circle one) polar nonpolar

**d. COCl<sub>2</sub>**

Lewis formula

sketch of 3D shape with dipoles

Molecular geometry: \_\_\_\_\_

Bond angles: \_\_\_\_\_

**e. CCl<sub>2</sub>F<sub>2</sub>**

Lewis formula

**COCl<sub>2</sub>** is \_\_\_\_\_.

(Circle one) polar nonpolar

sketch of 3D shape with dipoles

Molecular geometry: \_\_\_\_\_

**CCl<sub>2</sub>F<sub>2</sub>** is \_\_\_\_\_.

Bond angles: \_\_\_\_\_

(Circle one) polar nonpolar

f. **SOCl<sub>2</sub>**

Lewis formula

sketch of 3D shape with dipoles

Molecular geometry: \_\_\_\_\_

**COCl<sub>2</sub>** is \_\_\_\_\_.

Bond angles: \_\_\_\_\_

(Circle one) polar nonpolar

Ex. 3: Rank the following molecules in terms of increasing dipole moment:

CH<sub>2</sub>Cl<sub>2</sub>, CCl<sub>2</sub>F<sub>2</sub>, CH<sub>2</sub>F<sub>2</sub>, and CF<sub>4</sub>.

\_\_\_\_\_ < \_\_\_\_\_ < \_\_\_\_\_ < \_\_\_\_\_  
smallest dipole moment largest dipole moment

Ex. 4: Rank the following molecules in terms of increasing dipole moment:

COCl<sub>2</sub>, SO<sub>3</sub>, SOCl<sub>2</sub>, NF<sub>3</sub>, and NCl<sub>3</sub>.

\_\_\_\_\_ < \_\_\_\_\_ < \_\_\_\_\_ < \_\_\_\_\_ < \_\_\_\_\_  
smallest dipole moment largest dipole moment

## 9.4 VALENCE BOND THEORY

### Localized Electron Model

- a molecule is a collection of atoms that share electrons between their atomic orbitals
- “localized” because the electrons are assumed to exist between the atoms

## Valence Bond (VB) Theory

- assumes electrons in molecules occupy atomic orbitals of individual atoms in a bond
- accounts for changes in PE as distance between reacting atoms changes
- incomplete picture of all aspects of bonding but gives some insight

## Basic Theory

- a covalent bond consists of a pair of electrons in atomic orbitals

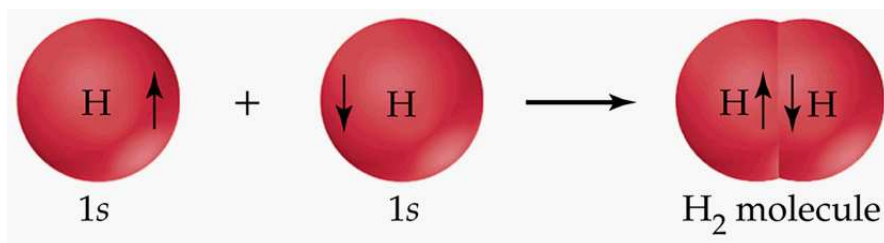
Ex. 1 H atom has the electron configuration:  $1s^1$

H atom has the atomic orbital diagram:  $\frac{\uparrow}{1s}$

Lewis formula for  $H_2$  molecule: **H—H**

Each H in a  $H_2$  molecule has the atomic orbital diagram:  $\frac{\uparrow\downarrow}{1s}$

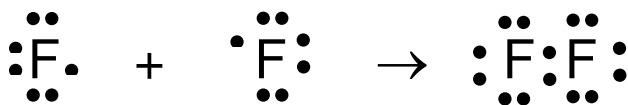
**S orbitals** are spherical, so two 1s orbitals for the two H atoms in  $H_2$  bond by having an overlapping region where the two electrons are shared.



Ex. 1 F atom has the electron configuration:  $1s^2 2s^2 2p^5$

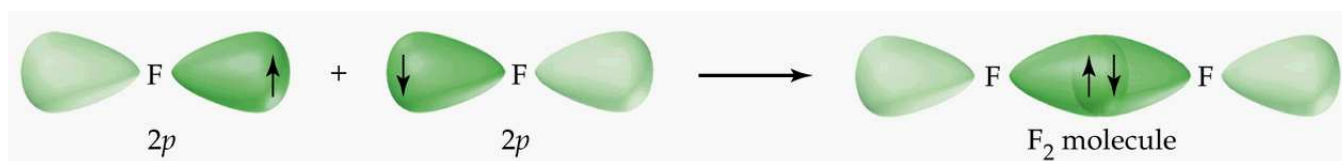
F atom has the atomic orbital diagram:  $\frac{\uparrow\downarrow}{1s} \frac{\uparrow\downarrow}{2s} \frac{\uparrow\downarrow}{2p} \frac{\uparrow}{2p}$

F atoms forming  $F_2$  molecule:



**P orbitals** are dumbbell-shaped, so two 2p orbitals for the two F atoms in  $F_2$  bond by having an overlapping region where the two electrons are shared.





### Case #1: BeH<sub>2</sub>

1. Draw the Lewis formula for the BeH<sub>2</sub> molecule below:

Lewis formula

Sketch of molecule

2. The BeH<sub>2</sub> molecule's shape is \_\_\_\_\_ and the bond angle is \_\_\_\_\_.

Sketch the molecule in the space provided above.

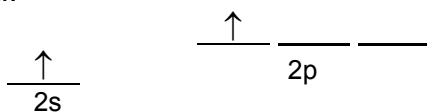
3. The electron configuration for Be: \_\_\_\_\_

4. The ground state orbital diagram for Be should be as follows:



– BUT this indicates that Be does not form covalent bonds with H since Be's electrons are already paired.

→ for Be to make two bonds, one of Be's 2s electrons must be promoted to the 2p orbital:



– Now there are two unpaired electrons available to bond to each H, but this orbital diagram indicates that the two Be–H bonds are different since one forms with a 2s orbital and other from a 2p orbital.

– BUT VSEPR predicts **BeH<sub>2</sub> is linear** and experiment indicates that **the two Be–H bonds are equivalent** → inconsistency between VSEPR and orbitals

How do you get two equivalent atomic orbitals that are oriented 180° from each other when s orbitals are spherical and p orbitals are dumbbell shaped?

→ **Hybridize the atomic orbitals!**

#### Hybridization of Atomic Orbitals

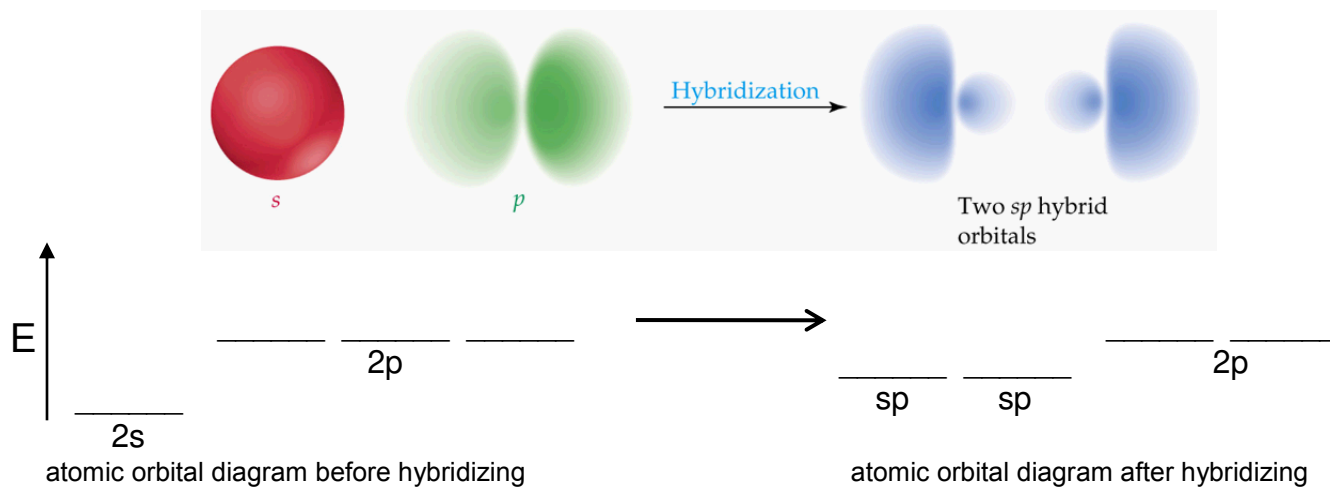
– The shape predicted by VSEPR does not match the bond angles given by pure s and pure p orbitals → atomic orbitals involved in bonding must be a combination of s and p orbitals

- To hybridize, mix s and p orbitals to get the same number of new hybridized orbitals (e.g. mix one s and one p → two sp orbitals)

**hybridization:** mixing of atomic orbitals in an atom (usually central atom) to generate a new set of atomic orbitals, called **hybrid orbitals**

**sp Hybridization:** mixing **one s** orbital and **one p** orbital → **two sp** orbitals

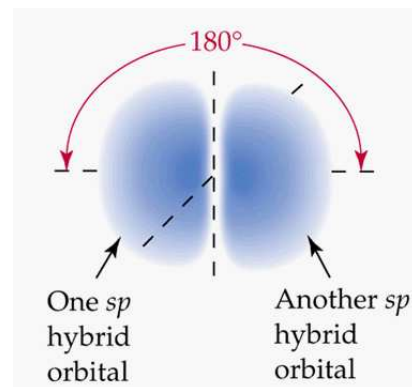
→ hybridize a 2s and a 2p orbital to get 2 equivalent **sp hybrid orbitals**:



The **two sp orbitals** in Be are oriented along a line to maximize the distance between electrons.

→ **linear shape (180° bond angle)** corresponding to a form a linear molecule when the H atoms are bonded to the Be atom.

Example: Sketch the BeH<sub>2</sub> molecule below by showing the Be atom with sp orbitals, the H atoms with s orbitals, & bonds as overlapping areas.



### Case #2: BH<sub>3</sub>

1. Draw the Lewis formula for the BH<sub>3</sub> molecule below:

Lewis formula

Sketch of molecule

- BH<sub>3</sub>'s shape is \_\_\_\_\_ and its bond angles are \_\_\_\_\_.  
Sketch the molecule above.
- Electron configuration for B (using core notation): \_\_\_\_\_
- Draw the atomic orbital diagram for the valence electrons in B:
- Promote electrons in the atomic orbital diagram for B, so B can form 3 bonds.

Although B now has unpaired electrons in 3 orbitals for bonding, the atomic orbital diagram indicates that two of the B–H bonds (from 2p) should be the same but one (from 2s) should be different.

But VSEPR predicts **BH<sub>3</sub> is trigonal planar** and experimental evidence indicates that the **three B–H bonds in BH<sub>3</sub> are equivalent**

→ hybridize one 2s and two 2p orbitals to get **3 equivalent sp<sup>2</sup> hybrid orbitals**

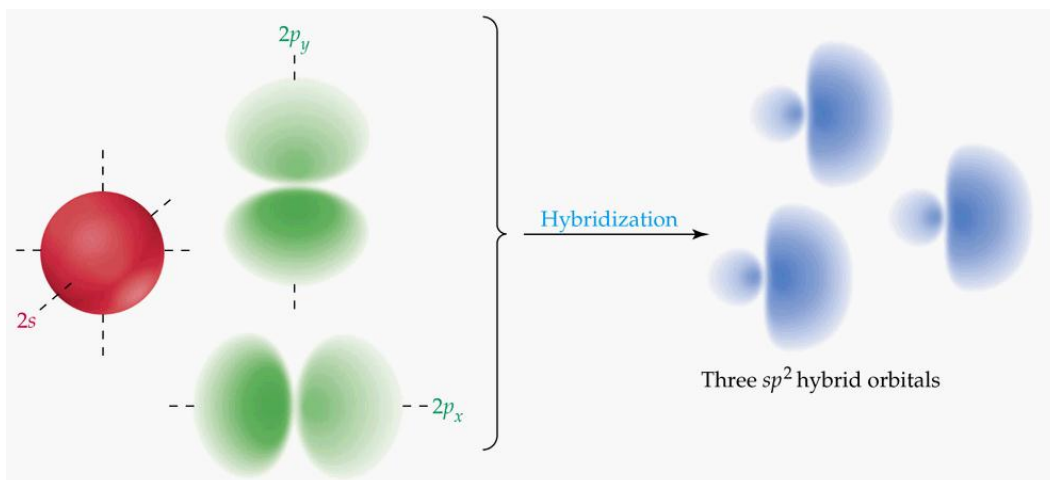
Show the atomic orbital diagrams for the hybridization below:

hybridization  
→

atomic orbital diagram before hybridizing

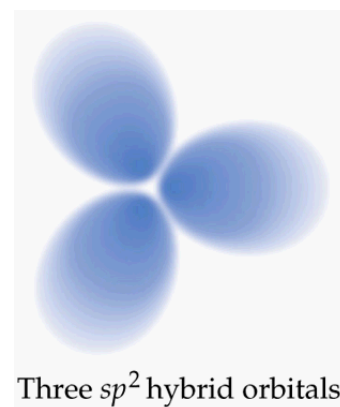
atomic orbital diagram after hybridizing

The hybridization of one s and two p orbitals to form three sp<sup>2</sup> hybrid orbitals



To maximize the distance between electrons in B, the **three  $sp^2$  orbitals** in the B atom are oriented in a triangular shape  
 → **trigonal planar shape ( $120^\circ$  bond angle)**  
 corresponds to  **$sp^2$  orbitals**

Example: Sketch the the  $BH_3$  molecule at the right by showing the the H atoms with s orbitals, & bonds as overlapping areas.



### Case #3: $CH_4$ :

1. Draw the Lewis formula for the  $CH_4$  molecule below:

Lewis formula

Sketch of molecule

2. The  $CH_4$  molecule's shape is \_\_\_\_\_ and the bond angles are \_\_\_\_\_.  
 Sketch the molecule above.
3. Electron configuration for C (using core notation): \_\_\_\_\_

4. Draw the atomic orbital diagram for the valence electrons in C:

5. Promote electrons in the atomic orbital diagram, so C can form 4 bonds.

Although C now has unpaired electrons in 4 orbitals for bonding, the atomic orbital diagram in step 5 indicates that three of the C–H bonds (from 2p) should be the same, but one (from 2s) should be different.

But VSEPR predicts **CH<sub>4</sub> is tetrahedral** and experimental evidence indicates that **the four C–H bonds are equivalent**

→ hybridize one 2s and three 2p orbitals to get **4 equivalent sp<sup>3</sup> hybrid orbitals**

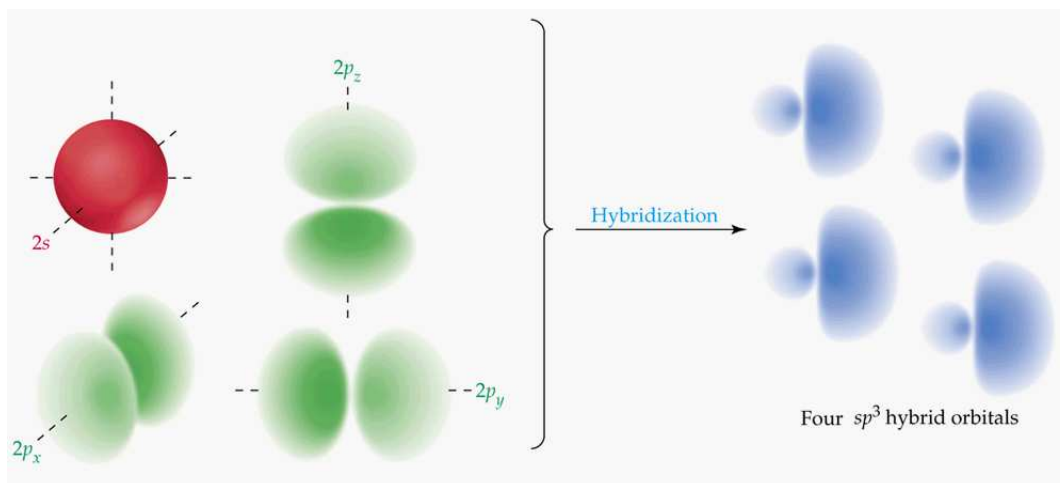
Show the atomic orbital diagrams for the hybridization below:

hybridization →

atomic orbital diagram before hybridizing

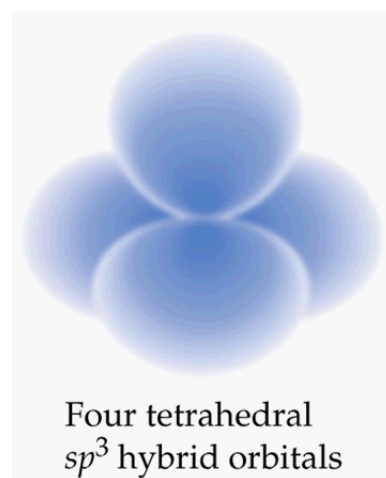
atomic orbital diagram after hybridizing

The hybridization of one s and three 2p orbitals to form four sp<sup>3</sup> hybrid orbitals

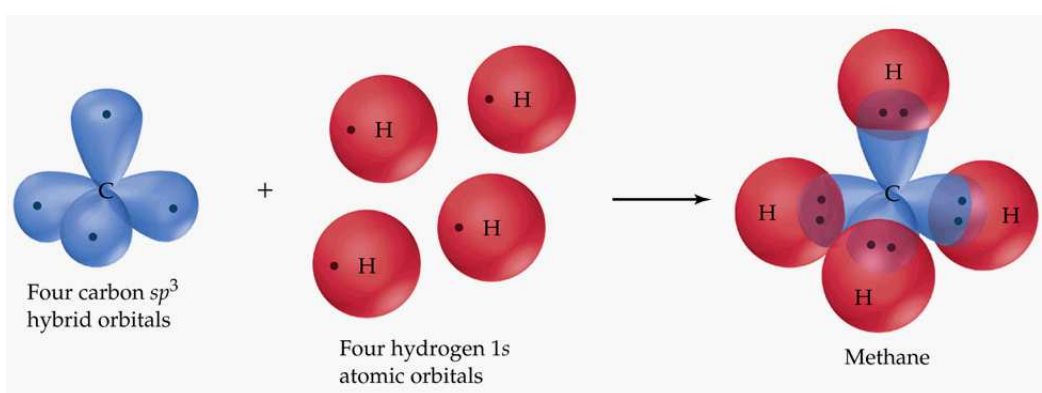


To maximize the distance between e<sup>-</sup>'s in C, the **four sp<sup>3</sup> orbitals** in the C atom are oriented to be **109.5°** away from one another in three dimensions

→ **tetrahedral shape** (with **109.5° bond angles**) corresponding to **four sp<sup>3</sup> orbitals** oriented towards the four corners of a 4-sided pyramid



The four hybrid sp<sup>3</sup> atomic orbitals for C are shown in blue below, along with the four 1s orbitals for the four H atoms to form the CH<sub>4</sub> molecule.



The C-H bonds are made from the electrons shared in the darker overlapping regions.

#### Case #4: PF<sub>5</sub>:

1. Draw the Lewis formula for the PF<sub>5</sub> molecule below:

Lewis formula

Sketch of molecule

2. PF<sub>5</sub>'s shape is \_\_\_\_\_ and its bond angles are \_\_\_\_\_.  
Sketch the molecule above.

3. Electron configuration for P (using core notation): \_\_\_\_\_

- Draw the atomic orbital diagram for the valence electrons in P:
- Promote electrons to 3d in the atomic orbital diagram, so P can form 5 bonds.

Although P now has unpaired electrons in 5 orbitals for bonding, the atomic orbital diagram in step 5 above indicates that three of the P–F bonds (from 3p) should be the same, but two (one from 3s and one from 3d) should be different.

But VSEPR predicts **PF<sub>5</sub> is trigonal bipyramidal** and experimental evidence indicates that **the five P–F bonds are equivalent**

→ hybridize one 3s, three 3p orbitals, and one 3d orbital to get **5 equivalent sp<sup>3</sup>d hybrid orbitals**

Show the atomic orbital diagrams for the hybridization below:

hybridization  
→

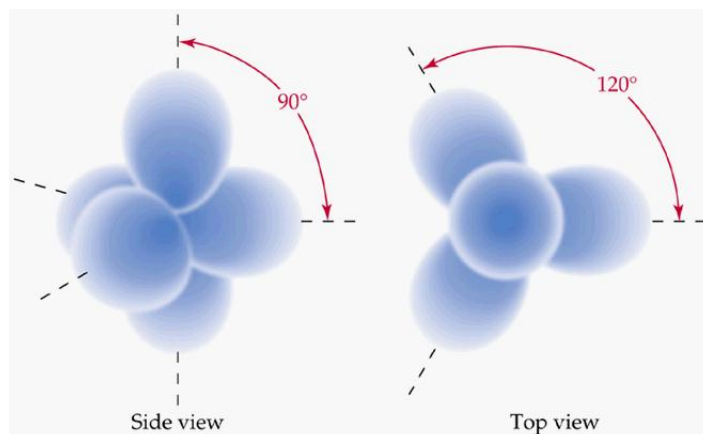
atomic orbital diagram before hybridizing

atomic orbital diagram after hybridizing

To maximize the distance between e<sup>-</sup>s in P, the **five sp<sup>3</sup>d orbitals** in the P atom are oriented as shown at the right

→ **trigonal bipyramidal shape** (with **120°** and **90°** bond angles)

→ to get **trigonal bipyramidal shape** (or variations like see-saw, T-shaped, etc.), must have **sp<sup>3</sup>d orbitals**



**Case #5: SF<sub>6</sub>:**

1. Draw the Lewis formula for the SF<sub>6</sub> molecule below:

Lewis formula

Sketch of molecule

2. The SF<sub>6</sub> molecule's shape is \_\_\_\_\_ and its bond angles are \_\_\_\_\_.  
Sketch the molecule above.
3. Electron configuration for S (using core notation): \_\_\_\_\_
4. Draw the atomic orbital diagram  
for the valence electrons in S:
5. Promote electrons in the atomic  
orbital diagram, so S can form 6 bonds.

Although S now has unpaired electrons in 6 orbitals for bonding, the atomic orbital diagram in step 5 indicates that three different types of the S–F bonds (one from 3s, three from 3p, two from 3d).

But VSEPR predicts **SF<sub>6</sub> is octahedral** and experimental evidence indicates that **the six S–F bonds are equivalent**

→ hybridize one 3s, three 3p orbitals, two 3d orbital to get **6 equivalent sp<sup>3</sup>d<sup>2</sup> hybrid orbitals**

Show the atomic orbital diagrams for the hybridization below:

→ hybridization →

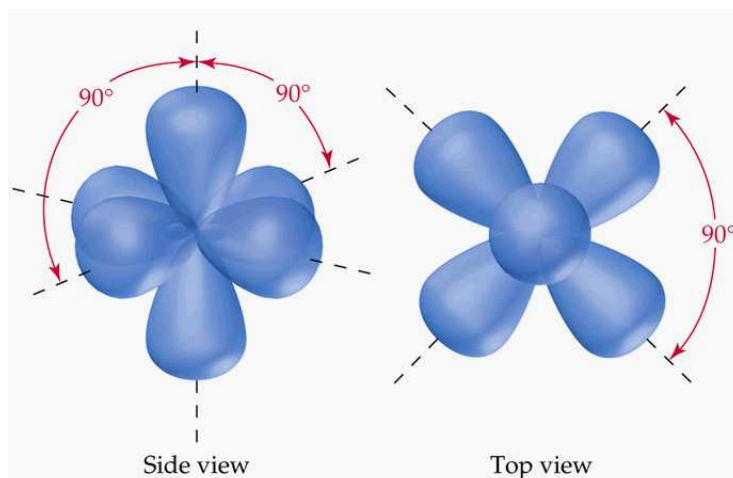
atomic orbital diagram before hybridizing

atomic orbital diagram after hybridizing



To maximize the distance between electrons in S, the **five  $sp^3d^2$  orbitals** in the S atom are oriented as follows:

- **octahedral shape**  
(with  $90^\circ$  bond angles)
- to get **octahedral shape** (or variations like square pyramid or square planar) must have  **$sp^3d^2$  orbitals**



### Predicting what hybrid orbitals form on central atom of molecules:

1. Draw Lewis structure to determine total number of bonds on central atom
2. Given the shape of molecule or bond angle from the VSEPR model, we can determine what hybrid orbitals must be involved:

Molecular Geometry (Shape)	Steric #	Hybrid Orbitals
<b>linear</b> (e.g. HCN, $BeCl_2$ , $CO_2$ ), central atom has 2 or 4 electron pairs	<b>2</b>	<b><math>sp</math></b>
<b>trigonal planar</b> ( $120^\circ$ bond angle or $120^\circ \angle$ ), <b>bent</b> ( $<120^\circ \angle$ )	<b>3</b>	<b><math>sp^2</math></b>
<b>tetrahedral</b> ( $109.5^\circ \angle$ ), <b>trigonal pyramid</b> , or <b>bent</b> ( $<109.5^\circ \angle$ )	<b>4</b>	<b><math>sp^3</math></b>
<b>trigonal bipyramidal</b> , <b>see-saw</b> , <b>T-shape</b> , <b>linear</b> (with expanded octet/more than 4 electron pairs on central atom)	<b>5</b>	<b><math>sp^3d</math></b>
<b>octahedral or square planar</b> ( $90^\circ \angle$ ), <b>square pyramid</b> ( $<90^\circ \angle$ )	<b>6</b>	<b><math>sp^3d^2</math></b>

- Example:
- i. Draw the Lewis structure.
  - ii. Use VSEPR to determine the molecule's shape and bond angles,
  - iii. Draw atomic orbital diagrams for valence electrons before and after hybridization.
  - iv. Indicate the atomic hybrid orbital for the central atom in each.
  - v. Sketch the molecule showing the hybrid atomic orbitals on the central atom and hybrid or unhybridized orbitals on the outer atoms.

**$H_2O$ :**

Sketch of molecule showing hybrid orbitals

shape = \_\_\_\_\_ bond angles = \_\_\_\_\_ hybrid orbital \_\_\_\_\_

hybridization →

before hybridizing

after hybridizing

---

**CH<sub>3</sub>F:**

Sketch of molecule showing hybrid orbitals

shape = \_\_\_\_\_ bond angles = \_\_\_\_\_ hybrid orbital \_\_\_\_\_

hybridization →

before hybridizing

after hybridizing

**NH<sub>3</sub>:**

Sketch of molecule showing hybrid orbitals

shape = \_\_\_\_\_ bond angles = \_\_\_\_\_ hybrid orbital \_\_\_\_\_

hybridization →

before hybridizing

after hybridizing

**SeF<sub>4</sub>:**

Sketch of molecule showing hybrid orbitals

shape = \_\_\_\_\_ bond angles = \_\_\_\_\_ hybrid orbital \_\_\_\_\_

hybridization →

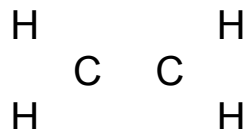
before hybridizing

after hybridizing

## 9.5 SHAPES AND BONDING IN LARGER MOLECULES

### Double Bond Case: C<sub>2</sub>H<sub>4</sub>:

1. Draw the Lewis structure for C<sub>2</sub>H<sub>4</sub> using the skeletal structure below:



- The shape around each C is \_\_\_\_\_, and the bond angle is \_\_\_\_\_.
- Electron configuration for C (using core notation): \_\_\_\_\_
- Draw the atomic orbital diagram for the valence electrons in C, promoting electrons in the atomic orbital diagram, so C can form 3 bonds.
- Given the shape around each C atom, C has \_\_\_\_\_ atomic hybrid orbitals.
- Show the atomic orbital diagrams forming the three hybrid orbitals for each C atom below:

hybridization →

atomic orbital diagram before hybridizing

atomic orbital diagram after hybridizing

### sigma (σ) bonds:

- covalent bond formed by directly overlapping orbitals
  - for example, all of the bonds we've seen between the hybrid orbitals on the central atom and the outer atoms' orbitals have all been sigma bonds
- The electron density is concentrated between the two nuclei of bonding atoms.
- single bonds are generally sigma bonds
- only the first bond in double and triple bonds can be a sigma bond

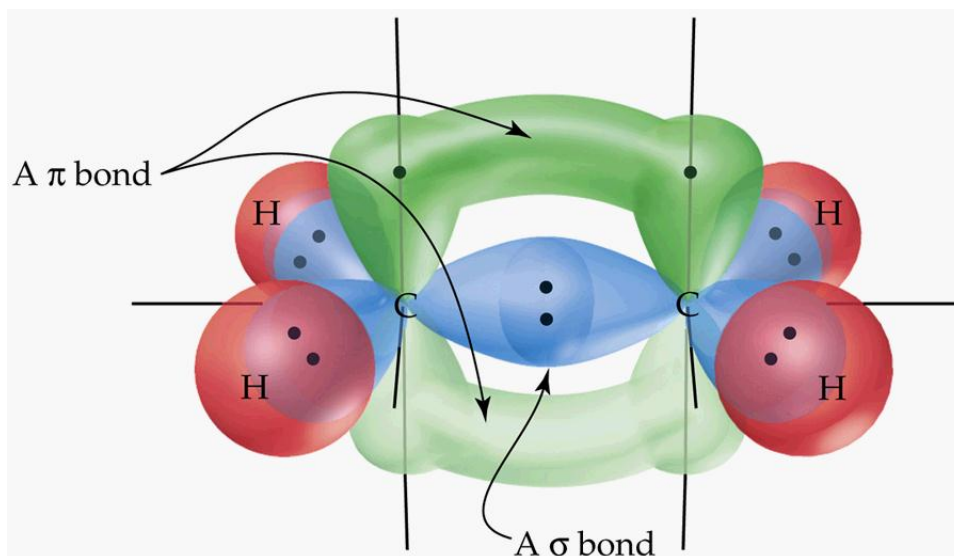
### pi (π) bond: (usually second and third bonds in double and triple bonds)

- covalent bond formed by sideways interaction between adjacent orbitals
- electron density concentrated above and below plane of the nuclei of bonding atoms

Example: Indicate the sigma and pi bonds in the ethylene molecule below:



Each C–H bond and the first C–C bond all have a region of direct overlap where the shared electrons are located—these are all sigma ( $\sigma$ ) bonds, as shown below:



Note: The atomic orbital diagram for each C atom drawn in step 6 C shows an unhybridized p orbital. The second C–C bond forms from the two electrons in the unhybridized p orbitals.

- Each C atom has an unpaired electron in the  $2p_z$  orbital, which is perpendicular to the  $sp^2$  orbitals forming the C–H and first C–C bond.
- These two electrons in the  $2p_z$  bond via a sideways overlap as shown above.

Note: The carbon-carbon double bond in  $C_2H_4$  is made up of the following:

The  $\sigma$  bond is the first C–C bond, and the two lobes above and below (indicated as  $\pi$  bond) together make up the  $\pi$  bond, which is the second C–C bond.

### Triple Bond Case: $C_2H_2$ :

1. Draw the Lewis structure for  $C_2H_2$  using the skeletal structure below:



2. The shape around each C is \_\_\_\_\_, and the bond angle is \_\_\_\_\_.
3. Electron configuration for C (using core notation): \_\_\_\_\_
4. Given the shape around each C atom, C has \_\_\_\_\_ atomic hybrid orbitals.
5. Draw the atomic orbital diagram for the valence electrons in C, promoting electrons, so C can form 2 bonds.

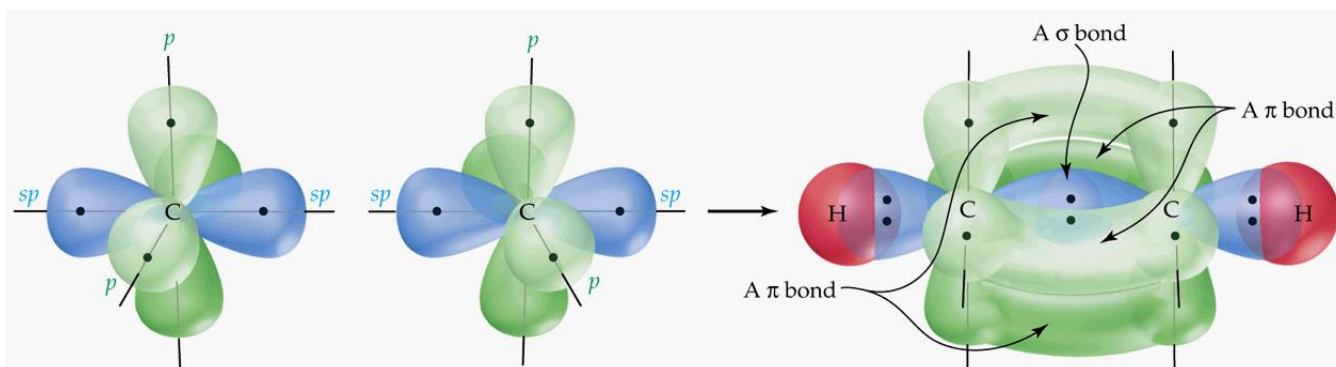
6. Show the atomic orbital diagrams for the formation of the three hybrid orbitals for each C atom below:

hybridization  
→

atomic orbital diagram before hybridizing

atomic orbital diagram after hybridizing

Each C–H bond and the first C–C bond are all sigma bonds, as shown below:



Note: The atomic orbital diagram for each C atom drawn in step 6 C shows two unhybridized p orbitals. The 2<sup>nd</sup> and 3<sup>rd</sup> C–C bonds form from the electrons in the unhybridized p orbitals.

- Each carbon has two unpaired electrons in unhybridized p orbitals (in the 2p<sub>y</sub> and 2p<sub>z</sub>), which are perpendicular to the sp orbitals forming the C–H and first C–C bond.
- These two electrons in the 2p<sub>y</sub> and 2p<sub>z</sub> bond to each other via a sideways overlap to make the 2<sup>nd</sup> and 3<sup>rd</sup> bond in the triple bond, as shown above.

Note: The carbon-carbon triple bond in C<sub>2</sub>H<sub>2</sub> consists of a σ bond (shown in blue) and two carbon-carbon π bonds (shown in green) made from the four lobes on the unhybridized p's.

Example: **HCN**

1. Draw the Lewis structure for HCN:
2. The shape around each C is \_\_\_\_\_, and the bond angle is \_\_\_\_\_.
3. Electron configuration for C (using core notation): \_\_\_\_\_
4. Given the shape around each C atom, C has \_\_\_\_\_ atomic hybrid orbitals.
5. Draw the atomic orbital diagram for the valence electrons in C, promoting electrons, so C can form 2 bonds.

6. Show the atomic orbital diagrams for the formation of the hybrid orbitals for the C atom below:

hybridization →

atomic orbital diagram before hybridizing

atomic orbital diagram after hybridizing

7. Sketch the molecule below showing the hybridized and unhybridized atomic orbitals on the carbon and nitrogen atoms.

## Bonding and Magnetism

- Ex. 1: Draw the Lewis electron-dot formulas for  $N_2$  and  $O_2$  below:

Lewis electron-dot formula for  $N_2$

Lewis electron-dot formula for  $O_2$

- Ex. 2: Write the electron configurations (using core notation) for N and O.

Electron Configuration for N: \_\_\_\_\_

Electron Configuration for O: \_\_\_\_\_

- Ex. 3: Draw the atomic orbital diagrams for the valence electrons in N and O below:

atomic orbital diagram for N

atomic orbital diagram for O

- Ex. 4: Draw the atomic orbital diagrams for the valence electrons in  $N_2$  and  $O_2$  below:

atomic orbital diagram each N in N<sub>2</sub>

atomic orbital diagram for each O in O<sub>2</sub>

### Magnetic Properties of Molecules

**paramagnetic:** substance contains unpaired electrons  
→ weakly attracted to magnetic field

**diamagnetic:** substance contains only paired electrons  
→ slightly repelled by a magnetic field

Ex. 5: Based on Ex. 4, the N<sub>2</sub> molecule is \_\_\_\_\_,      paramagnetic      diamagnetic  
and the O<sub>2</sub> molecule is \_\_\_\_\_.      paramagnetic      diamagnetic

Ex. 6: Based on your answers to Ex. 5 above, predict what will happen when liquid nitrogen is poured over magnetic field. Will it stick or not? Explain.

Ex. 7: Based on your answers to Ex. 5 above, predict what will happen when liquid oxygen is poured over magnetic field. Will it stick or not? Explain.

Ex. 8: Based on the YouTube video showing the magnetic properties of liquid N<sub>2</sub> and liquid O<sub>2</sub>,  
the N<sub>2</sub> molecule is \_\_\_\_\_,      paramagnetic      diamagnetic  
and the O<sub>2</sub> molecule is \_\_\_\_\_.      paramagnetic      diamagnetic

### 9.6 MOLECULAR ORBITAL (MO) MODEL



### Problems with the Localized Electron Model

- Does not address resonance
- Does not correctly explain molecules with unpaired electrons (paramagnetic molecules)
- Provides not information on bond energies (i.e., why some molecules don't form)

### Molecular Orbital (MO) Model (or MO Theory)

- Molecules exist as positively charged nuclei sharing all of the electrons within the molecule
- Electrons are contained within "molecular orbitals", not localized between 2 atoms.
- MO Theory correctly predicts relative bond strength, magnetism, and bond polarity.

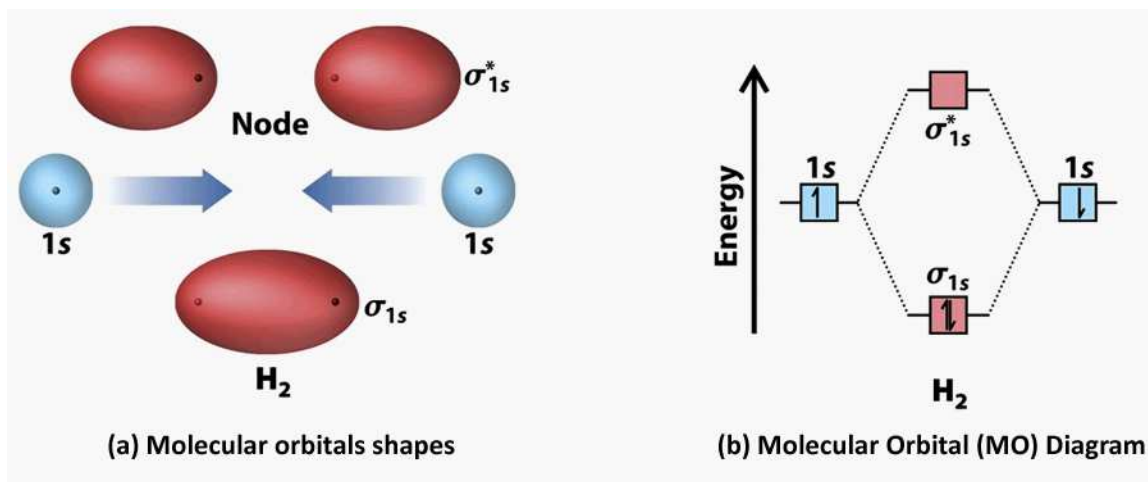
### Characteristics of Molecular Orbitals (MOs) are similar to atomic orbitals.

- Each molecular orbital can hold 2 electrons.
- Pauli Exclusion Principle applies → electrons in same MO must have opposite spins.
- Hund's Rule applies → one  $e^-$ s in each degenerate orbital with same spin before pairing.
- The square of the MO wave function ( $\psi^2$ ) gives the probability density or "electron cloud"
- Like hybrid atomic orbitals, the # of MOs formed equals the original # of atomic orbitals.
- When 2 atoms form a molecule, their electrons can only occupy the new MOs.

1s atomic orbitals → 2 new MOs: bonding  $\sigma_{1s}$  and antibonding  $\sigma_{1s}^*$

We can also show the formation of the MOs using orbitals diagrams and H<sub>2</sub> as an example.

Isolated H atoms are shown in blue, and the H<sub>2</sub> molecule is shown in red.



The two 1s orbitals from each H atom form two new molecular orbitals:  $\sigma_{1s}$  and  $\sigma_{1s}^*$

- Because the lower MO results from **direct overlap**, it is called a **bonding  $\sigma_{1s}$**  MO.
  - A **bonding MO is lower in energy** than the original atomic orbitals.
- A node between the nuclei in the upper MO results in a **antibonding  $\sigma_{1s}^*$**  MO.
  - An **antibonding MO is higher in energy** than the original atomic orbitals.
- Aufbau (Building-Up) Principle applies → bonding  $\sigma_{1s}$  MO fills before antibonding  $\sigma_{1s}^*$  MO.

### Electron Configurations for Molecules using MO Diagrams

Just like for individual atoms, electron configurations can be written for molecules, and the electron configurations are based on the occupied orbitals in the molecule's MO diagram.

Since there are 2 electrons in the  $\sigma_{1s}$  molecular orbital for the H<sub>2</sub> molecules, its electron configuration shows the  $\sigma_{1s}$  MO in parentheses followed by the superscript 2.

Electron configuration for H<sub>2</sub>:  $(\sigma_{1s})^2$

### Bond Order and Bond Strength

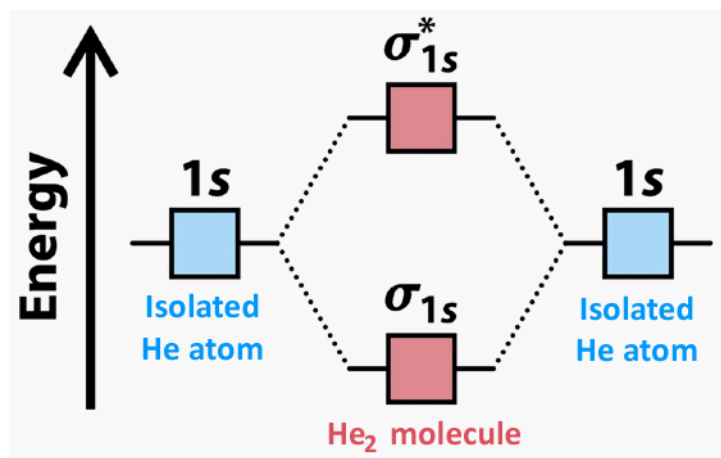
- MO Theory allows determination of bond order, a measure of the relative bond strength.
  - **The higher the bond order, the stronger the bond.**
- The bond order is given as follows (with the number of electrons being **divided by 2** since **bonds consist of electron pairs**).

$$\text{bond order} = \frac{\text{\# of bonding electrons} - \text{\# of antibonding electrons}}{2}$$

Ex. 1: Use the MO diagram for H<sub>2</sub> to calculate its bond order.

Ex. 2: Consider the He atom and why the He<sub>2</sub> molecule does not form.

- Write the electron configuration for helium: \_\_\_\_\_
- Fill in the MO diagram for the He<sub>2</sub> molecule below:

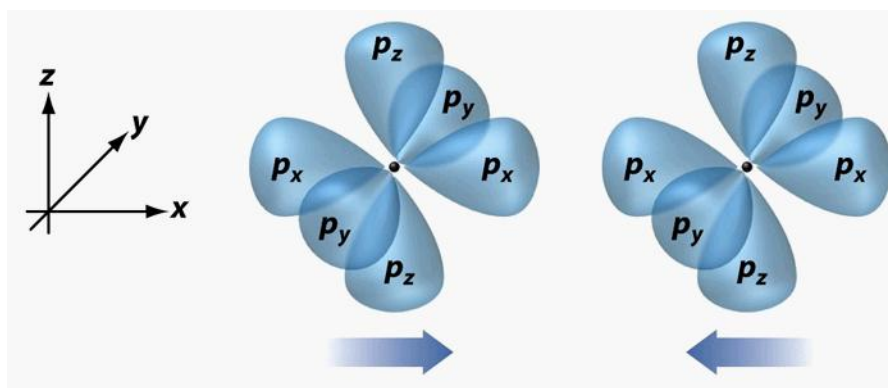


- Calculate the bond order for the He<sub>2</sub> molecule.

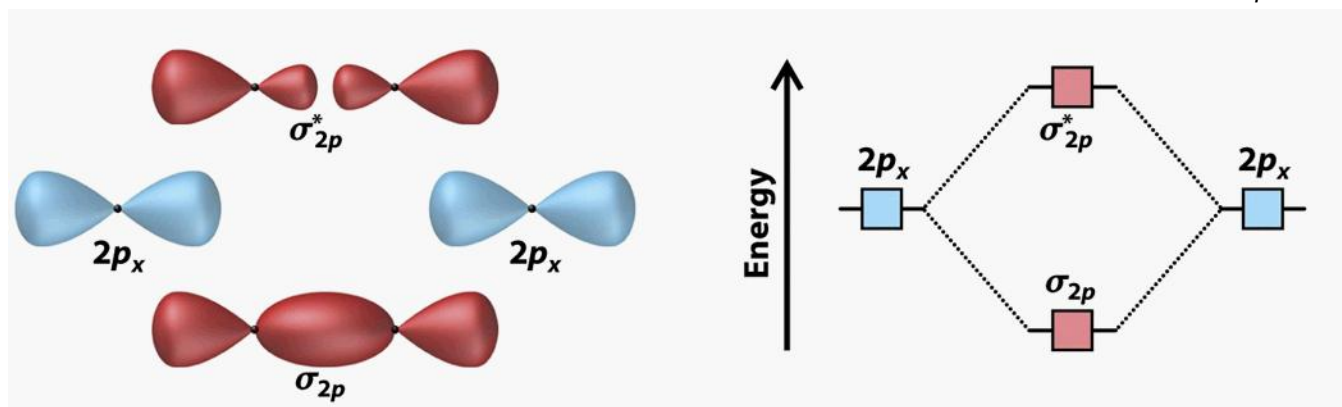
d. Using the bond order determined for the He<sub>2</sub> molecule, explain why it is not stable.

## MOLECULAR ORBITALS IN HOMONUCLEAR DIATOMIC MOLECULES

Consider when two sets of p orbitals come together and overlap to form  $\sigma$  and  $\pi$  bonds.



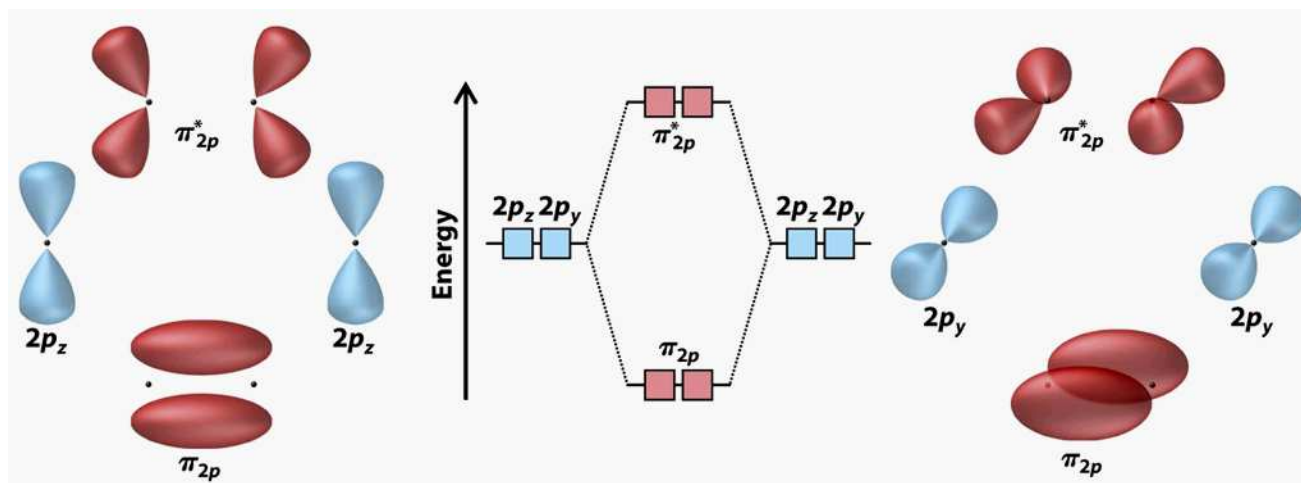
$2p_x$  atomic orbitals  $\rightarrow$  2 new molecular orbitals: bonding  $\sigma_{2p}$  and antibonding  $\sigma_{2p}^*$



- Because the lower MO results from **direct overlap**, it is called a **bonding  $\sigma_{2p}$**  MO.
  - A **bonding MO is lower in energy** than the original atomic orbitals.
- A node between the nuclei in the upper MO results in an **antibonding  $\sigma_{2p}^*$**  MO.
  - An **antibonding MO is higher in energy** than the original atomic orbitals.

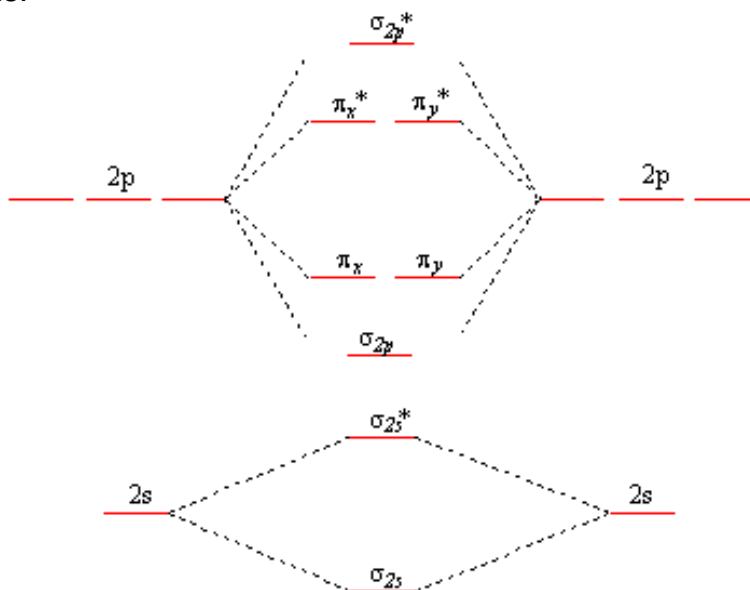
$2p_z$  and  $2p_y$  atomic orbitals  $\rightarrow$  4 new MOs: two bonding  $\pi_{2p}$  and two antibonding  $\pi_{2p}^*$ ,

which are each offset from the  $2p_x$  MOs and one another by  $90^\circ$ .



- Because the lower MO results from **indirect overlap**, it is called a **bonding  $\pi_{2p}$**  MO.
  - A **bonding MO is lower in energy** than the original atomic orbitals.
- A node between the nuclei in the upper MO results in a **antibonding  $\pi_{2p}^*$**  MO.
  - An **antibonding MO is higher in energy** than the original atomic orbitals.

The following molecular orbital diagram shows the energy levels resulting from two sets of 2s and 2p atomic orbitals:



- Because of the **direct (or head-on) overlap** in the **bonding  $\sigma_{2p}$** , the interaction between the  $2p_x$  molecular orbitals is stronger than in the  $2p_x$  and  $2p_y$ , so the **bonding  $\sigma_{2p}$**  is lower in energy than either of the **bonding  $\pi_{2p}$**  molecular orbitals.

Ex. 1: Write the electron configurations (using core notation) for N and O.

Electron Configuration for N: \_\_\_\_\_

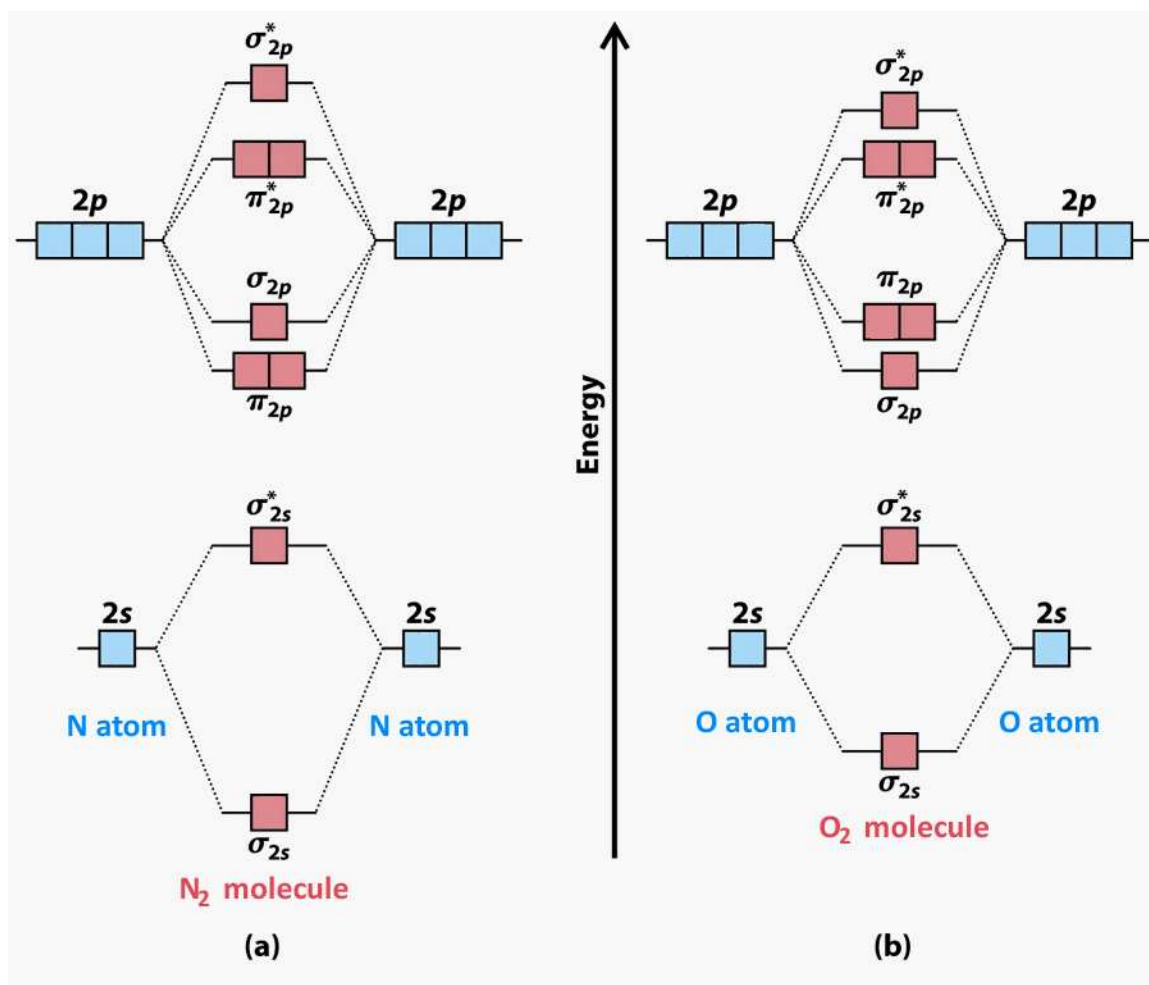
Electron Configuration for O: \_\_\_\_\_

Ex. 2: Draw the atomic orbital diagrams for the valence electrons in N and O below:

atomic orbital diagram for N

atomic orbital diagram for O

Ex. 3: Fill in the MO diagrams for N<sub>2</sub> and O<sub>2</sub> below using the atomic orbital diagrams drawn for each N and O atom in Ex. 2.



Ex. 4: How does the MO diagram for O<sub>2</sub> explain what happens when liquid O<sub>2</sub> is poured between the poles of a strong magnet?

Ex. 5: Write the electron configurations for  $N_2$  and  $O_2$  below:

$N_2$ : \_\_\_\_\_

$O_2$ : \_\_\_\_\_

Ex. 6: Calculate the bond orders for  $N_2$  and  $O_2$ .

### 9.5 COMBINING THE LOCALIZED ELECTRON AND MOLECULAR ORBITAL MODELS (TO EXPLAIN RESONANCE)

1a. Draw the resonance structures for the ozone molecule,  $O_3$ .

resonance structures

Sketch of molecule

b.  $O_3$ 's shape is \_\_\_\_\_ and its bond angle is \_\_\_\_\_.  
Sketch the molecule above.

c. Given  $O_3$ 's shape, the central atom in  $O_3$  must have \_\_\_\_\_ atomic hybrid orbitals.

d. Electron configuration for O (using core notation): \_\_\_\_\_

e. Draw the ground state atomic orbital  
diagram for the valence electrons in O:

- f. Show the atomic orbital diagrams for the hybridization of orbitals in the central O atom:  
(Note: The central O atom has a pair of electrons in the unhybridized p orbital.)

hybridization  
—————→

atomic orbital diagram before hybridizing

atomic orbital diagram after hybridizing

- g. Sketch the 3D ball-and-stick arrangement of the three O atoms in  $O_3$  then draw the molecular orbitals containing the delocalized electrons.

2a. Draw the resonance structures for **carbonate ion**,  $CO_3^{2-}$ .

resonance structure

Sketch of molecule

- b.  $\text{CO}_3^{2-}$ 's shape is \_\_\_\_\_ and its bond angles are \_\_\_\_\_.
- c. Sketch the molecule above.
- d. Sketch the 3D arrangement of atoms in the **carbonate ion**,  $\text{CO}_3^{2-}$  using ball-and-stick representations, then draw the following:
- The atomic hybrid orbitals for the C atom
  - The unhybridized p orbitals for the C atom and the three outer O atoms and the resulting MOs holding the delocalized electrons—i.e., electrons shared by all four atoms.
  - Indicate  $\sigma$  and  $\pi$  bonds in the polyatomic ion.