

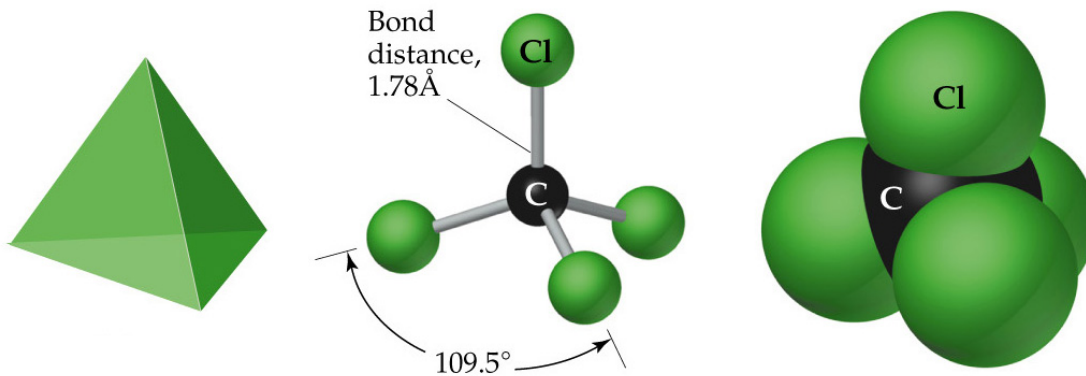
# Chapter 9

## Molecular Geometry and Bonding Theories

- How to describe **molecular geometries**
- Molecular shapes - the **VSEPR** model
- **Polar vs nonpolar** molecules
- Why molecules form bonds and have the shapes they do – **valence-bond theory**
- Overlap of atomic orbitals – **sigma bonds** and **pi bonds**
- **Hybridization** of atomic orbitals
- Electronic structure of molecules – **molecular orbital theory**

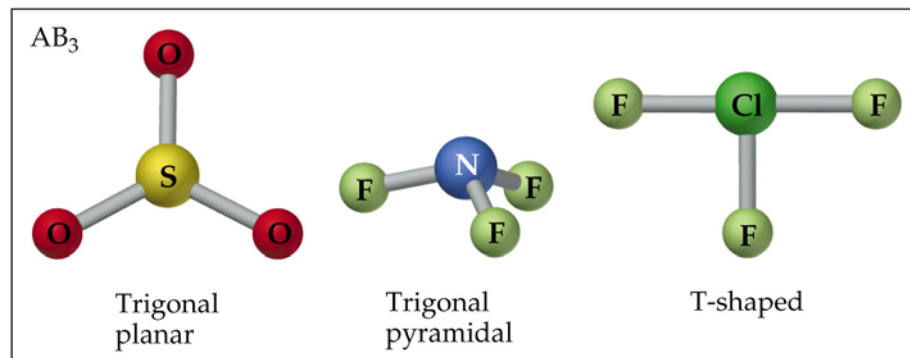
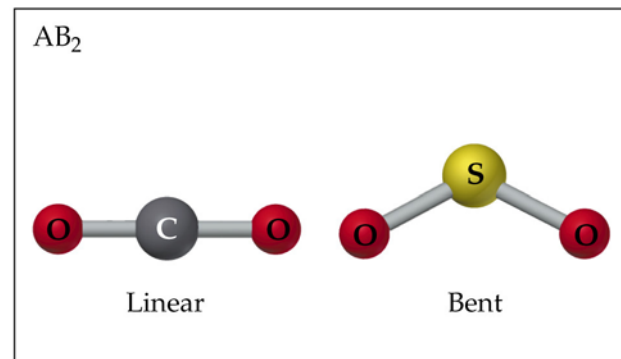
# Molecular Shapes

- **Lewis structures** give atomic connectivity: they tell us **which atoms are physically connected** to which.
- The **shape** of a molecule is determined by its **bond angles**.
- Consider **CCl<sub>4</sub>**: experimentally we find all **Cl-C-Cl bond angles are 109.5°**.
- Therefore, the molecule **cannot be planar** and all Cl atoms are located at the vertices of a **tetrahedron** with the C at its center.



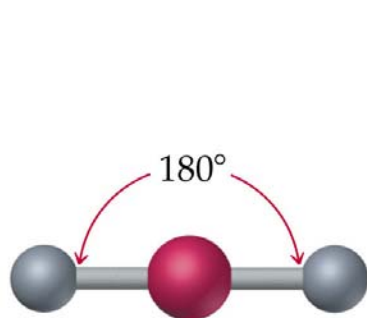
# Molecular Shapes

- In order to **predict molecular shape**, we assume the **valence electrons repel** each other. Therefore, the molecule adopts 3D geometry to **minimize this repulsion**.
- We call this process **Valence Shell Electron Pair Repulsion (VSEPR)** theory.
- There are **simple shapes** for **AB<sub>2</sub>** and **AB<sub>3</sub>** molecules.

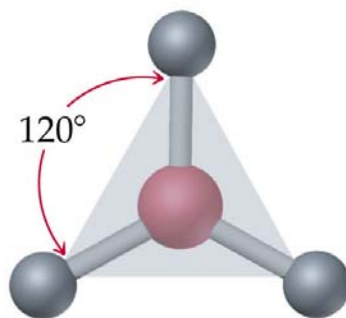


# Molecular Shapes

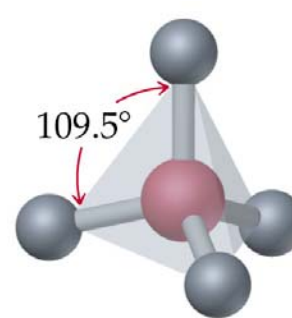
- There are **five fundamental geometries** for molecular shape:



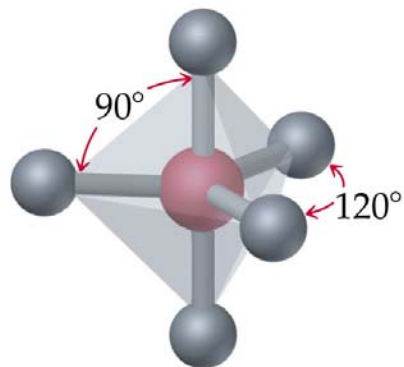
Linear



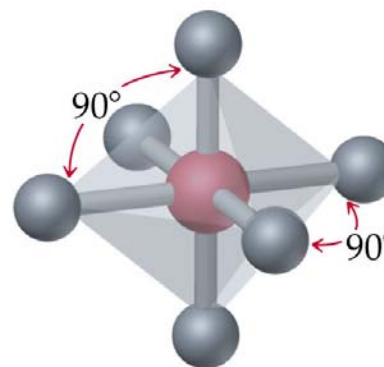
Trigonal planar



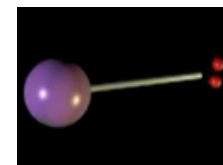
Tetrahedral



Trigonal bipyramidal

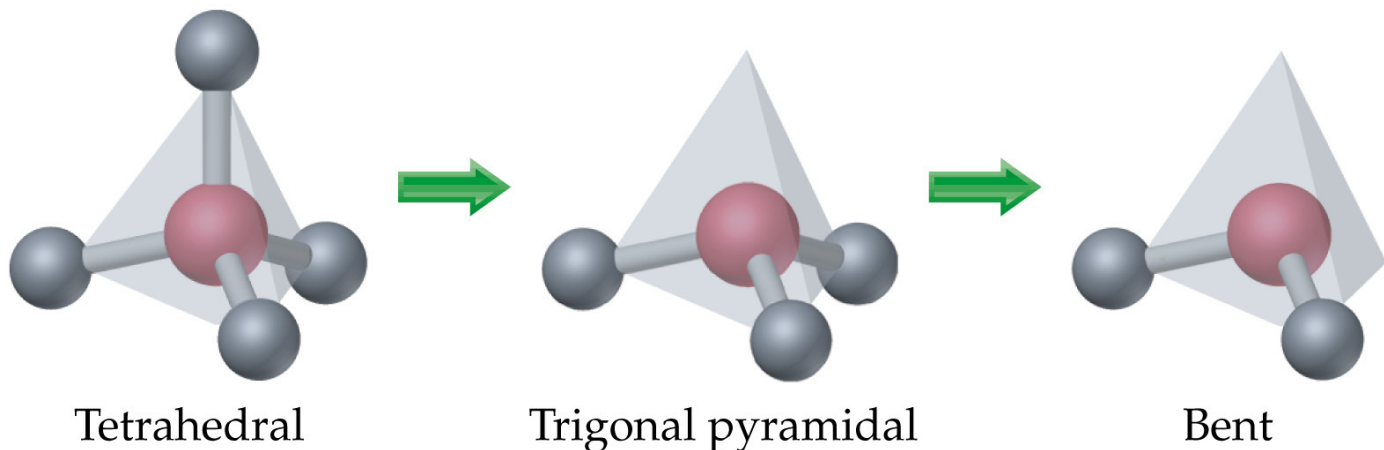


Octahedral



# Molecular Shapes

- When **considering the geometry** about the central atom, we **consider all electrons** (lone pairs and bonding pairs).
- When **naming the molecular geometry**, we focus only on the **positions of the atoms**.
- **Additional molecular shapes** can be obtained by **removing corner atoms** from the basic geometries.

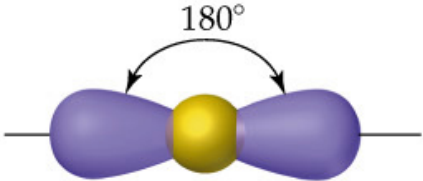
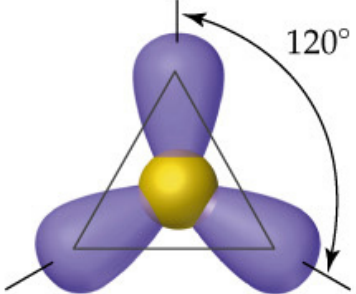
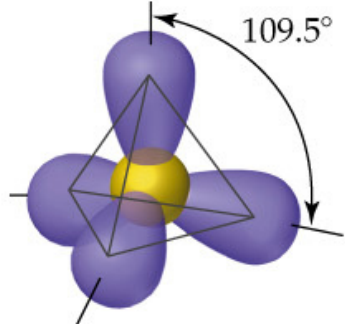


# VSEPR Model

- To **determine the shape** of a molecule, we **do not distinguish between lone pairs** (nonbonding) of electrons **and bonding pairs**.
- **Regions** where these electrons are most likely to be found are called **electron domains**.
- We define the **electron domain geometry** by the positions in 3D space of **ALL electron pairs** (bonding or non-bonding).
- The electrons adopt an arrangement in space to **minimize e<sup>-</sup>-e<sup>-</sup> repulsion**.

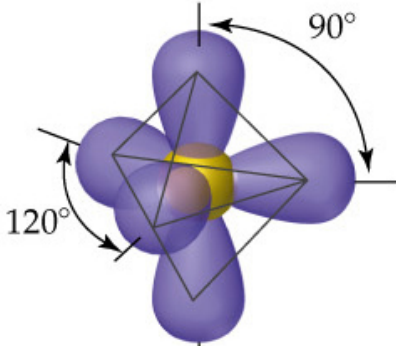
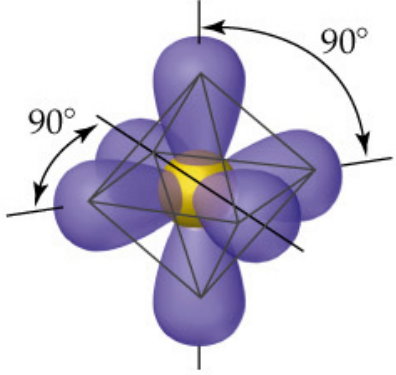
# VSEPR Model

TABLE 9.1 Electron-Domain Geometries as a Function of the Number of Electron Domains

Number of Electron Domains	Arrangement of Electron Domains	Electron-Domain Geometry	Predicted Bond Angles
2		Linear	$180^\circ$
3		Trigonal planar	$120^\circ$
4		Tetrahedral	$109.5^\circ$

# VSEPR Model

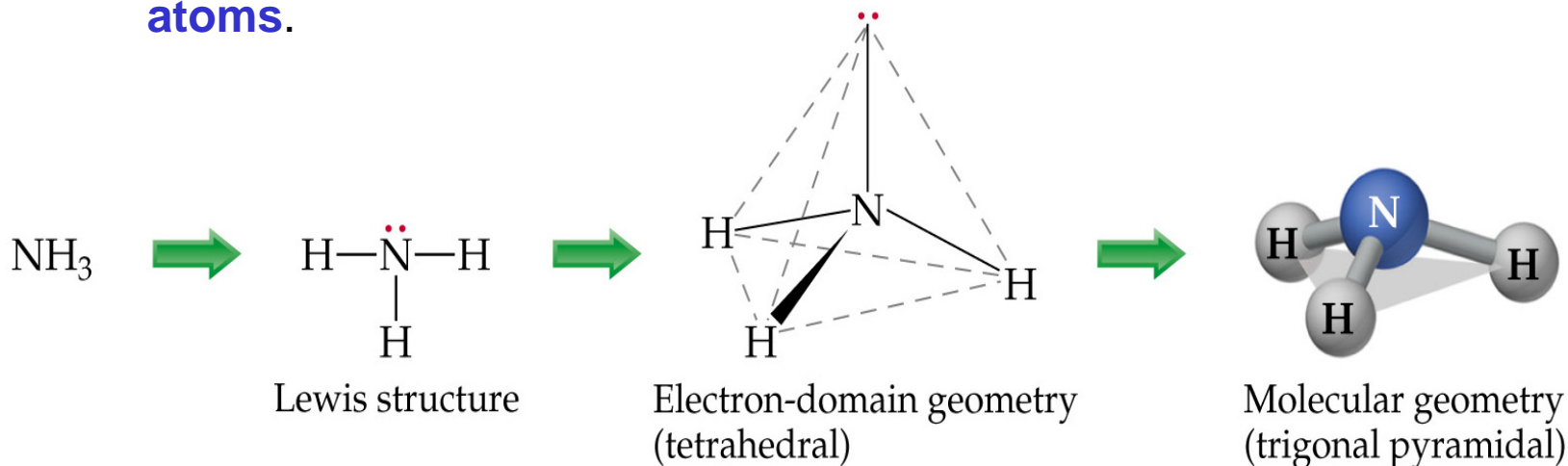
TABLE 9.1 Electron-Domain Geometries as a Function of the Number of Electron Domains

Number of Electron Domains	Arrangement of Electron Domains	Electron-Domain Geometry	Predicted Bond Angles
5		Trigonal bipyramidal	120° 90°
6		Octahedral	90°



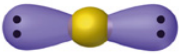

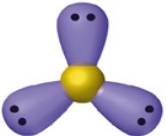
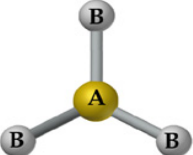
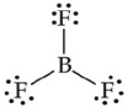
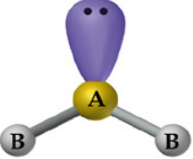
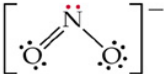
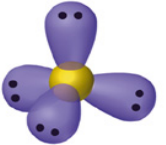
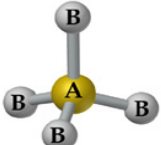
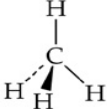
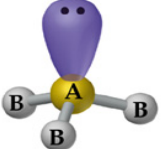
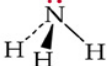
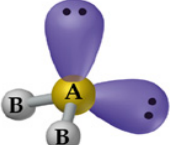

# VSEPR Model

- To determine the **electron-domain** and **molecular geometries**:
  - Draw the **Lewis structure**.
  - Count the **total number of electron domains** around the **central atom** (non-bonding pair, single bond, or multiple bond).
  - Determine **electron-domain geometry** by arranging the **electron domains** to **minimize e<sup>-</sup>e<sup>-</sup> repulsion**.
  - Determine the **molecular geometry** by the arrangement of the **bonded atoms**.



# VSEPR Model

TABLE 9.2 Electron-Domain Geometries and Molecular Shapes for Molecules with Two, Three, and Four Electron Domains Around the Central Atom

Number of Electron Domains	Electron-Domain Geometry	Bonding Domains	Nonbonding Domains	Molecular Geometry	Example
2	 Linear	2	0	 Linear	$\ddot{\text{O}}=\text{C}=\ddot{\text{O}}$
3	 Trigonal planar	3	0	 Trigonal planar	
		2	1	 Bent	
4	 Tetrahedral	4	0	 Tetrahedral	
		3	1	 Trigonal pyramidal	
		2	2	 Bent	

# VSEPR Model

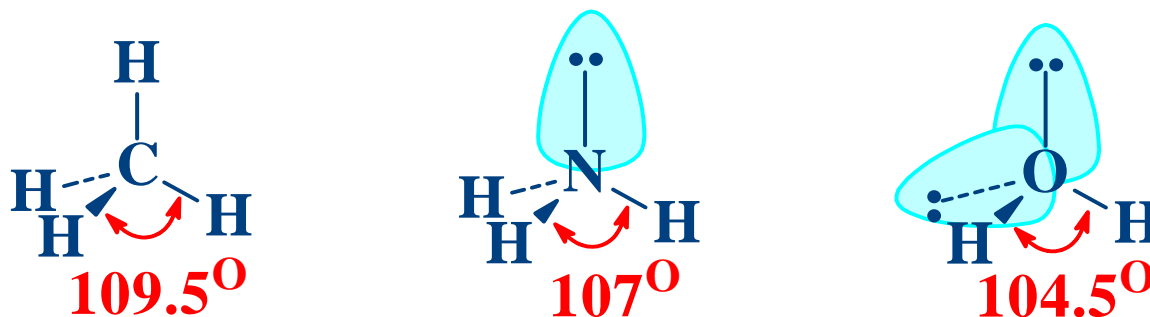
## The Effect of Nonbonding Electrons and Multiple Bonds on Bond Angles

- Determine the **electron domain** geometry only by looking at **electrons**.
- Name the **molecular geometry** by the positions of **atoms**.
- **Ignore lone pairs** in the **molecular geometry**.
- All the atoms that obey the **octet rule** have **tetrahedral** electron domain geometries.

# VSEPR Model

## The Effect of Nonbonding Electrons and Multiple Bonds on Bond Angles

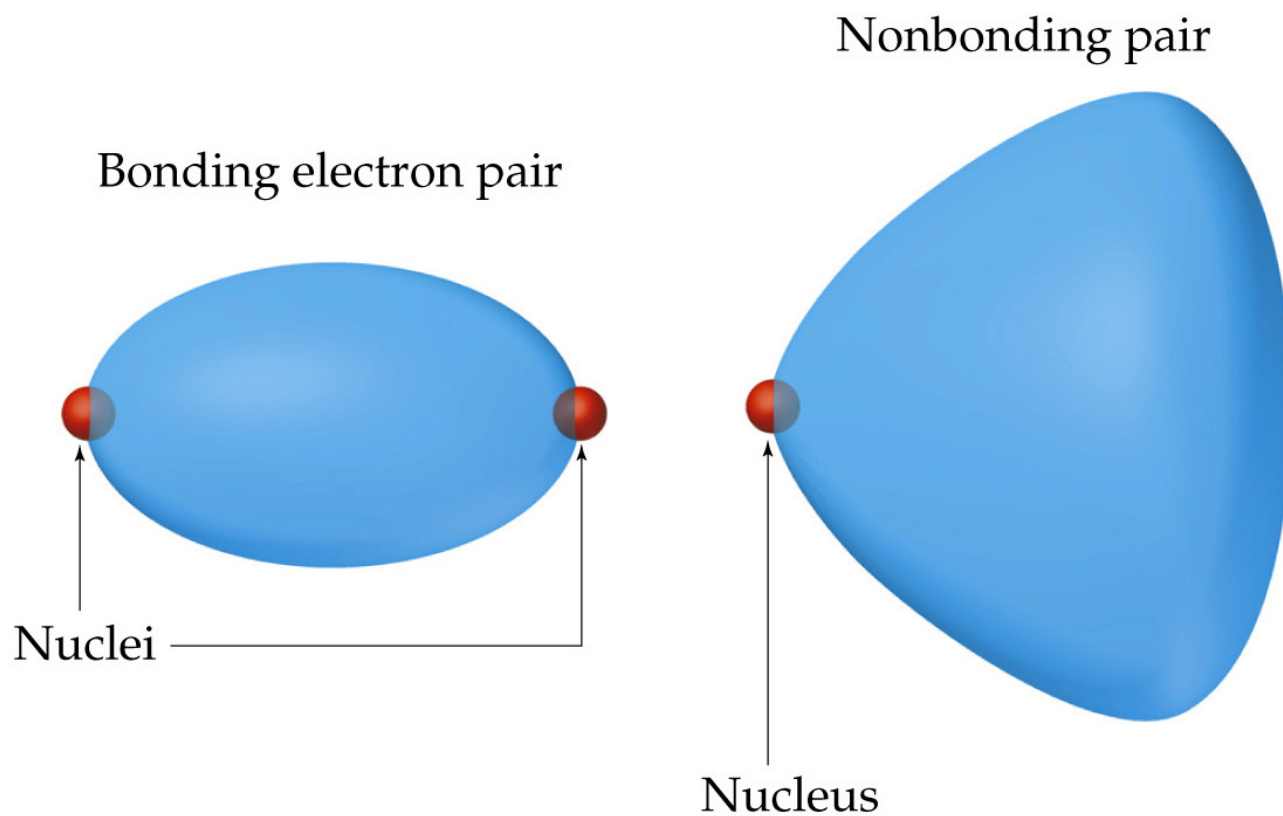
- By **experiment**, the H-X-H bond angle decreases on moving from C to N to O:



- Since electrons in a bond are attracted by two nuclei, they **do not repel as much as lone pairs**.
- Therefore, the **bond angle decreases** as the number of **lone pairs increase**.

# VSEPR Model

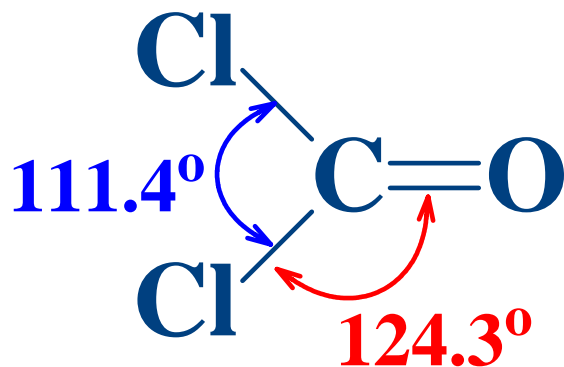
## The Effect of Nonbonding Electrons and Multiple Bonds on Bond Angles



# VSEPR Model

## The Effect of Nonbonding Electrons and Multiple Bonds on Bond Angles

- Similarly, electrons in **multiple bonds** repel more than electrons in single bonds.



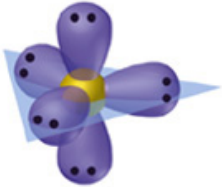
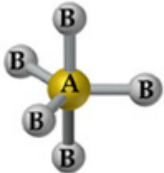
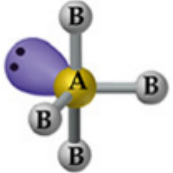
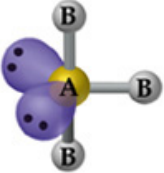
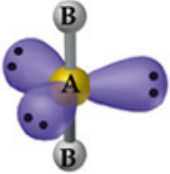
# VSEPR Model

## Molecules with Expanded Valence Shells

- Atoms that have **expanded octets** have **AB<sub>5</sub>** (trigonal bipyramidal) or **AB<sub>6</sub>** (octahedral) electron domain geometries.
- For **trigonal bipyramidal** structures there is a plane containing three electron pairs. The fourth and fifth electron pairs are located above and below this plane.
- For **octahedral structures**, there is a plane containing four electron pairs. Similarly, the fifth and sixth electron pairs are located above and below this plane.

# VSEPR Model

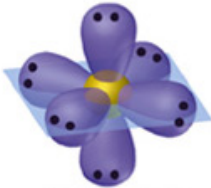
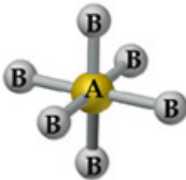
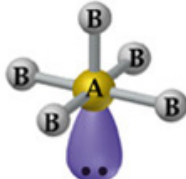
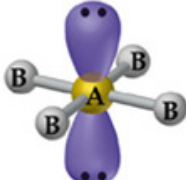
TABLE 9.3 Electron-Domain Geometries and Molecular Shapes for Molecules with Five and Six Electron Domains Around the Central Atom

Total Electron Domains	Electron-Domain Geometry	Bonding Domains	Nonbonding Domains	Molecular Geometry	Example
5	 <p>Trigonal bipyramidal</p>	5	0	 <p>Trigonal bipyramidal</p>	$\text{PCl}_5$
		4	1	 <p>Seesaw</p>	$\text{SF}_4$
		3	2	 <p>T-shaped</p>	$\text{ClF}_3$
		2	3	 <p>Linear</p>	$\text{XeF}_2$



# VSEPR Model

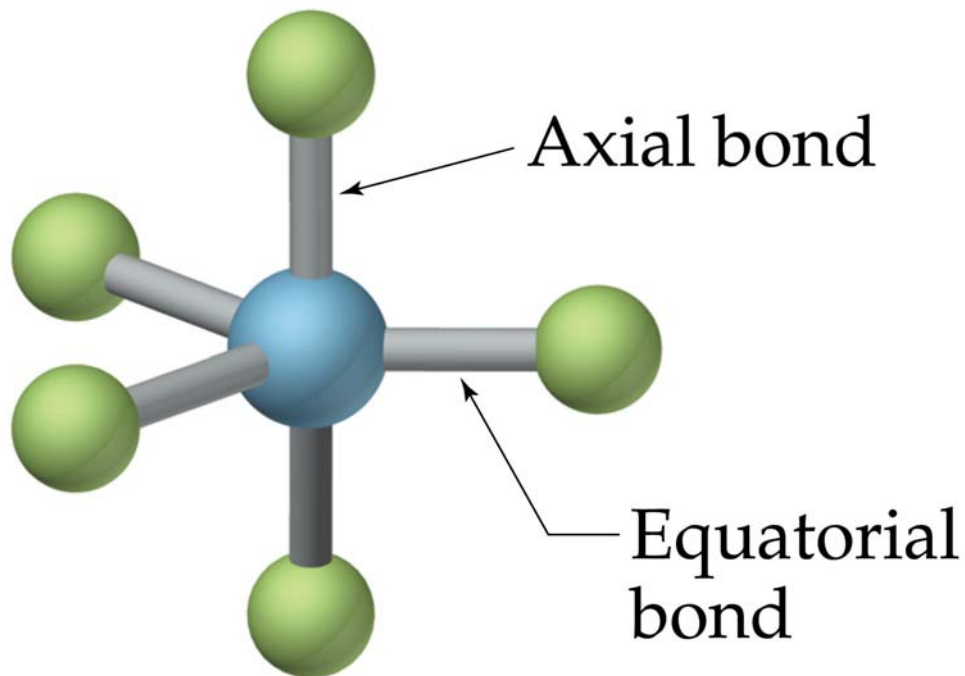
TABLE 9.3 Electron-Domain Geometries and Molecular Shapes for Molecules with Five and Six Electron Domains Around the Central Atom

Total Electron Domains	Electron-Domain Geometry	Bonding Domains	Nonbonding Domains	Molecular Geometry	Example
6	 <p>Octahedral</p>	6	0	 <p>Octahedral</p>	$\text{SF}_6$
		5	1	 <p>Square pyramidal</p>	$\text{BrF}_5$
		4	2	 <p>Square planar</p>	$\text{XeF}_4$

# VSEPR Model

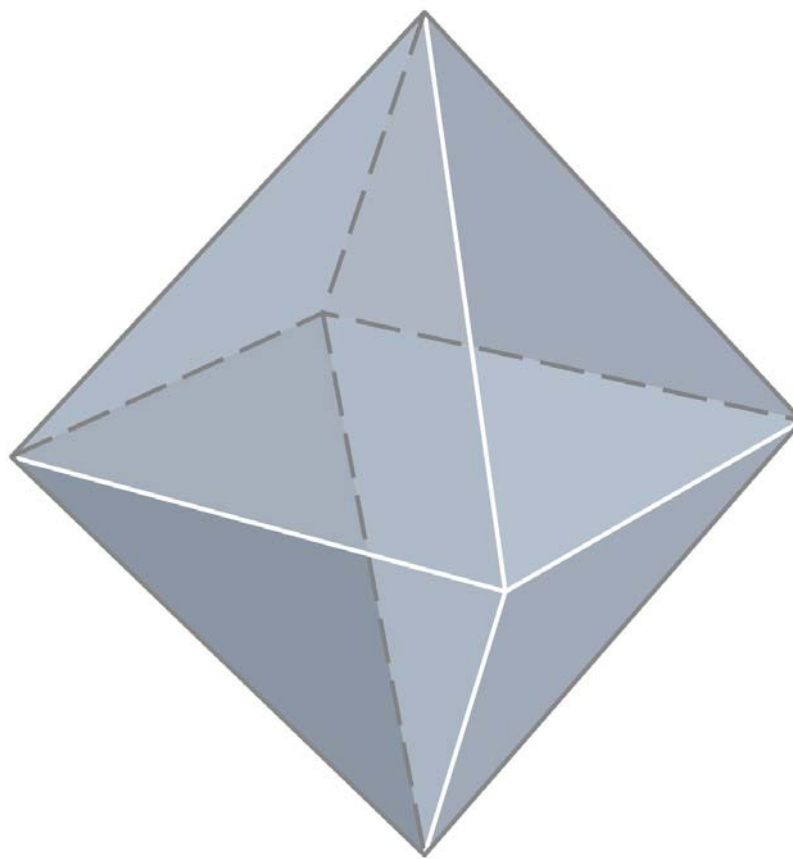
## Molecules with Expanded Valence Shells

- To minimize e<sup>-</sup>-e<sup>-</sup> repulsion, **lone pairs** are always placed in **equatorial positions**.



# VSEPR Model

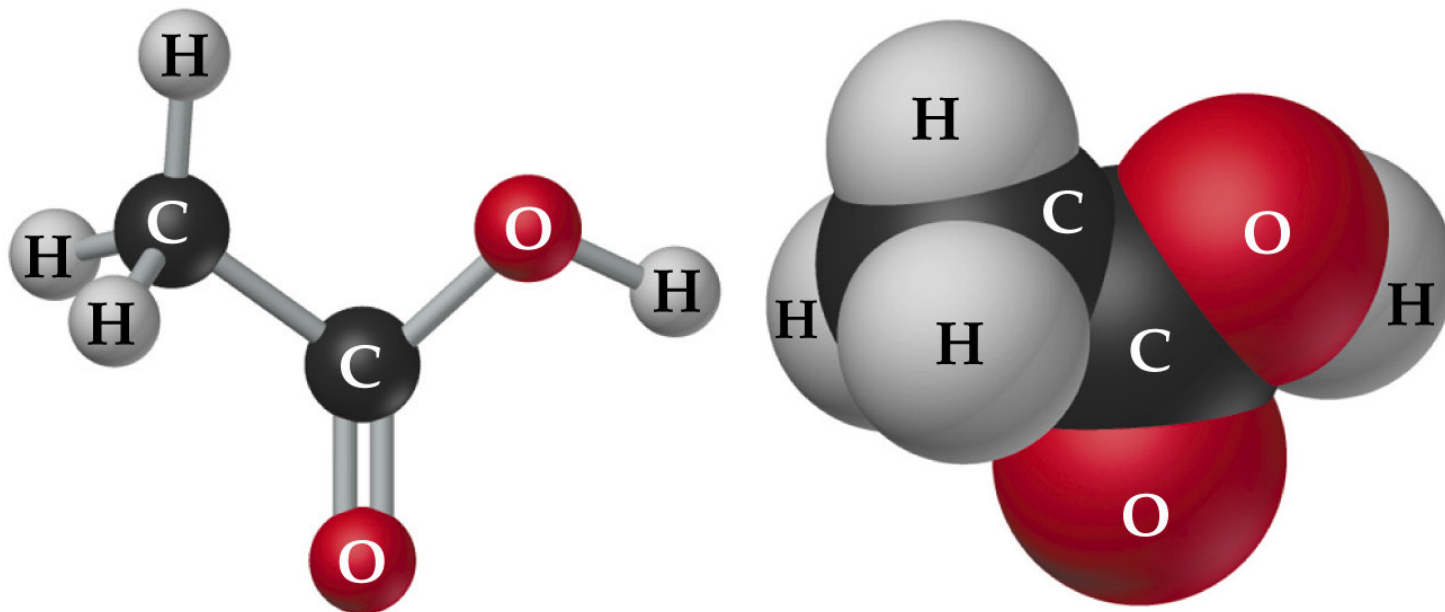
## Molecules with Expanded Valence Shells



# VSEPR Model

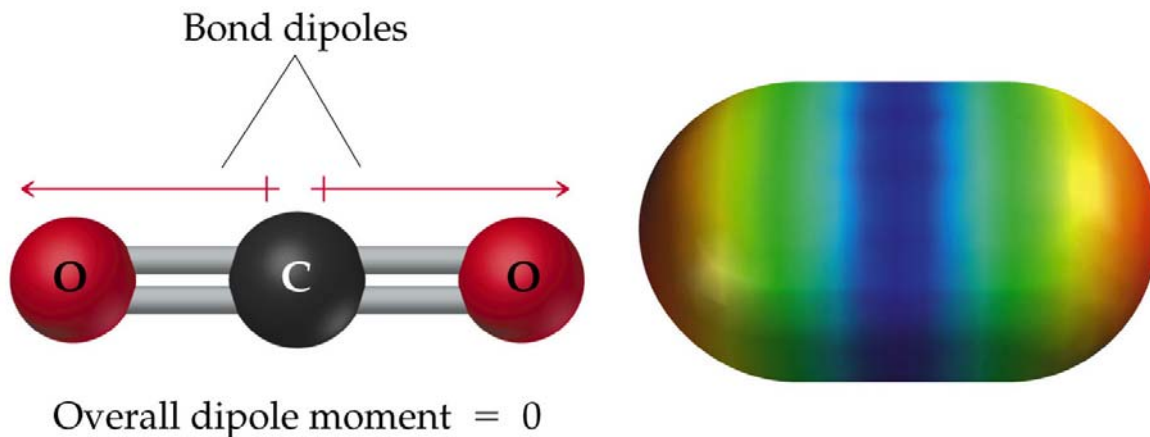
## Shapes of Larger Molecules

- In **acetic acid**,  $\text{CH}_3\text{COOH}$ , there are **three central atoms**.
- We assign the geometry about **each central atom separately**.



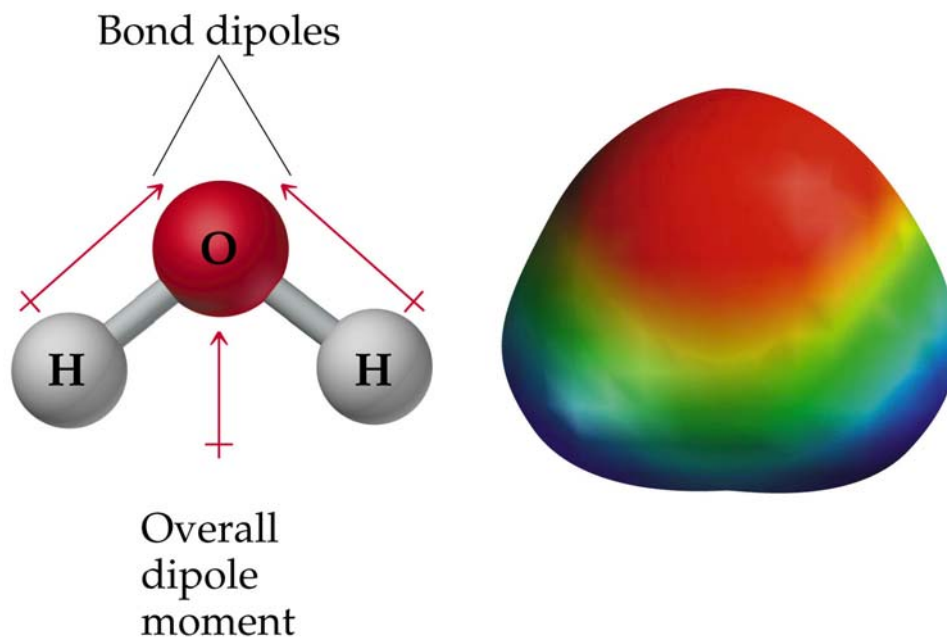
# Molecular Shape and Molecular Polarity

- When there is a **difference in electronegativity** between two atoms, then the bond between them is **polar**.
- It is possible for a molecule to **contain polar bonds**, but not be **polar**.
- For example, the **bond dipoles in CO<sub>2</sub> cancel** each other because CO<sub>2</sub> is linear.



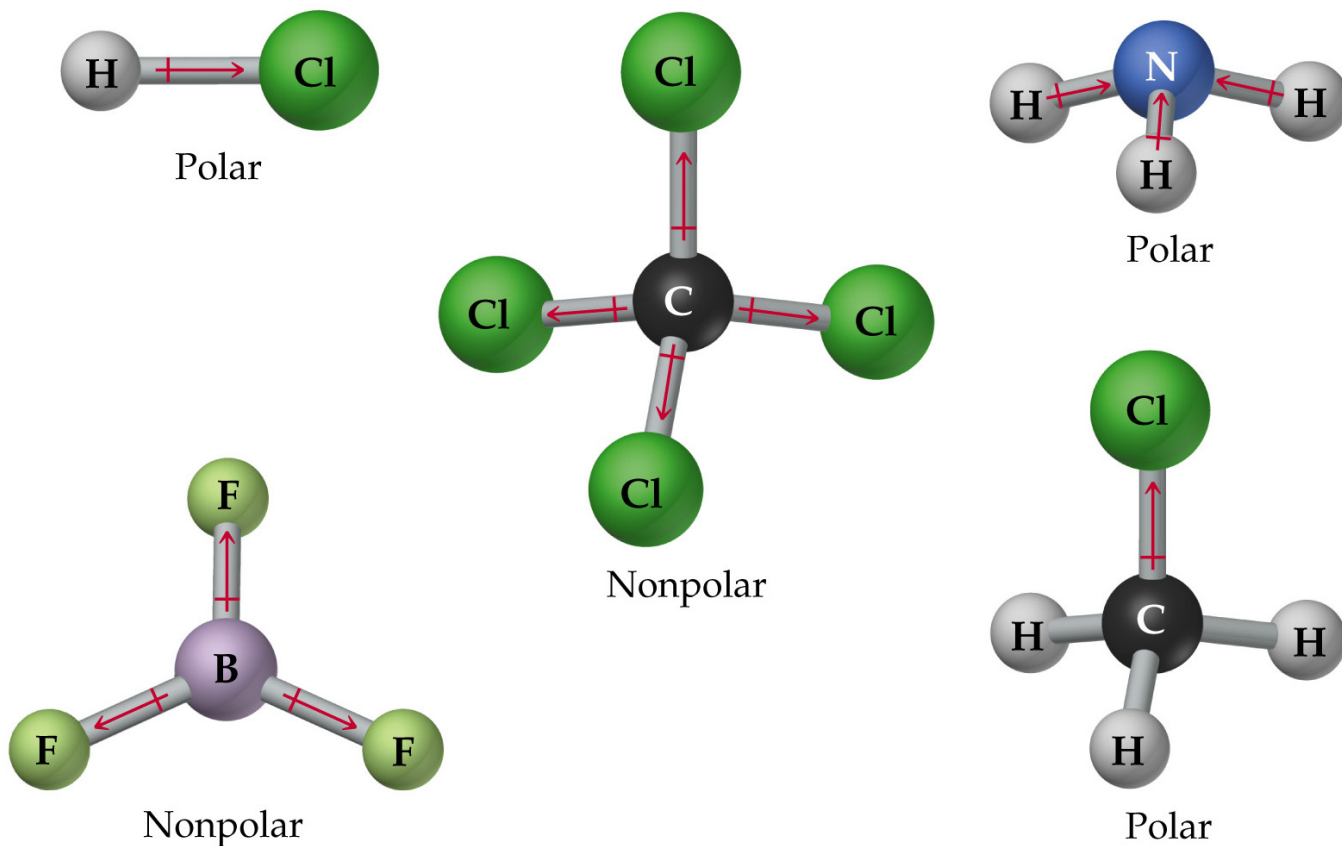
# Molecular Shape and Molecular Polarity

- In **water**, the molecule is not linear and the bond dipoles **do not cancel** each other.
- Therefore, water is a **polar molecule**.



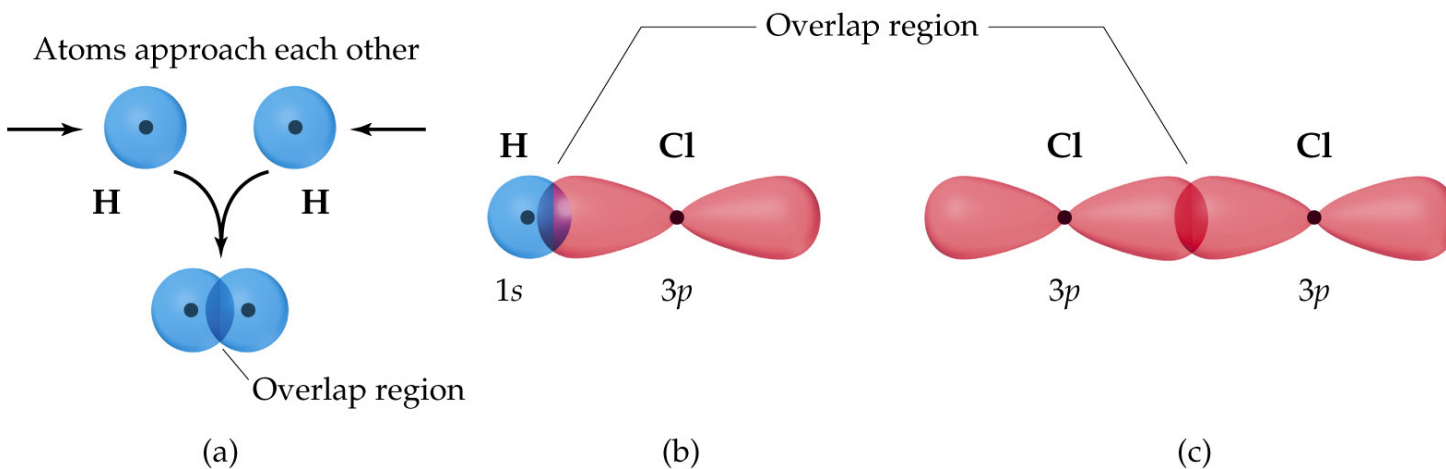
# Molecular Shape and Molecular Polarity

- The **overall polarity** of a molecule depends on its **molecular geometry**.



# Covalent Bonding and Orbital Overlap

- Lewis structures and VSEPR do not **explain why a bond forms**.
- How do we account for **shape** in terms of **quantum mechanics**?
- What are the orbitals that are **involved in bonding**?
- We use **Valence Bond Theory**:
  - **Bonds form** when orbitals on atoms **overlap**.
  - There are **two electrons of opposite spin** in the orbital overlap.



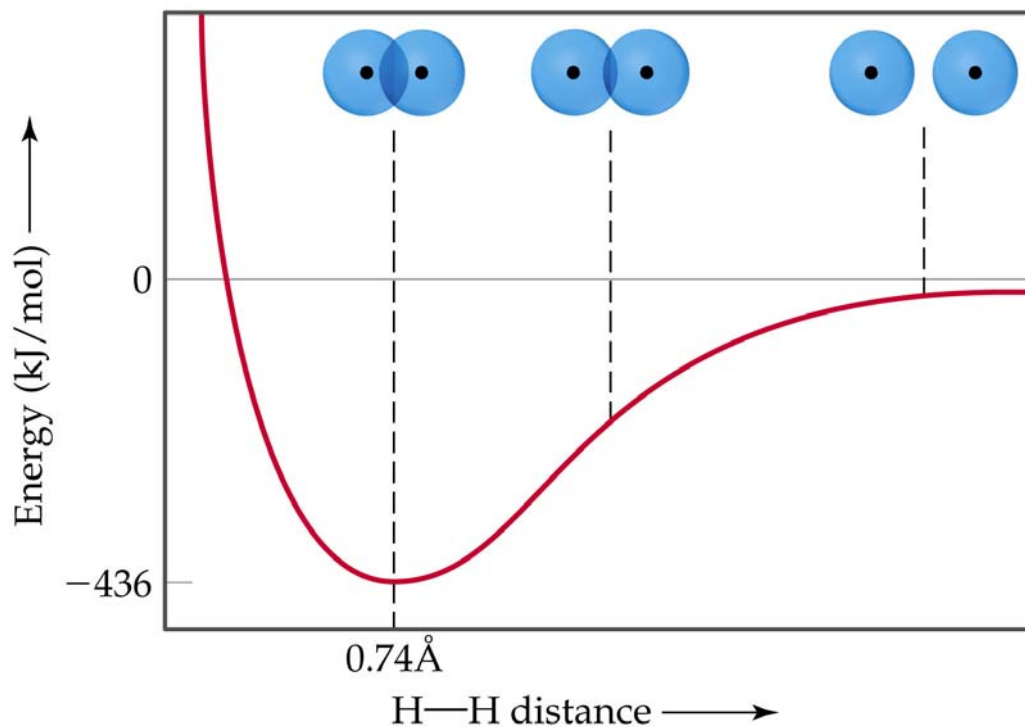


# Covalent Bonding and Orbital Overlap

- As two **nuclei approach** each other their **atomic orbitals overlap**.
- As the amount of overlap increases, the energy of the interaction decreases.
- At some distance the **minimum energy** is reached.
- The **minimum energy** corresponds to the **bonding distance** (or bond length).
- As the two atoms get closer, their nuclei begin to repel and the energy increases.

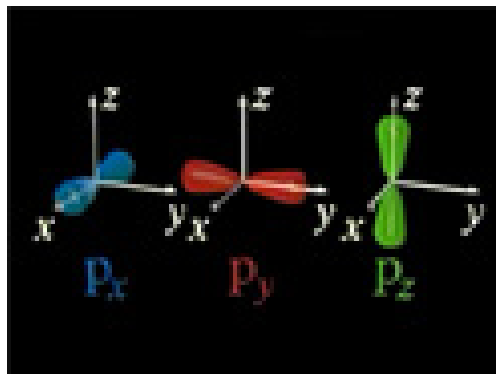
# Covalent Bonding and Orbital Overlap

- At the **bonding distance**, the **attractive forces** between nuclei and electrons just **balance** the **repulsive forces** (nucleus-nucleus, electron-electron).



# Hybrid Orbitals

- Atomic orbitals can **mix** or **hybridize** in order to adopt an **appropriate geometry** for bonding.
- **Hybridization** is determined by the **electron domain geometry**.



# Hybrid Orbitals

## sp Hybrid Orbitals

- Consider the **BeF<sub>2</sub>** molecule (experimentally known to exist):
  - Be has a **1s<sup>2</sup>2s<sup>2</sup>** electron configuration.
  - There is **no unpaired electron** available for bonding.
  - We conclude that the **atomic orbitals are not adequate** to describe orbitals in the molecule.
- We know that the **F-Be-F bond angle should be 180°** (VSEPR theory).
- We also know that **one electron from Be** is shared with each **one of the unpaired electrons from F**.

# Hybrid Orbitals

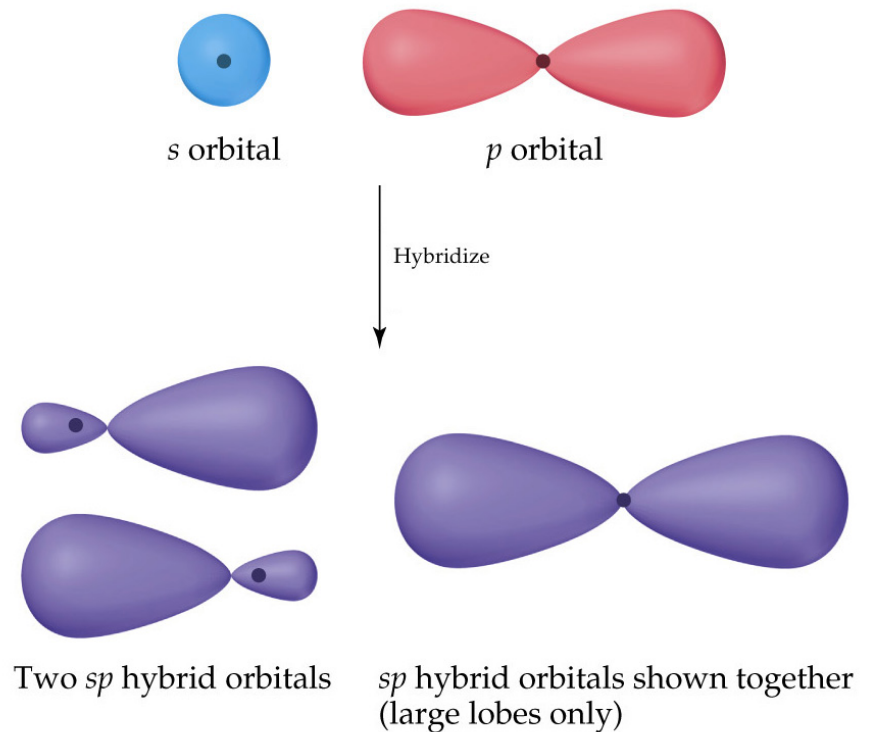
## sp Hybrid Orbitals

- We assume that the Be orbitals in the Be-F bond are **180° apart**.
- We could **promote an electron** from the 2s orbital on Be to the 2p orbital to **get two unpaired electrons** for bonding.
- BUT the **geometry** is still **not explained**.
- We can solve the problem by allowing the 2s and one 2p orbital on Be to mix or form a **hybrid orbital**.
- The hybrid orbital comes from an s and a p orbital and is called an **sp hybrid orbital**.

# Hybrid Orbitals

## sp Hybrid Orbitals

- The lobes of **sp hybrid orbitals** are  $180^\circ$  apart.
- Since only one of the Be  $2p$  orbitals has been used in hybridization, there are **two unhybridized  $p$  orbitals remaining** on Be.



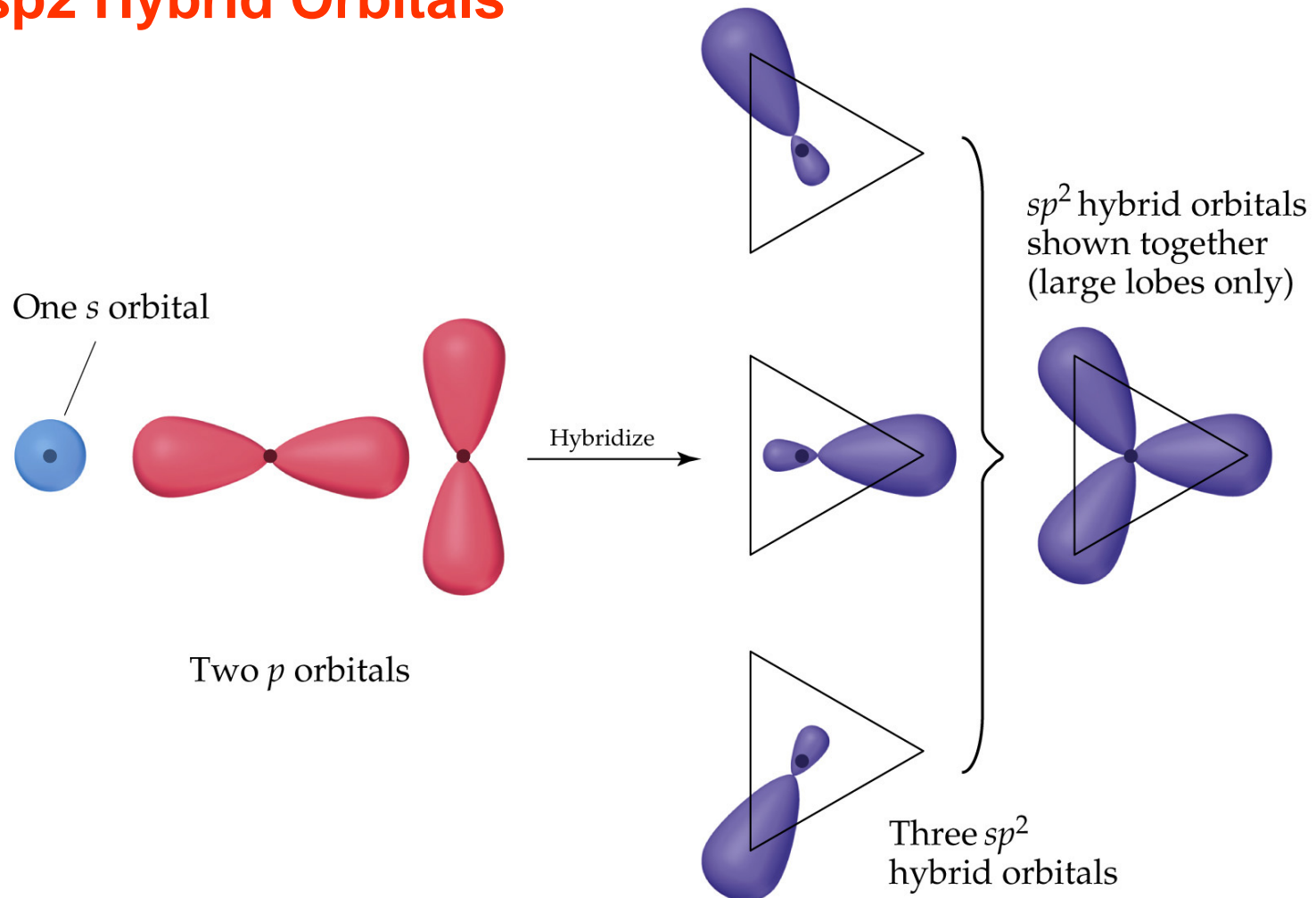
# Hybrid Orbitals

## $sp^2$ Hybrid Orbitals

- *Important:* when we mix  $n$  atomic orbitals we must get  $n$  hybrid orbitals.
- $sp^2$  hybrid orbitals are formed with one s and two p orbitals. (Therefore, there is one unhybridized p orbital remaining.)
- The large lobes of  $sp^2$  hybrids lie in a trigonal plane.
- All molecules with trigonal planar electron pair geometries have  $sp^2$  orbitals on the central atom.

# Hybrid Orbitals

## sp<sup>2</sup> Hybrid Orbitals

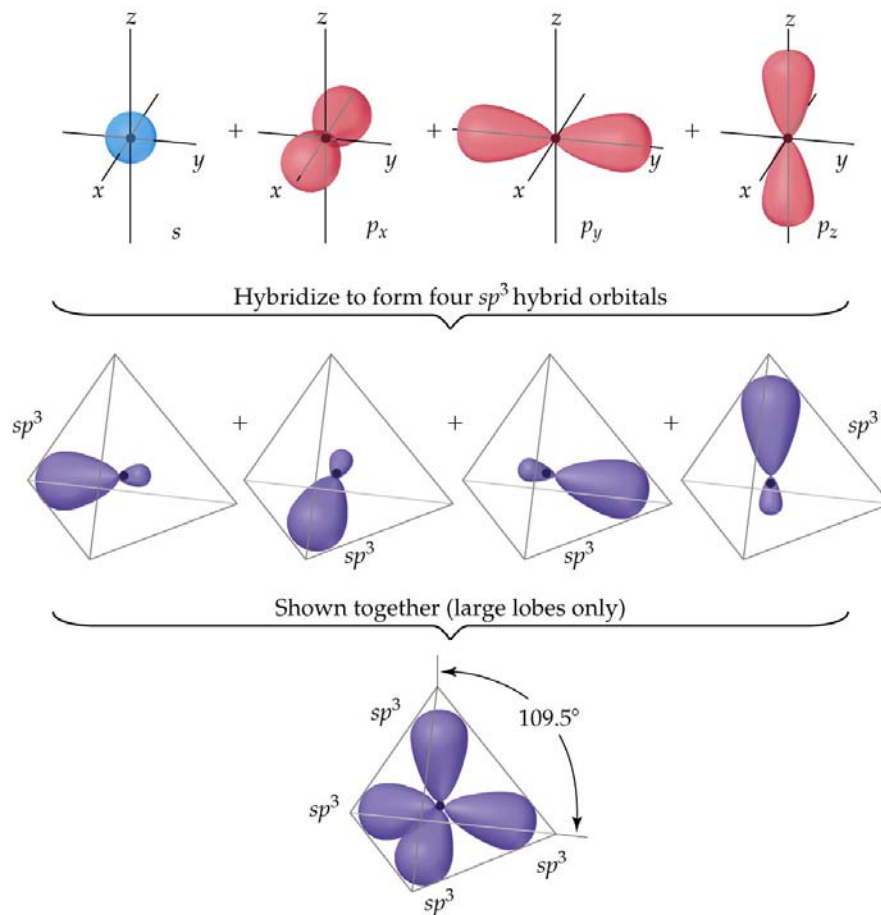




# Hybrid Orbitals

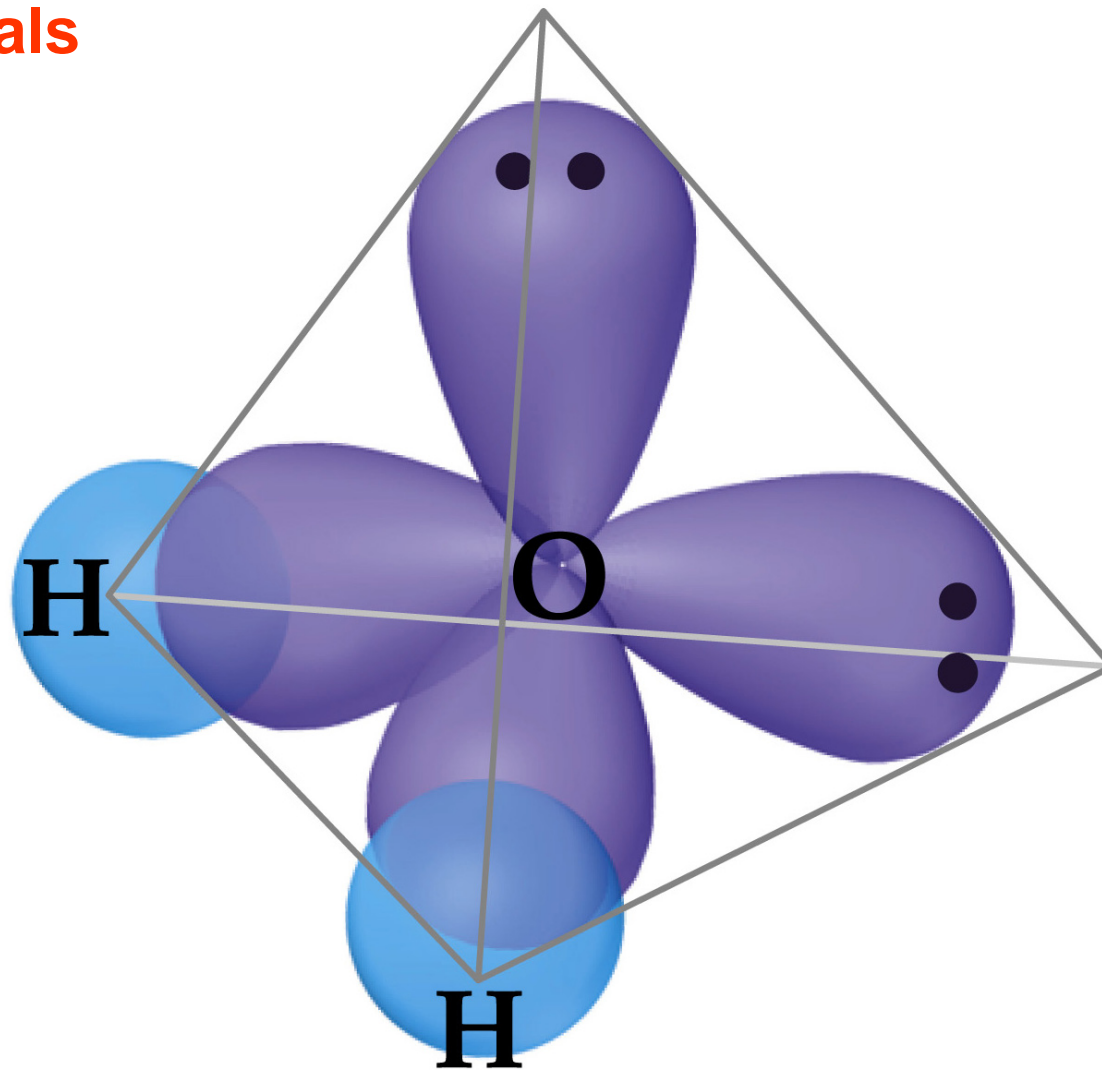
## $sp^3$ Hybrid Orbitals

- $sp^3$  Hybrid orbitals are formed from one  $s$  and three  $p$  orbitals.
- Therefore, there are **four large lobes**.
- Each lobe points towards a vertex of a **tetrahedron**.
- The **angle** between the large lobes is  **$109.5^\circ$** .
- All molecules with tetrahedral electron pair geometries are  $sp^3$  hybridized.



# Hybrid Orbitals

$sp^3$  Hybrid Orbitals

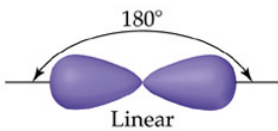
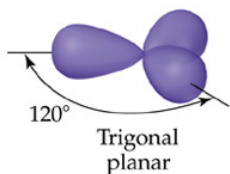
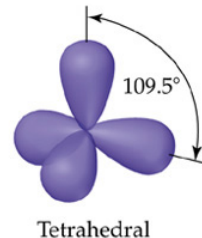
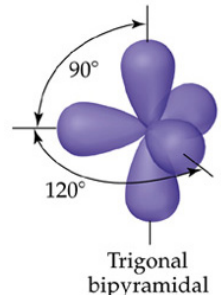
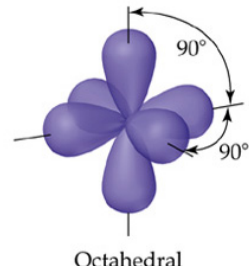


# Hybrid Orbitals

## Hybridization Involving d Orbitals

- Since there are only three  $p$ -orbitals, **trigonal bipyramidal** and **octahedral** electron domain geometries must **involve  $d$ -orbitals**.
- **Trigonal bipyramidal** electron domain geometries require  **$sp^3d$  hybridization**.
- **Octahedral** electron domain geometries require  **$sp^3d^2$  hybridization**.

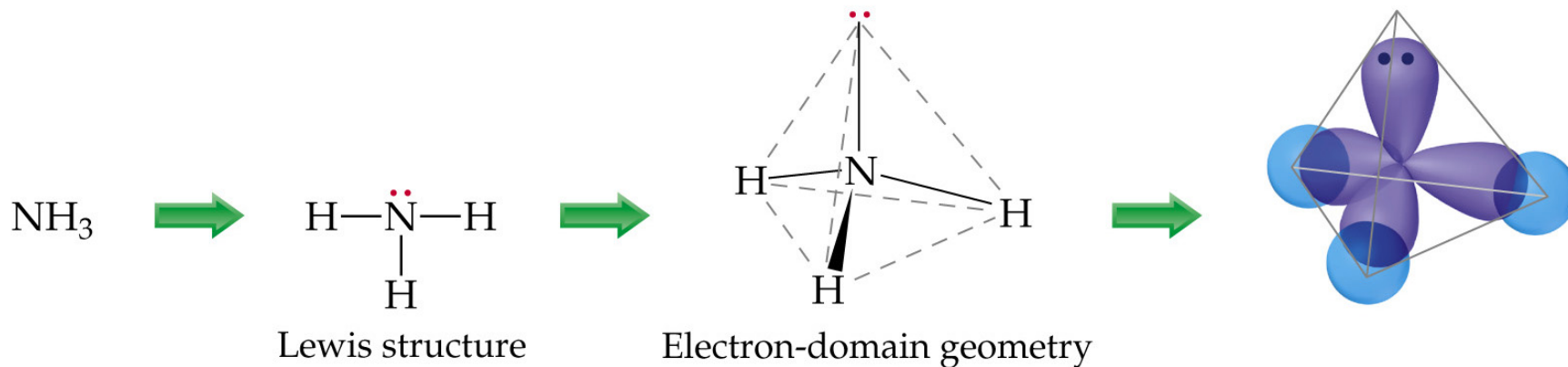
TABLE 9.4 Geometric Arrangements Characteristic of Hybrid Orbital Sets

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

# Hybrid Orbitals

## Predicting Hybrid Orbitals

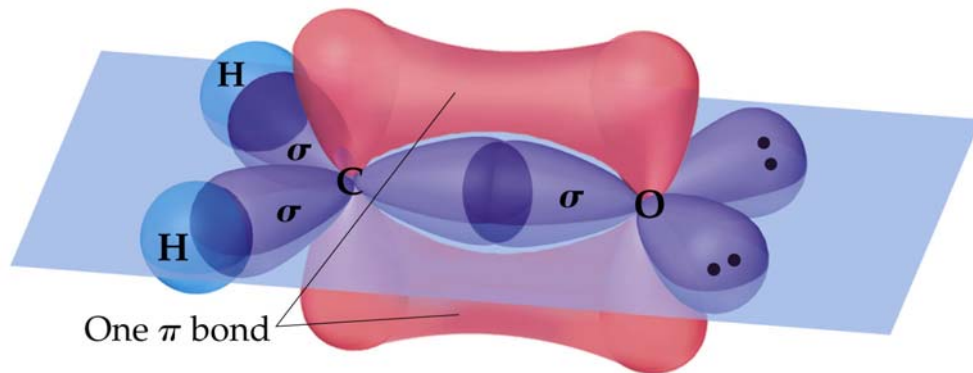
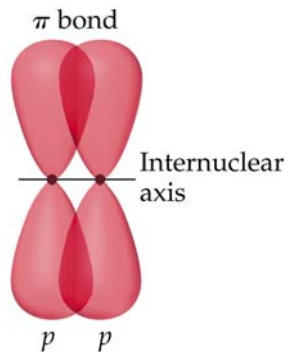
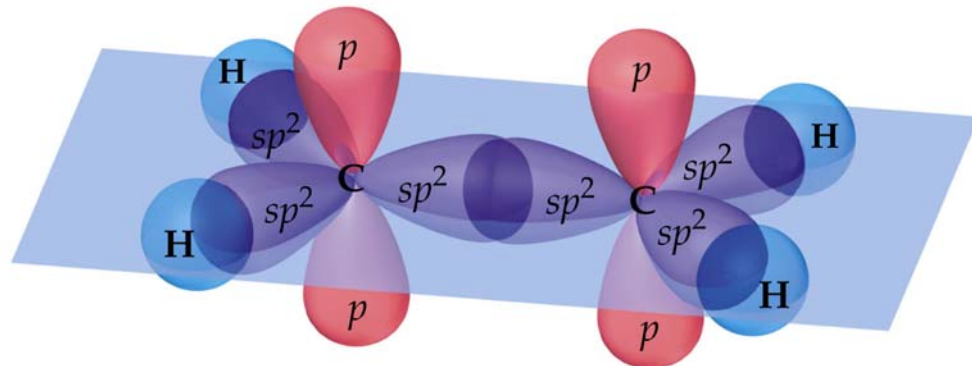
1. Draw the **Lewis structure**.
2. Determine the **electron domain geometry** with VSEPR.
3. Specify the **hybrid orbitals required** for the electron pairs based on the electron domain geometry (Table 9.4).



# Multiple Bonds

Ethylene,  $C_2H_4$ , has:

- **one  $\sigma$ - and one  $\pi$ -bond;**
- **both C atoms  $sp^2$  hybridized;**
- **both C atoms with trigonal planar electron domain and molecular geometries.**

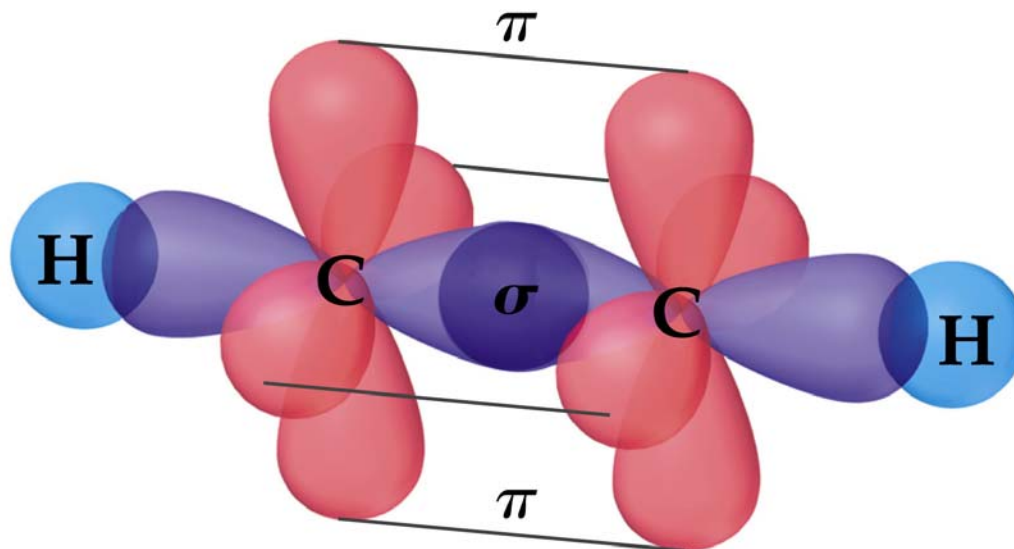


# Multiple Bonds

Consider **acetylene**,  $C_2H_2$

- the electron domain geometry of each C is **linear**;
- therefore, the C atoms are **sp hybridized**;
- the sp hybrid orbitals form the **C-C and C-H  $\sigma$ -bonds**;
- there are **two unhybridized p-orbitals**;
- both unhybridized p-orbitals form the **two  $\pi$ -bonds**;
- one  $\pi$ -bond is **above and below** the plane of the nuclei;
- one  $\pi$ -bond is **in front and behind** the plane of the nuclei.

# Multiple Bonds



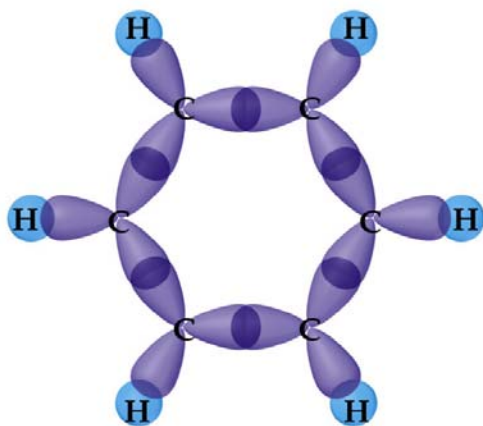
Acetylene, C<sub>2</sub>H<sub>2</sub>

**Note:** When triple bonds form (e.g. C<sub>2</sub>H<sub>2</sub> or N<sub>2</sub>), one π-bond is always above and below and the other is in front and behind the plane of the nuclei.

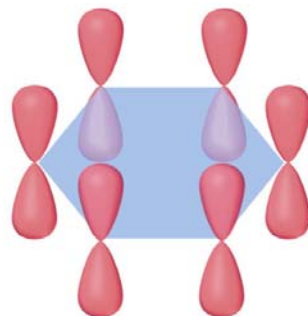
# Multiple Bonds

## Delocalized $\pi$ Bonding

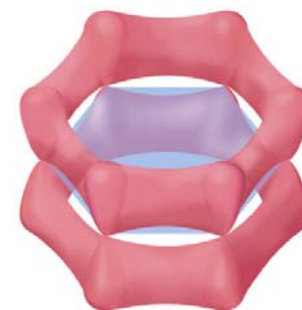
- So far all the bonds we have encountered are localized between two nuclei.
- In the case of **benzene**
  1. there are **6 C-C  $\sigma$  bonds**, **6 C-H  $\sigma$  bonds**,
  2. each C atom is  **$sp^2$  hybridized**,
  3. and there are **6 unhybridized  $p$  orbitals** on each C atom.



(a)  $\sigma$  bonds



(b)  $2p$  atomic orbitals



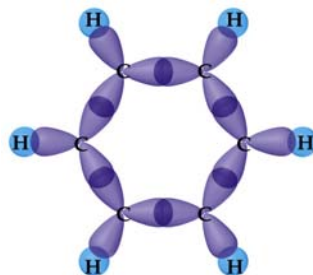
(c) Delocalized  $\pi$  bonds



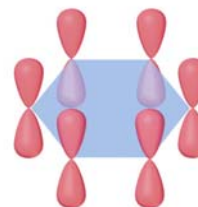
# Multiple Bonds

## Delocalized $\pi$ Bonding

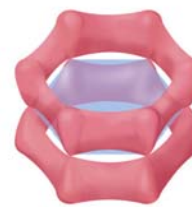
- In benzene there are **two options for the 3  $\pi$  bonds**:
  1. **localized** between C atoms or
  2. **delocalized** over the entire ring (i.e. the  $\pi$  electrons are **shared by all 6 C atoms**).
- Experimentally, **all C-C bonds** are the **same length** in benzene.
- Therefore, **all C-C bonds** are of the **same type** (recall single bonds are longer than double bonds).



(a)  $\sigma$  bonds



(b)  $2p$  atomic orbitals



(c) Delocalized  $\pi$  bonds

# Multiple Bonds

## General Conclusions

- Every two atoms share **at least 2 electrons**.
- Two electrons between atoms on the **same axis as the nuclei are  $\sigma$  bonds**.
- **$\sigma$ -Bonds** are always **localized**.
- If two atoms share **more than one pair** of electrons, the **second and third pair form  $\pi$ -bonds**.
- When **resonance** structures are possible, **delocalization** is also possible.

# Molecular Orbitals

- **Some aspects** of bonding are **not explained** by Lewis structures, VSEPR theory and hybridization (e.g., magnetic behavior and color).
- For these molecules, we use **Molecular Orbital (MO) Theory**.
- Just as electrons in atoms are found in **atomic orbitals**, electrons in molecules are found in **molecular orbitals**.
- Molecular orbitals:
  1. contain a maximum of **two electrons**;
  2. have **definite energies**;
  3. can be visualized with **contour diagrams**;
  4. are associated with an **entire molecule**.

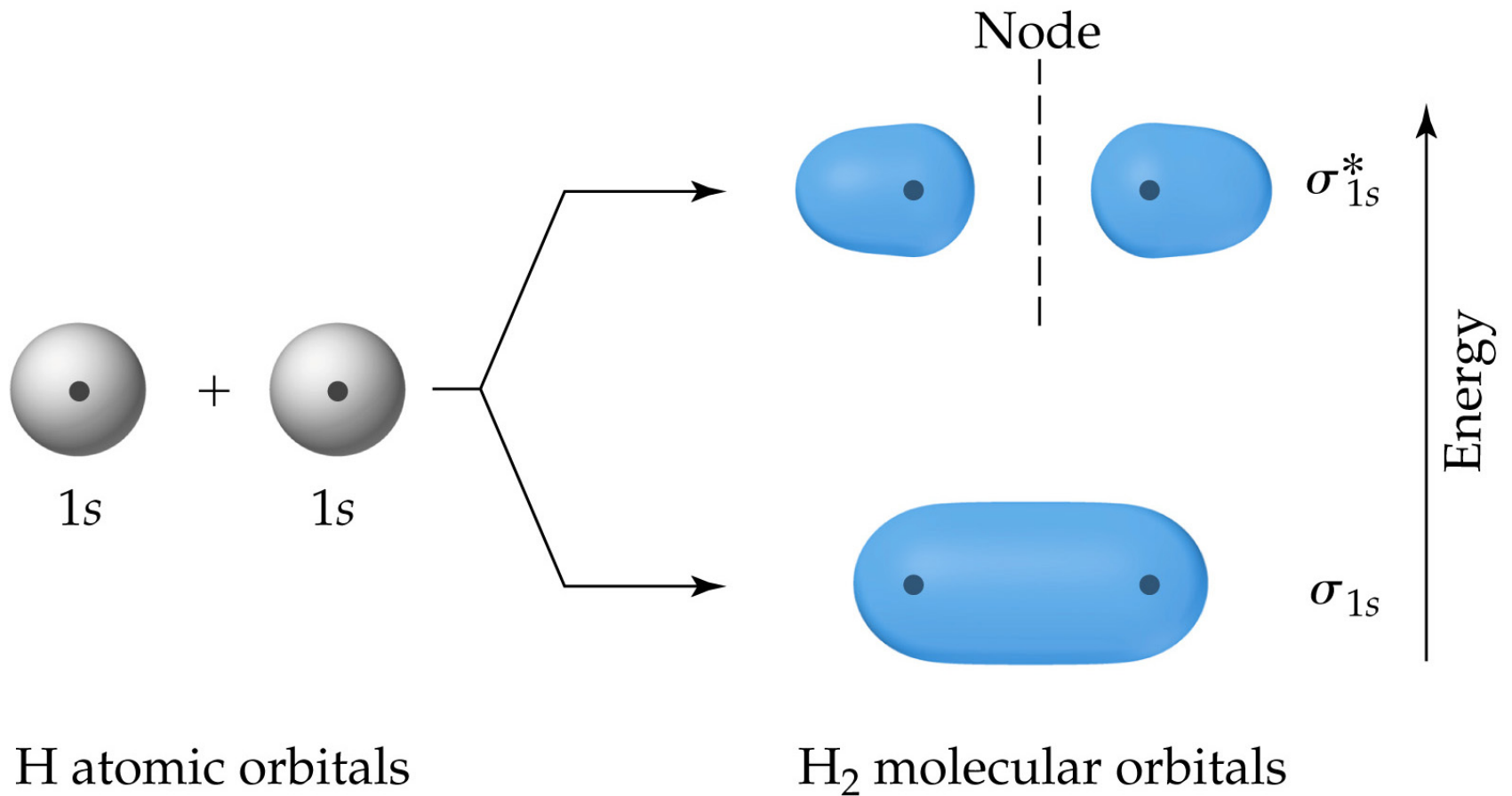
# Molecular Orbitals

## The Hydrogen Molecule

- When **two atomic orbitals** overlap, **two molecular orbitals** form.
- Therefore, **1s (H) + 1s (H)** must result in **two MOs for H<sub>2</sub>**:
  - one has electron density primarily between nuclei (**bonding MO**);
  - one has little electron density between nuclei (**antibonding MO**).
- MOs resulting from **s orbitals** are  **$\sigma$  MOs**.
- **$\sigma$**  (bonding) MO is **lower energy** than  **$\sigma^*$**  (antibonding) MO.

# Molecular Orbitals

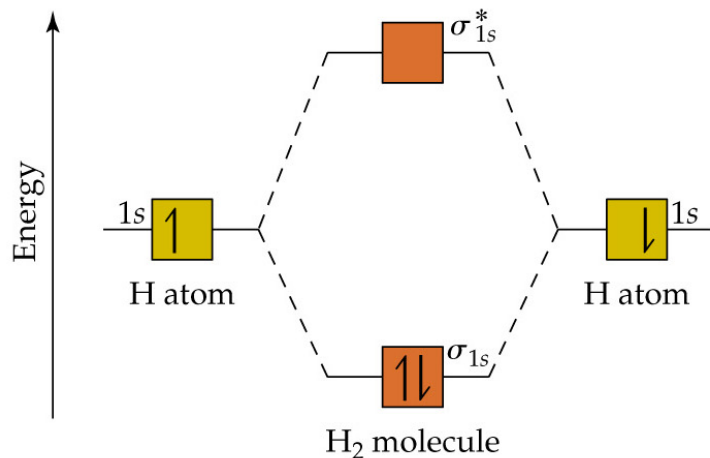
## The Hydrogen Molecule



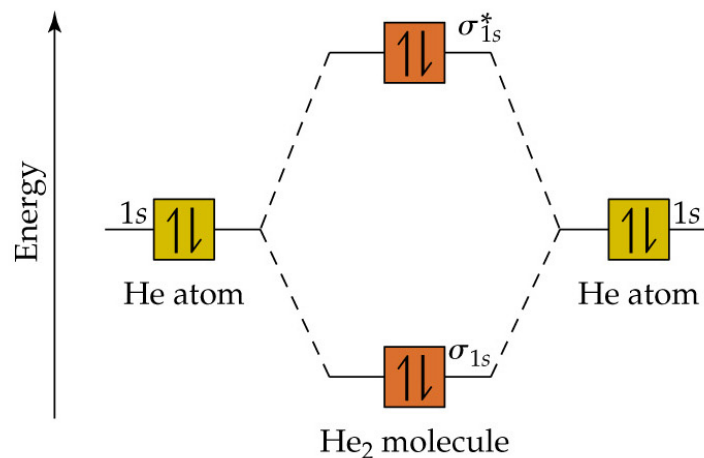
# Molecular Orbitals

## The Hydrogen Molecule

- **Energy-level diagrams** (aka MO diagrams) show orbital energies and electron assignments.
- The electrons from the atoms are placed in the MOs starting at the **lowest energy** ( $\sigma_{1s}$ ) (Note: electrons in MOs have opposite spins).



(a)



(b)

# Molecular Orbitals

## Bond Order

- We define **bond order** as:

$$\text{Bond order} = \frac{1}{2} (\text{bonding electrons} - \text{antibonding electrons})$$

- Bond order = **1 for single bond**.
- Bond order = **2 for double bond**.
- Bond order = **3 for triple bond**.
- **Fractional bond orders** are possible.

# Molecular Orbitals

## Bond Order

- For H<sub>2</sub>:

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

Therefore, **H<sub>2</sub> has a single bond.**

- For He<sub>2</sub>:

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

Therefore, **He<sub>2</sub> is not a stable molecule.**



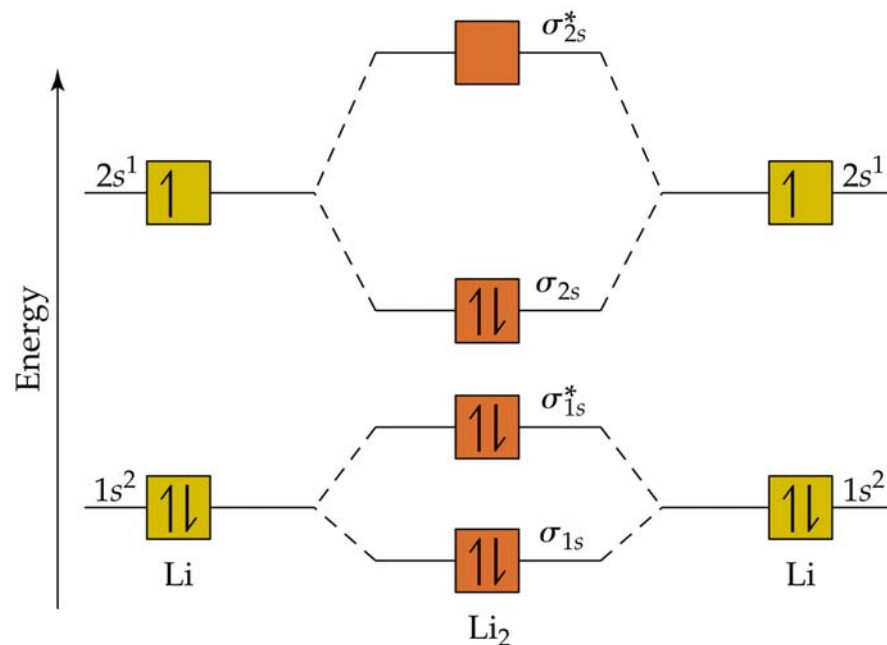
# Second-Row Diatomic Molecules

- First consider **homonuclear diatomic** molecules (e.g.  $\text{Li}_2$ ,  $\text{Be}_2$ ,  $\text{B}_2$  etc.).
- **AOs combine** according to the following **rules**:
  1. The **number of MOs = number of AOs**;
  2. AOs of **similar energy combine** most effectively;
  3. As **overlap increases**, the **energy** of the MO **decreases**;
  4. Each MO has at most **two electrons**, with **spins paired** (Pauli)
  5. For **degenerate orbitals**, each MO is **first occupied singly** (Hund)

# Second-Row Diatomic Molecules

## Molecular Orbitals for $\text{Li}_2$

- **1s orbitals** combine to give **one  $\sigma_{1s}$**  and **one  $\sigma_{1s}^*$**  orbital, both of which are occupied ( $\text{Li} = 1s^2 2s^1$ ).
- **2s orbitals** combine to give **one  $\sigma_{2s}$**  and **one  $\sigma_{2s}^*$**  orbital.
- The **energies of the 1s and 2s** orbitals are sufficiently different so that there is **no cross-mixing** of orbitals.



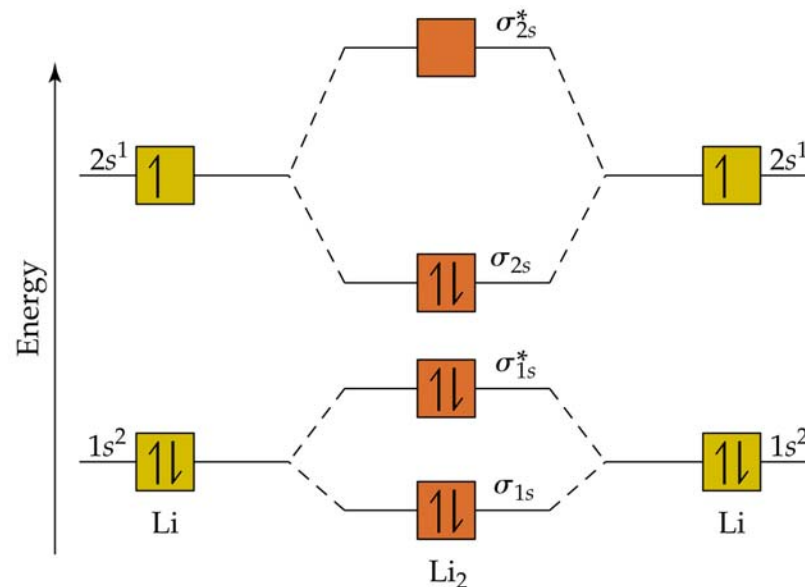
# Second-Row Diatomic Molecules

## Molecular Orbitals for $\text{Li}_2$

There are a total of 6 electrons in  $\text{Li}_2$ :

- 2 electrons in  $\sigma_{1s}$ ;
- 2 electrons in  $\sigma_{1s}^*$ ;
- 2 electrons in  $\sigma_{2s}$ ; and
- 0 electrons in  $\sigma_{2s}^*$ .

$$\text{Bond order} = \frac{1}{2}(4 - 2) = 1$$



- Since the  $1s$  AOs are completely filled, the  $\sigma_{1s}$  and  $\sigma_{1s}^*$  are filled.
- We generally ignore core electrons in MO diagrams.

# Second-Row Diatomic Molecules

## Molecular Orbitals for Be<sub>2</sub>

- There are a total of **8 electrons in Be<sub>2</sub>**:
  - **2 electrons in  $\sigma_{1s}$** ;
  - **2 electrons in  $\sigma^*_{1s}$** ;
  - **2 electrons in  $\sigma_{2s}$** ; and
  - **2 electrons in  $\sigma^*_{2s}$** .

$$\text{Bond order} = \frac{1}{2}(4 - 4) = 0$$

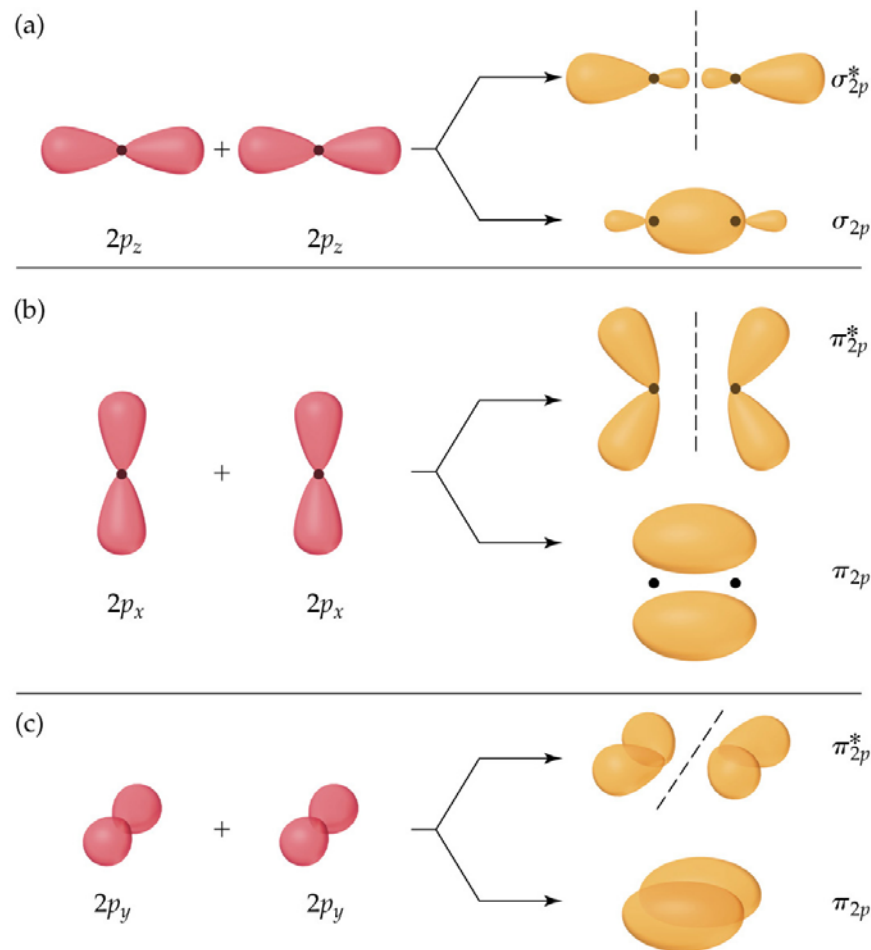
- Since the bond order is zero, **Be<sub>2</sub> does not exist**.

# Second-Row Diatomic Molecules

## Molecular Orbitals from 2p Atomic Orbitals

There are **two ways** in which two  $p$  orbitals **overlap**:

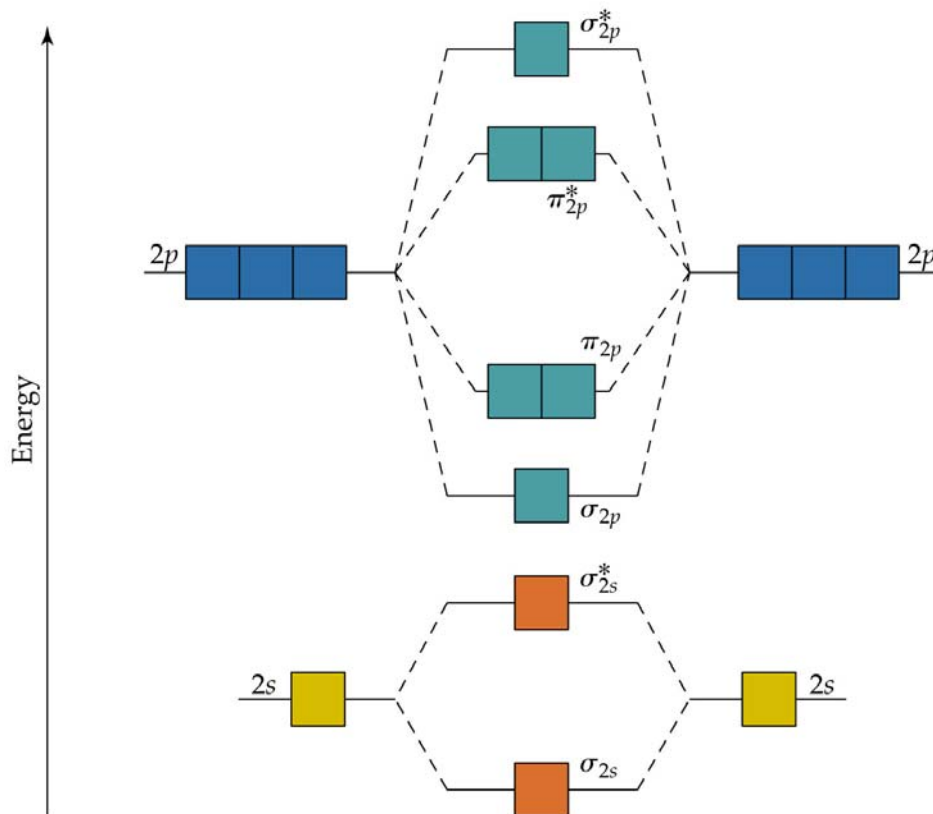
1. **end-on** so that the resulting MO has electron density on the axis between nuclei (i.e.  $\sigma$  type orbital);
2. **sideways** so that the resulting MO has electron density above and below, or to the sides, of the axis between nuclei (i.e.  $\pi$  type orbital).



# Second-Row Diatomic Molecules

## Molecular Orbitals from 2p Atomic Orbitals

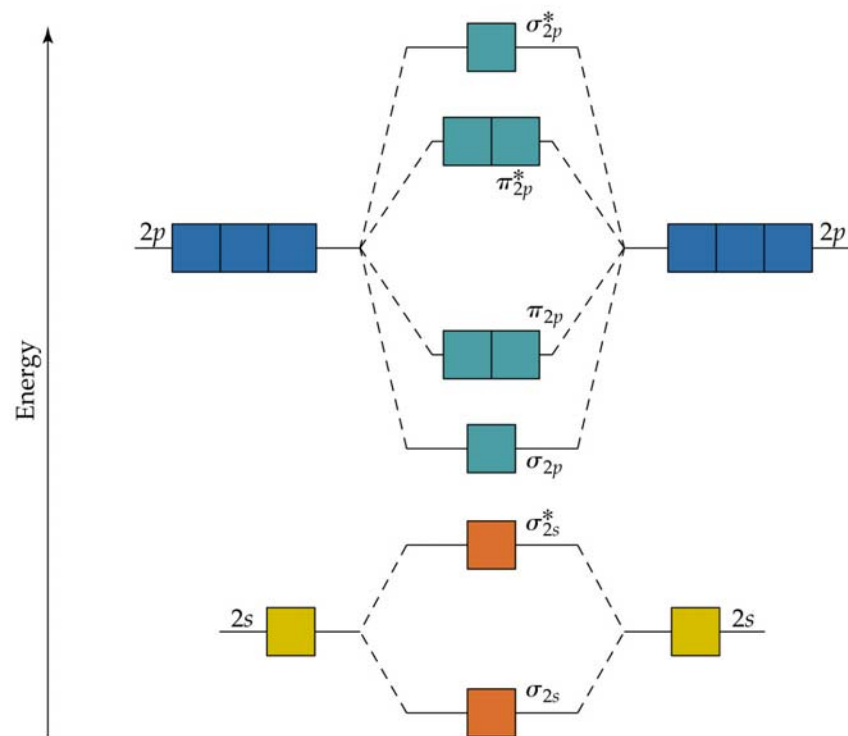
- The **six p-orbitals** (two sets of 3) must give rise to **6 MOs**:  $\sigma$ ,  $\sigma^*$ ,  $\pi$ ,  $\pi^*$ ,  $\pi$ , and  $\pi^*$ .
- Therefore, there is a **maximum of 2  $\pi$  bonds** that can come from p-orbitals.
- The **relative energies** of these six orbitals **can change**.



# Second-Row Diatomic Molecules

## Configurations for $B_2$ Through $Ne_2$

- As with 2s and 2p atomic orbitals,  $\sigma_{2s}$  orbitals are lower in energy than  $\sigma_{2p}$  orbitals.
- $2p_z$  Orbitals have greater overlap (they point directly towards one another) so the  $\sigma_{2p}$  MO is lower in energy than the  $\pi_{2p}$  orbitals.
- For the same reason, the  $\sigma_{2p}^*$  MO is higher in energy than the  $\pi_{2p}^*$  orbitals.
- The  $\pi_{2p}$  and  $\pi_{2p}^*$  orbitals are doubly degenerate.



# Second-Row Diatomic Molecules





































## Configurations for B<sub>2</sub> Through Ne<sub>2</sub>

- As **atomic number** decreases, it is more likely that a **2s orbital** on one atom can **interact** with the **2p orbital** on the other.
- As this **2s-2p interaction** increases, the  $\sigma_{2s}$  MO lowers in energy and the  $\sigma_{2p}$  MO increases in energy.
- For **B<sub>2</sub>, C<sub>2</sub> and N<sub>2</sub>** the  $\sigma_{2p}$  orbital is **higher** in energy than the  $\pi_{2p}$ .
- For **O<sub>2</sub>, F<sub>2</sub> and Ne<sub>2</sub>** the  $\sigma_{2p}$  orbital is **lower** in energy than the  $\pi_{2p}$ .
- Once the relative orbital energies are known, the required number of electrons can be added to the MOs, taking into account Pauli's exclusion principle and Hund's rule.



# Second-Row Diatomic Molecules

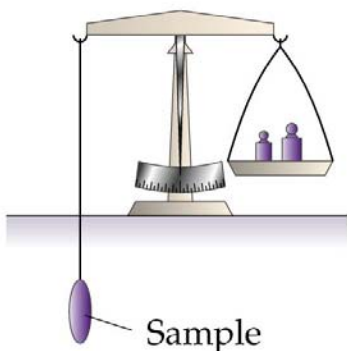
## Configurations for B<sub>2</sub> Through Ne<sub>2</sub>

	Large 2s-2p interaction			Small 2s-2p interaction		
	B <sub>2</sub>	C <sub>2</sub>	N <sub>2</sub>	O <sub>2</sub>	F <sub>2</sub>	Ne <sub>2</sub>
$\sigma_{2p}^*$						
$\pi_{2p}^*$						
$\sigma_{2p}$						
$\pi_{2p}$						
$\sigma_{2s}^*$						
$\sigma_{2s}$						
Bond order	1	2	3	2	1	0
Bond enthalpy (kJ/mol)	290	620	941	495	155	—
Bond length (Å)	1.59	1.31	1.10	1.21	1.43	—
Magnetic behavior	Paramagnetic	Diamagnetic	Diamagnetic	Paramagnetic	Diamagnetic	—

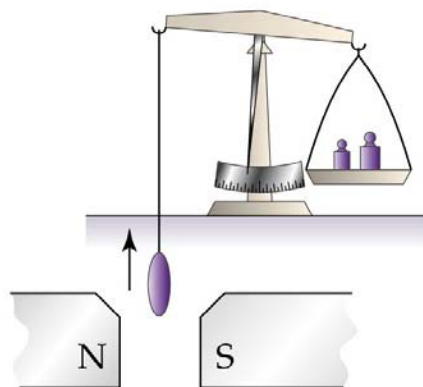
# Second-Row Diatomic Molecules

## Electron Configurations and Molecular Properties

- Two types of magnetic behavior:
  1. **paramagnetism** (unpaired electrons in molecule): **strong attraction** between magnetic field and molecule;
  2. **diamagnetism** (no unpaired electrons in molecule): **weak repulsion** between magnetic field and molecule.
- Magnetic behavior is **detected** by determining the **mass** of a sample in the presence and absence of **magnetic field**:

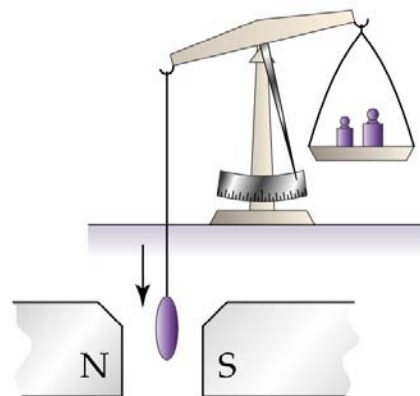


(a)



(b)

**Diamagnetic** – small decrease in mass



(c)

**Paramagnetic** – large increase in mass

# Second-Row Diatomic Molecules

## Electron Configurations and Molecular Properties

- Experimentally **O<sub>2</sub> is paramagnetic**.
- The **Lewis structure** for O<sub>2</sub> shows **no unpaired electrons**.
- The **MO diagram** for O<sub>2</sub> shows **2 unpaired electrons** in the  **$\pi_{2p}^*$  orbital**.
- Experimentally, **O<sub>2</sub> has a short bond length** (1.21 Å) and **high bond dissociation energy** (495 kJ/mol). This suggests a double bond.
- The **MO diagram** for O<sub>2</sub> **predicts both** paramagnetism and the double bond (bond order = 2).