

# Types of Chemical Bonding

***Ionic bonding*** involves the ***transfer*** of electrons and is usually observed when a ***metal*** bonds to a ***nonmetal***.

***Covalent bonding*** involves the ***sharing*** of electrons and is usually observed when a ***nonmetal*** bonds to a ***nonmetal***.

***Metallic bonding*** involves ***electron pooling*** and occurs when a ***metal*** bonds to another ***metal***.



# Figure 8.24 Electronegativity and atomic size.

Copyright © The McGraw-Hill Companies, Inc. Permission required for reproduction or display.

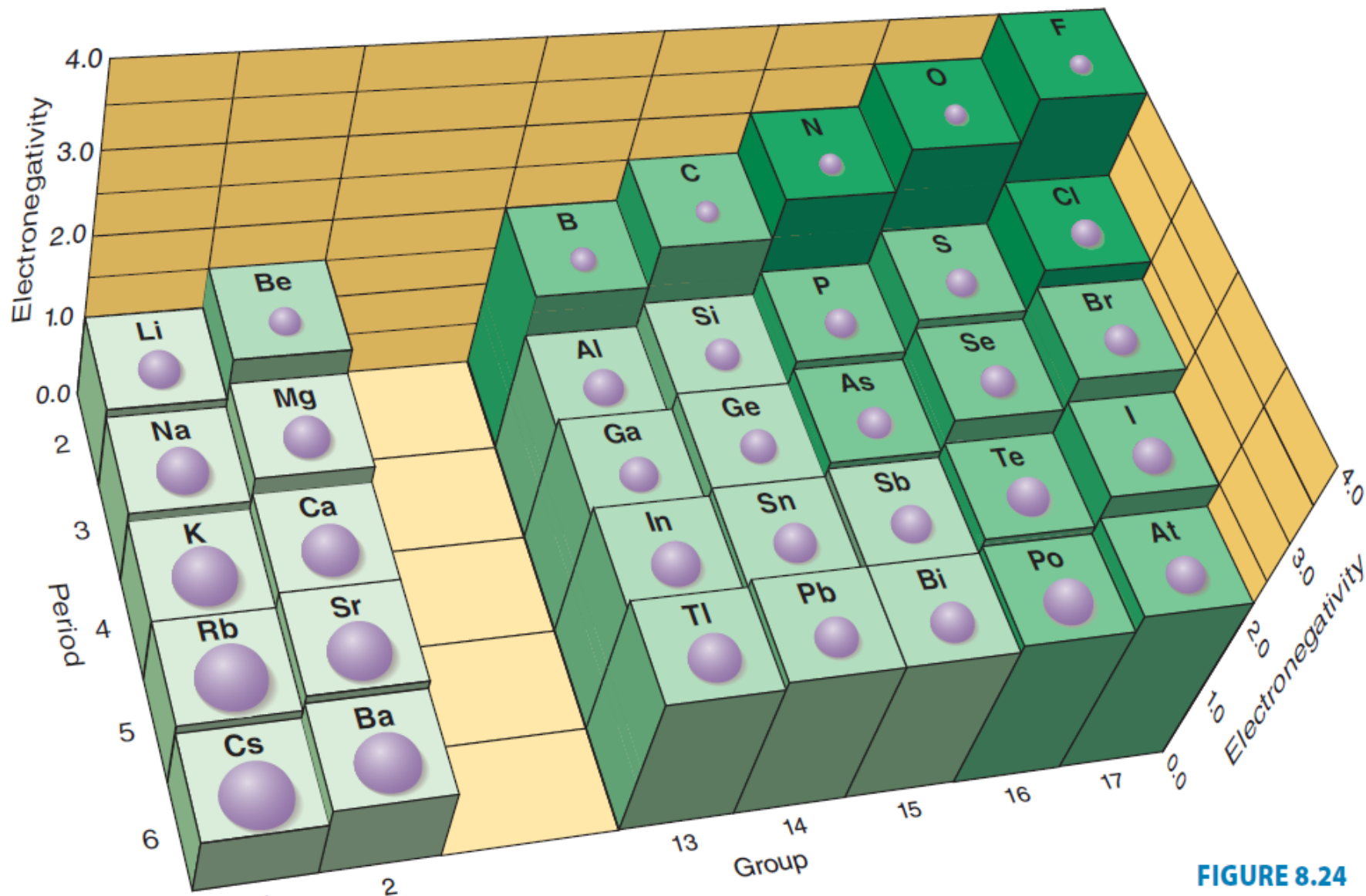


FIGURE 8.24

# Electronegativity and Oxidation Number

Electronegativities can be used to assign oxidation numbers:

- The more electronegative atom is assigned ***all*** the ***shared*** electrons.
- The less electronegative atom is assigned ***none*** of the shared electrons.
- Each atom in a bond is assigned ***all*** of its ***unshared*** electrons.
- $\text{O.N.} = \# \text{ of valence } e^- (\# \text{ of shared } e^- + \# \text{ of unshared } e^-)$





Cl is more electronegative than H, so for Cl:

$$\text{valence } e^- = 7$$

$$\text{shared } e^- = 2$$

$$\text{unshared } e^- = 6$$

$$\text{O.N.} = 7 - (2 + 6) = -1$$

H is less electronegative than Cl, so for H:

$$\text{valence } e^- = 1$$

$$\text{shared } e^- = 0 \text{ (all shared } e^- \text{ assigned to Cl)}$$

$$\text{unshared } e^- = 0$$

$$\text{O.N.} = 1 - (0 + 0) = +1$$





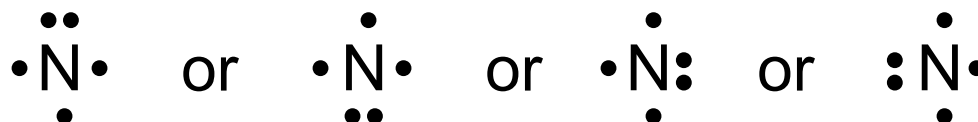
# Lewis Electron-Dot Symbols

To draw the Lewis symbol for any main-group element:

- Note the A-group number, which gives the number of valence electrons.
- Place one dot at a time on each of the four sides of the element symbol.
- Keep adding dots, pairing them, until all are used up.

Example:

Nitrogen, N, is in Group 5A and therefore has 5 valence electrons.



# Figure 8.5

## Lewis electron-dot symbols for elements in Periods 2 and 3.

Copyright © The McGraw-Hill Companies, Inc. Permission required for reproduction or display.

		1	2						
		$ns^1$	$ns^2$						
Period	2	• Li	• Be •	13	14	15	16	17	18
	3	• Na	• Mg •	$ns^2np^1$	$ns^2np^2$	$ns^2np^3$	$ns^2np^4$	$ns^2np^5$	$ns^2np^6$
				• B •	• C •	• N •	• O •	• F •	• Ne •
				• Al •	• Si •	• P •	• S •	• Cl •	• Ar •



## 8.2

# The Ionic Bonding Model

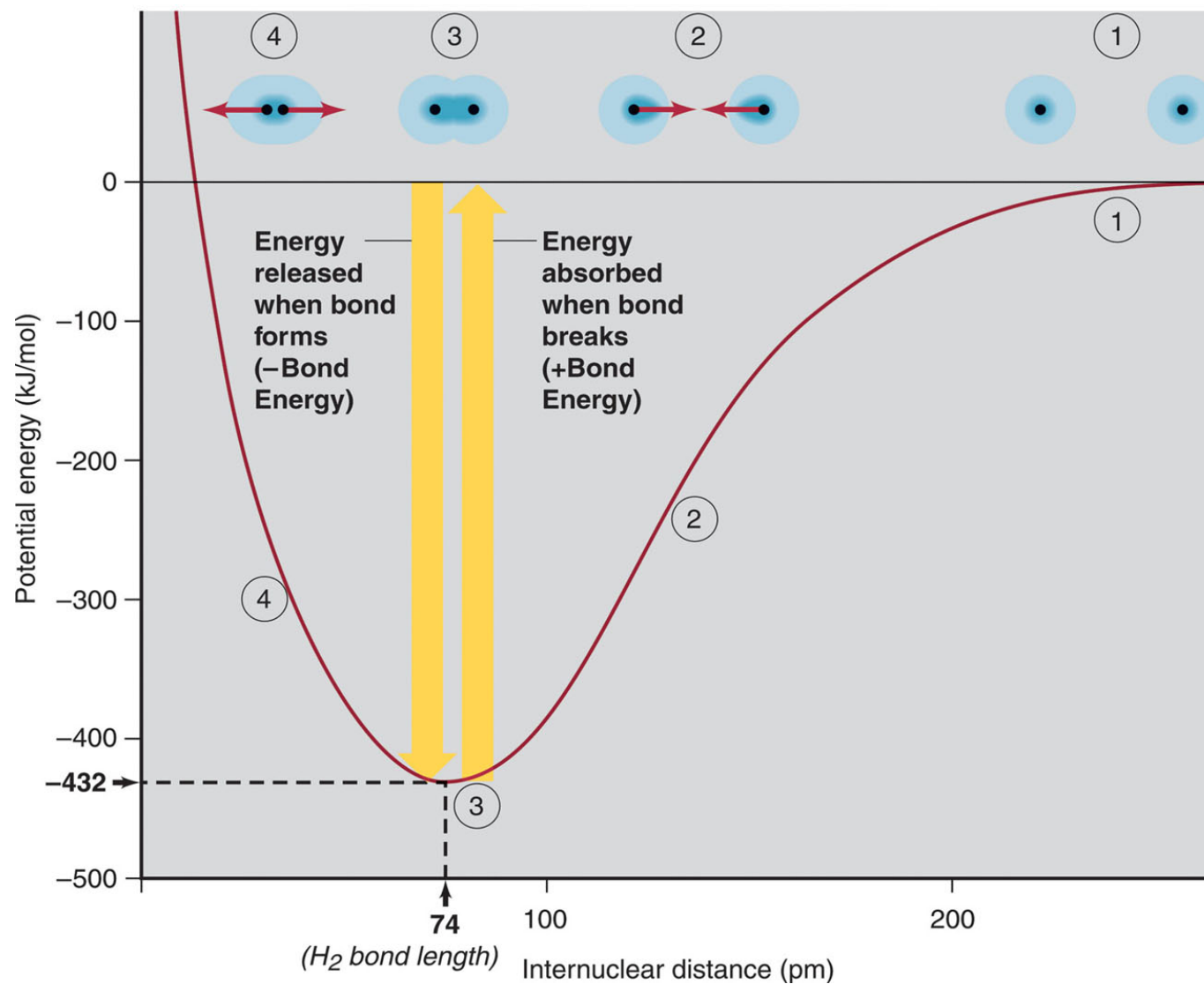
An ionic bond is formed when a metal ***transfers*** electrons to a nonmetal to form ***ions***, which attract each other to give a solid compound.

The total number of electrons lost by the metal atom(s) equals the total number of electrons gained by the nonmetal atoms.



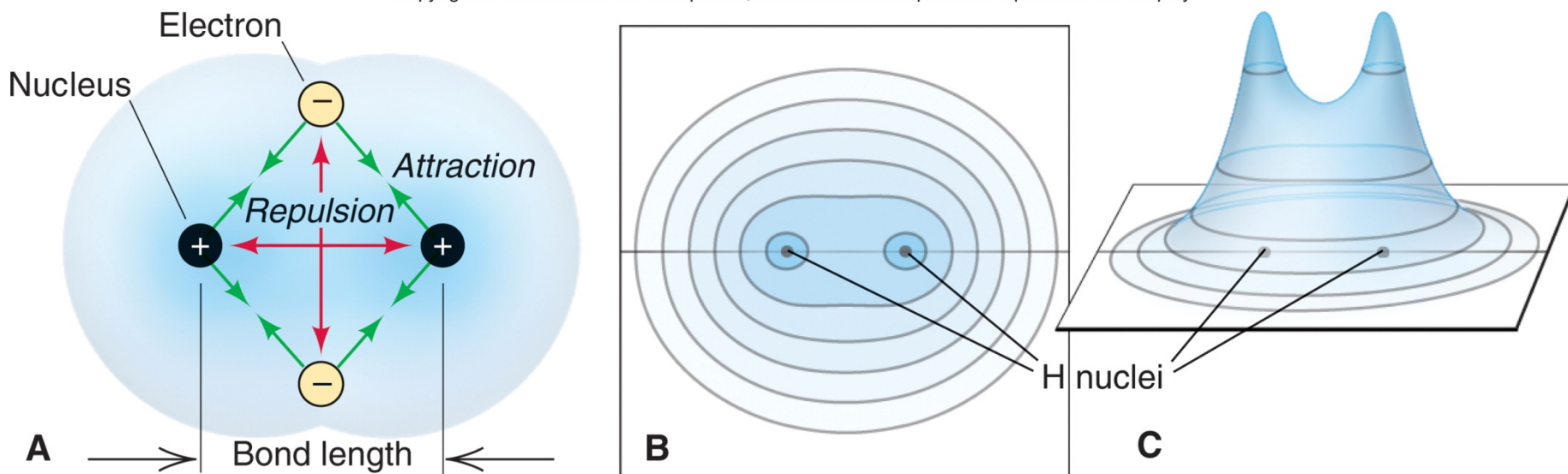
# 8.3

Figure 8.13 Covalent bond formation in  $H_2$ .



**Figure 8.14**      **Distribution of electron density in  $H_2$ .**

Copyright © The McGraw-Hill Companies, Inc. Permission required for reproduction or display.



At some distance (bond length),  
attractions balance repulsions.

Electron density is high around  
and between the nuclei.



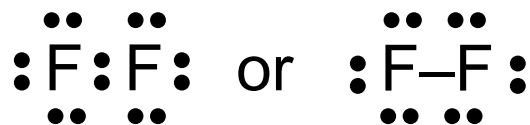
## Bonding Pairs and Lone Pairs

Atoms share electrons to achieve a full outer level of electrons. The shared electrons are called a ***shared pair*** or ***bonding pair***.

The shared pair is represented as a pair of dots or a line:

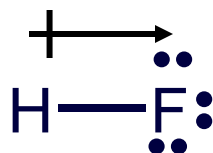


An outer-level electron pair that is not involved in bonding is called a ***lone pair***, or ***unshared pair***.

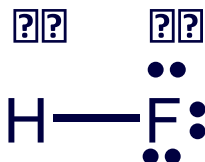


## Depicting Polar Bonds

The unequal sharing of electrons can be depicted by a polar arrow. The head of the arrow points to the ***more electronegative element***.

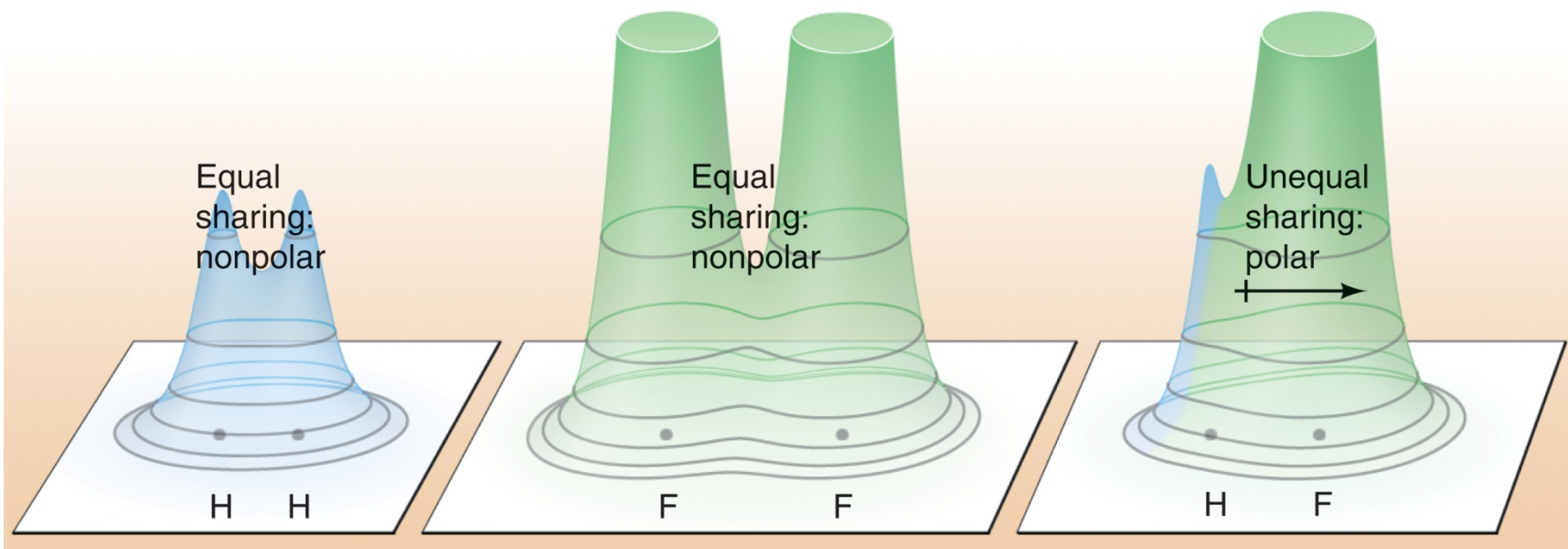


A polar bond can also be marked using  $\delta^+$  and  $\delta^-$  symbols.



## Figure 8.25 Electron density distributions in $\text{H}_2$ , $\text{F}_2$ , and $\text{HF}$ .

Copyright © The McGraw-Hill Companies, Inc. Permission required for reproduction or display.



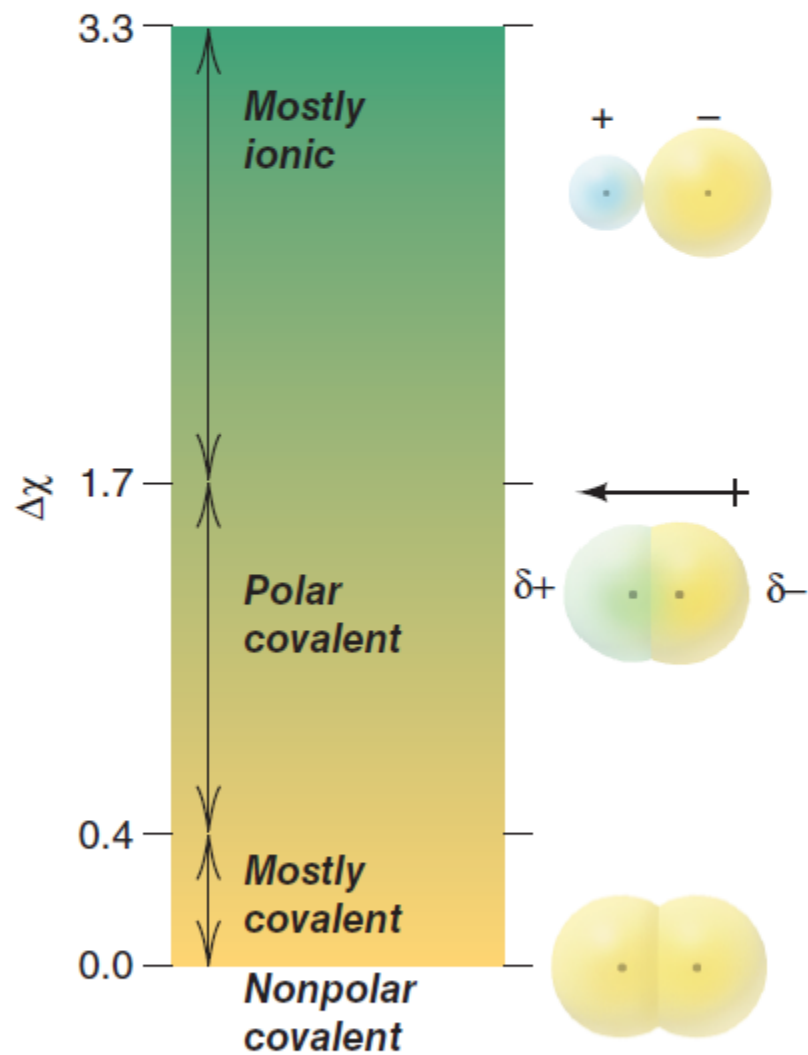
In  $\text{HF}$ , the electron density shifts from  $\text{H}$  to  $\text{F}$ .

The  $\text{H}-\text{F}$  bond has partial ionic character.



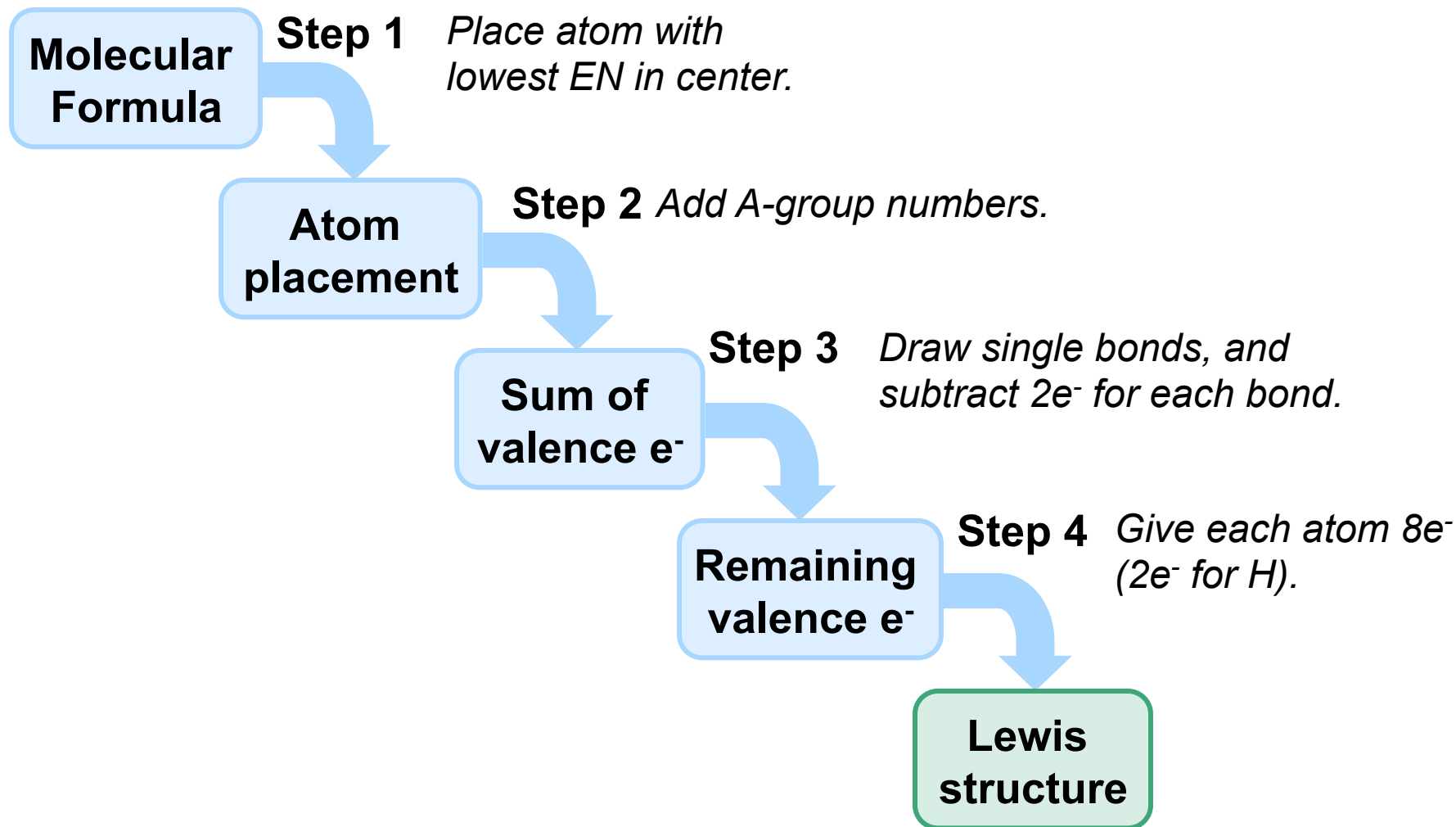


**Figure 8.26**  $\Delta\chi$  ranges for classifying the partial ionic character of bonds.



## 8.6

**Figure 8.30** The steps in converting a molecular formula into a Lewis structure.



## Example: $\text{NF}_3$

**Molecular  
Formula**

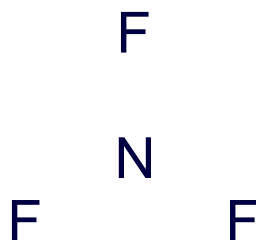
**Atom  
placement**

**Sum of  
valence  $e^-$**

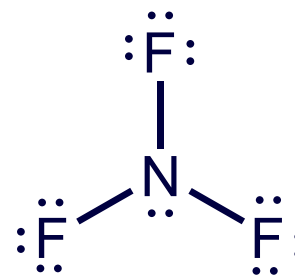
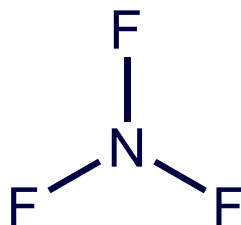
**Remaining  
valence  $e^-$**

**Lewis  
structure**

N has a lower EN than F, so N is placed in the center.



$$\begin{array}{rcl} 1 \times \text{N} & = & 1 \times 5 = 5e^- \\ 3 \times \text{F} & = & 3 \times 7 = 21e^- \\ \hline \text{Total} & & = 28e^- \end{array}$$

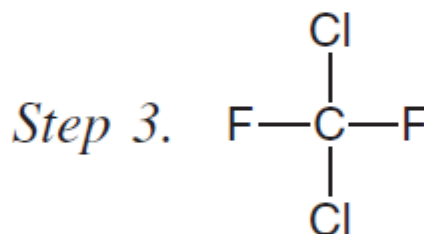
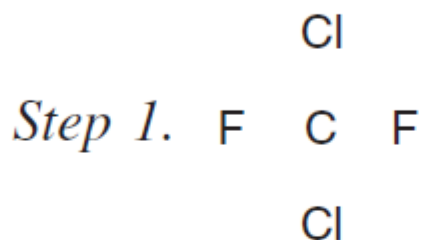


## Sample Problem 8.6

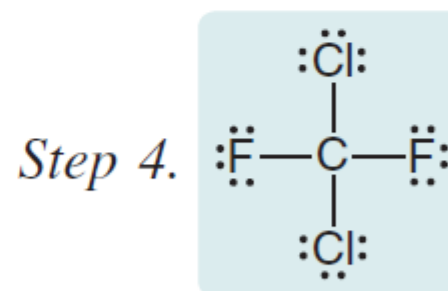
### Writing a Lewis Structure for a Molecule with One Central Atom.

**Problem :** Write the lewis structure for  $\text{CCl}_2\text{F}_2$  , one of the compounds responsible for the depletion of stratospheric ozone.

**Solution:**



*Step 2.* Total valence electrons = 32.



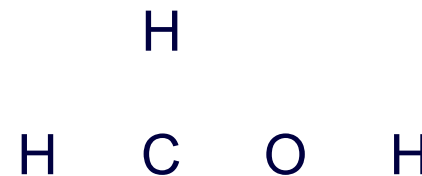
## Sample Problem 8.7

## Writing a Lewis Structures for a Molecule with More than One Central Atom

**PROBLEM:** Write the Lewis structure for methanol (molecular formula  $\text{CH}_4\text{O}$ ), an important industrial alcohol that is being used as a gasoline alternative in car engines.

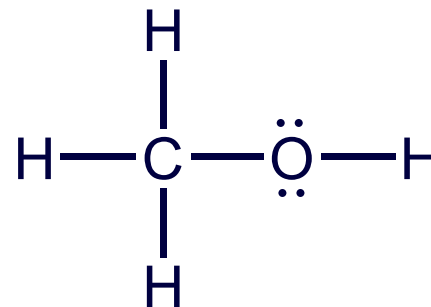
### SOLUTION:

*Step 1:* Place the atoms relative to each other. H can only form one bond, so C and O must be central and adjacent to each other.



*Step 2:*  $[1 \times \text{C}(4e^-)] + [1 \times \text{O}(6e^-)] + [4 \times \text{H}(1e^-)]$   
= 14 valence  $e^-$

*Step 3-4:* Add single bonds, then give each atom (other than H) a full octet.



## Multiple Bonds

If there are not enough electrons for the ***central*** atom to attain an octet, a multiple bond is present.

*Step 5:* If the central atom does not have a full octet, change a lone pair on a surrounding atom into another bonding pair to the central atom, thus forming a multiple bond.



## Sample Problem 8.8

## Writing Lewis Structures for Molecules with Multiple Bonds

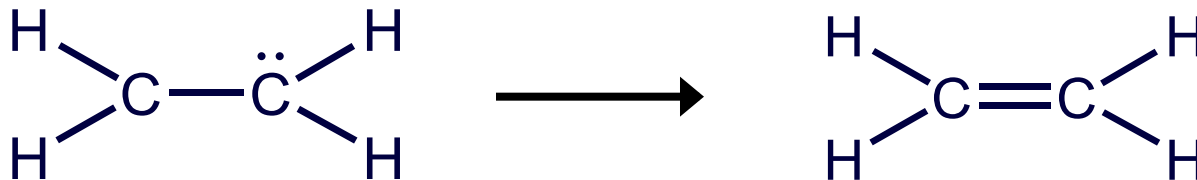
**PROBLEM:** Write Lewis structures for the following:

- (a) Ethylene ( $\text{C}_2\text{H}_4$ ), the most important reactant in the manufacture of polymers
- (b) Nitrogen ( $\text{N}_2$ ), the most abundant atmospheric gas( about 78 %)

**PLAN:** After following steps 1 to 4 we see that the central atom does not have a full octet. We must therefore add step 5, which involves changing a lone pair to a bonding pair.

### SOLUTION:

- (a)  $\text{C}_2\text{H}_4$  has  $2(4) + 4(1) = 12$  valence  $e^-$ . H can have only one bond per atom.



## Sample Problem 8.8 con' t

(b)  $\text{N}_2$  has  $2(5) = 10$  valence  $e^-$ .

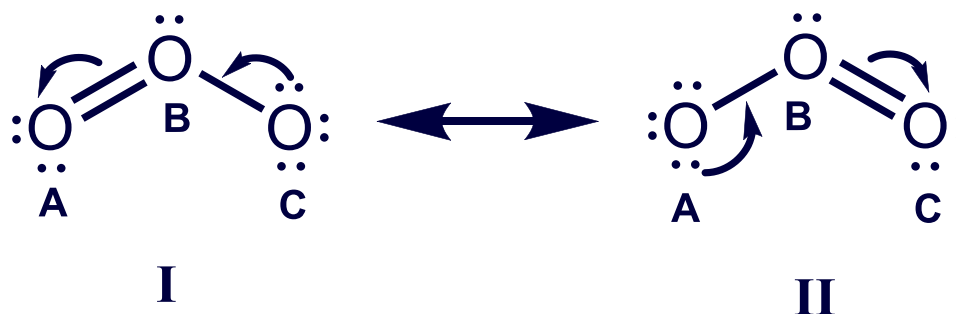




# Resonance Structures

The structure of  $O_3$  is shown more correctly using both Lewis structures, called ***resonance structures***.

A two-headed resonance arrow is placed between them.



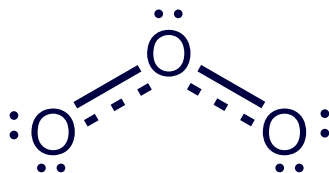
Resonance structures have the *same relative placement of atoms but different locations of bonding and lone electron pairs*.



# Electron Delocalization

Lewis structures depict electrons as **localized** either on an individual atom (lone pairs) or in a bond between two atoms (shared pair).

In a resonance hybrid, electrons are **delocalized**: their density is “spread” over a few adjacent atoms.



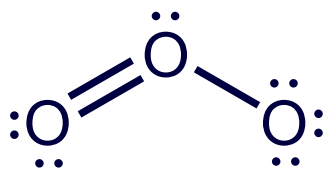
Dotted lines are used to show delocalized electrons.



## Fractional Bond Orders

Resonance hybrids often have ***fractional bond orders*** due to partial bonding.

$$\text{For O}_3, \text{ bond order} = \frac{3 \text{ electron pairs}}{2 \text{ bonded-atom pairs}} = 1\frac{1}{2}$$



## Sample Problem 8.9

## Writing Resonance Structures

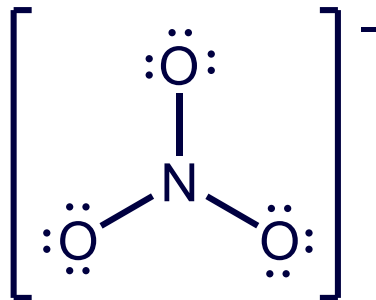
**PROBLEM:** Write resonance structures for the nitrate ion,  $\text{NO}_3^-$  and find the bond order.

**PLAN:** Write the Lewis structure, remembering to add  $1e^-$  to the total number of valence  $e^-$  for the  $-1$  charge. We apply Step 5 to form multiple bonds. Since multiple bonds can be formed in more than one location, there are resonance forms.

### SOLUTION:

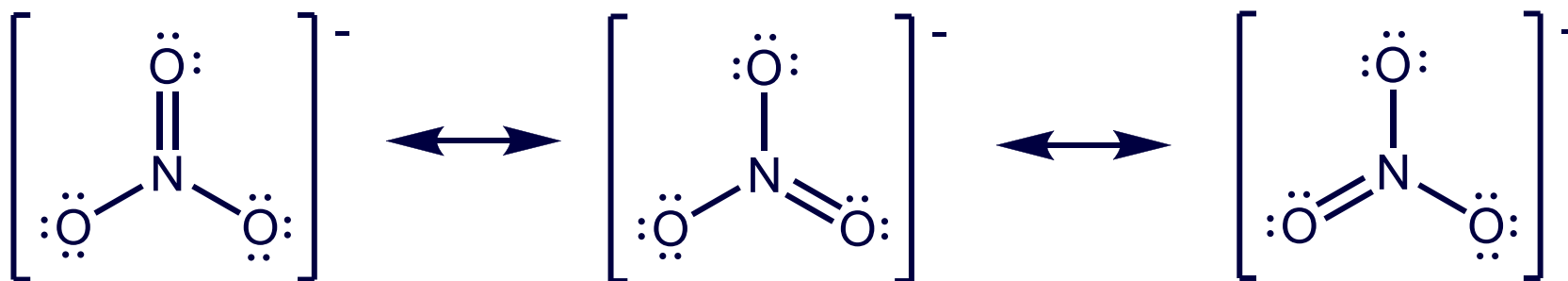
Nitrate has  $[1 \times \text{N}(5e^-)] + [3 \times \text{O}(6e^-)] + 1e^- = 24$  valence  $e^-$

After Steps 1-4:



### Sample Problem 8.9

*Step 5.* Since N does not have a full octet, we change a lone pair from O to a bonding pair to form a double bond.



$$\text{Bond order} = \frac{4 \text{ shared electron pairs}}{3 \text{ bonded-atom pairs}} = 1\frac{1}{3}$$

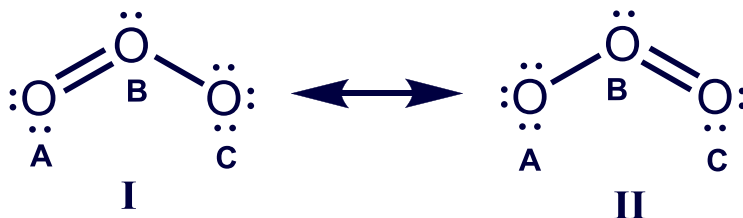


# Formal Charge

**Formal charge** is the charge an atom would have if all electrons were shared **equally**.

Formal charge of atom =

# of valence  $e^-$  - (# of unshared valence  $e^-$  +  $\frac{1}{2}$  # of shared valence  $e^-$ )



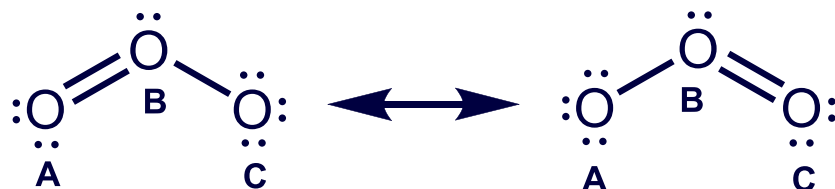
For O<sub>A</sub> in resonance form I, the formal charge is given by

$$6 \text{ valence } e^- - (4 \text{ unshared } e^- + \frac{1}{2}(4 \text{ shared } e^-)) = 6 - 4 - 2 = 0$$



# Formal Charge

Formal charges must sum to the actual charge on the species for ***all*** resonance forms.



$$\text{O}_A [6 - 4 - \frac{1}{2}(4)] = 0$$

$$\text{O}_B [6 - 2 - \frac{1}{2}(6)] = +1$$

$$\text{O}_C [6 - 6 - \frac{1}{2}(2)] = -1$$

$$\text{O}_A [6 - 6 - \frac{1}{2}(2)] = -1$$

$$\text{O}_B [6 - 2 - \frac{1}{2}(6)] = +1$$

$$\text{O}_C [6 - 4 - \frac{1}{2}(4)] = 0$$

For both these resonance forms the formal charges sum to zero, since  $\text{O}_3$  is a neutral molecule.



# Choosing the More Important Resonance Form

- Smaller formal charges (positive or negative) are preferable to larger ones.
- The **same** nonzero formal charges on adjacent atoms are not preferred.

Avoid like charges on adjacent atoms.

- A more negative formal charge should reside on a more electronegative atom.

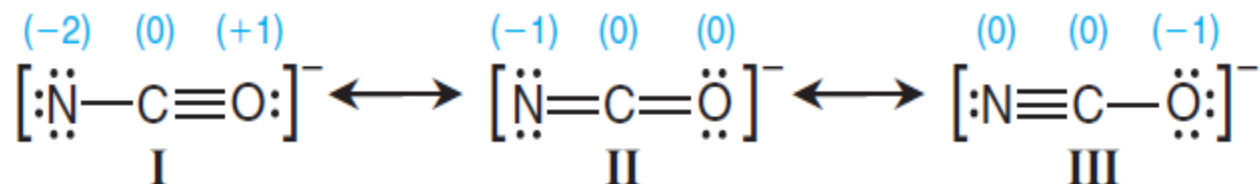




Example:  $\text{NCO}^-$  has 3 possible resonance forms:

Formal charges:

Resonance forms:



Resonance forms with smaller formal charges are preferred.  
Resonance form I is therefore **not** an important contributor.

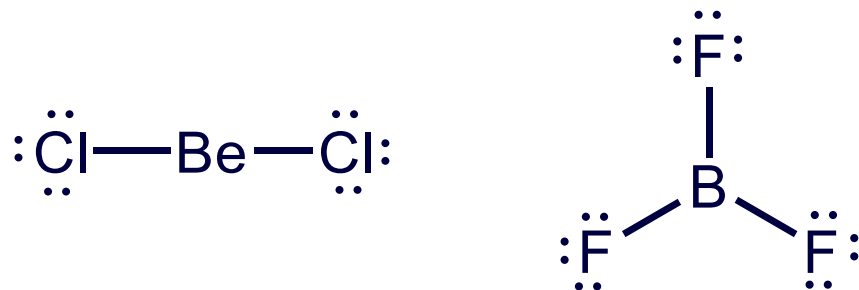
A negative formal charge should be placed on a more electronegative atoms, so resonance form III is preferred to resonance form II.

The overall structure of the  $\text{NCO}^-$  ion is still an **average** of all three forms, but **resonance form III** contributes **most** to the average.



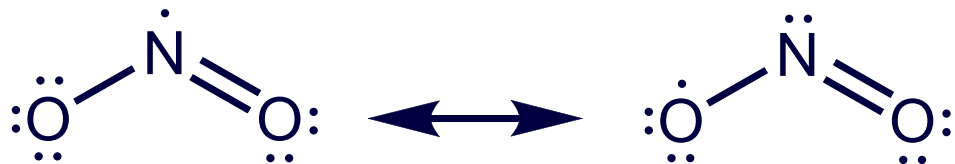
# Exceptions to the Octet Rule

## Molecules with Electron-Deficient Atoms



B and Be are commonly electron-deficient.

## Odd-Electron Species

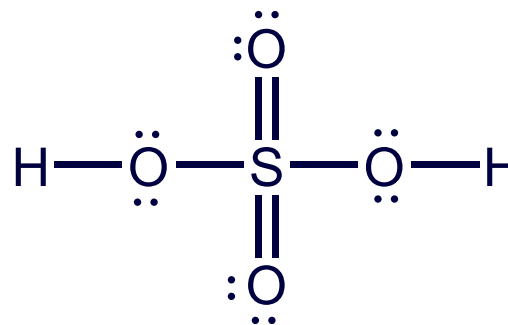
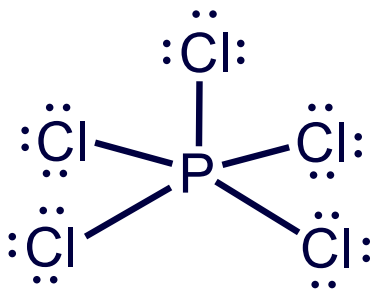


A molecule with an odd number of electrons is called a **free radical**.



# Exceptions to the Octet Rule

## Expanded Valence Shells



An expanded valence shell is only possible for ***nonmetals from Period 3 or higher*** because these elements have available ***d orbitals***.



## Sample Problem 8.10

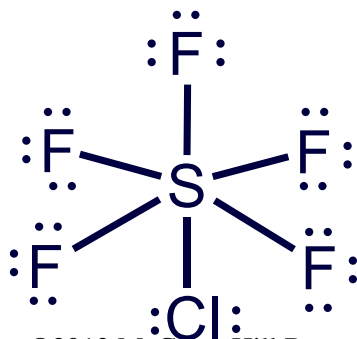
## Writing Lewis Structures for Octet-Rule Exceptions

**PROBLEM:** Write a Lewis structure and identify the octet-rule exception for **(a)**  $\text{SClF}_5$ ; **(b)**  $\text{H}_3\text{PO}_4$  (draw two resonance forms and select the more important); **(c)**  $\text{BFCl}_2$ .

**PLAN:** Draw each Lewis structure and examine it for exceptions to the octet rule. Period 3 elements can have an expanded octet, while B commonly forms electron-deficient species.

### SOLUTION:

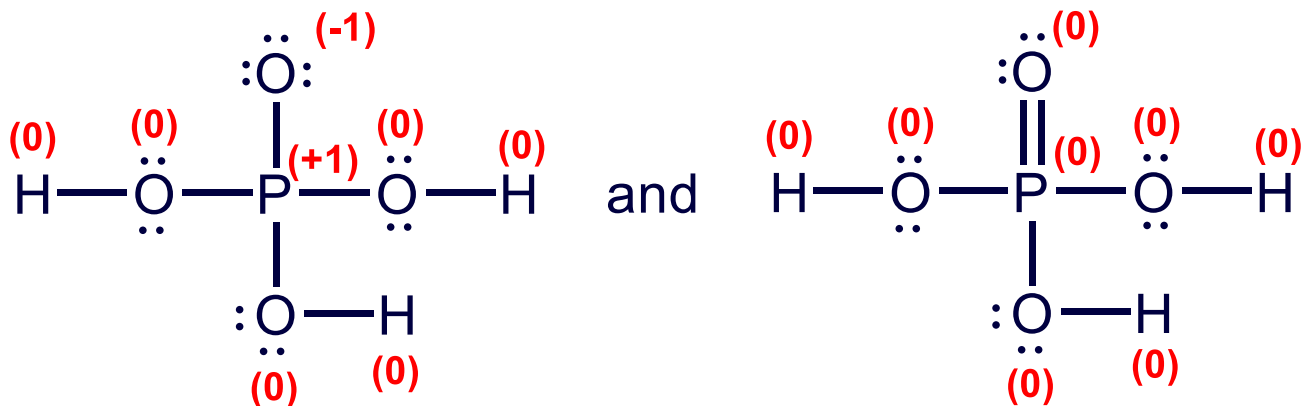
**(a)** The central atom is S, which is in Period 3 and can have an expanded valence shell.



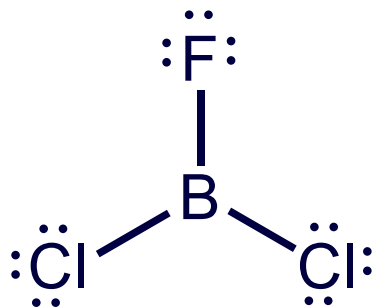
©2013 McGraw-Hill Ryerson Limited

## Sample Problem 8.10

(b)  $\text{H}_3\text{PO}_4$  has two resonance forms and formal charges indicate the more important form.



(c)  $\text{BFCl}_2$  is an electron-deficient molecule. B has only six electrons surrounding it.



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

Each group of valence electrons around a central atom is located as far as possible from the others, to minimize repulsions.

A “group” of electrons is any number of electrons that occupies a localized region around an atom.

A single bond, double bond, triple bond, lone pair, or single electron all count as a single group.



# Electron-group Arrangement and Molecular Shape

The ***electron-group arrangement*** is defined by both bonding and nonbonding electron groups.

The ***molecular shape*** is the three-dimensional arrangement of nuclei joined by the bonding groups. This is defined only by the relative positions of the nuclei.

Molecular shape is classified using the designation



A = central atom

X = surrounding atom

E = nonbonding valence-electron group

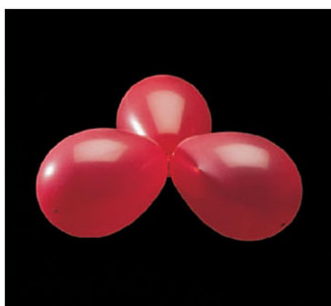
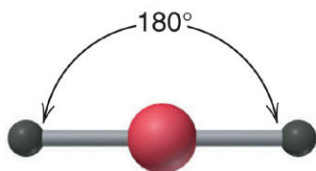
*m* and *n* are integers



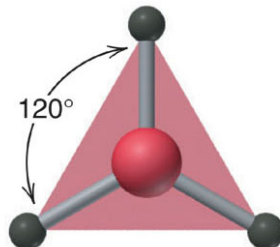
**Figure 9.2**      **Electron-group repulsions and molecular shapes.**



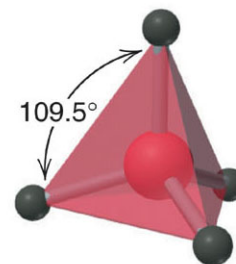
*linear*



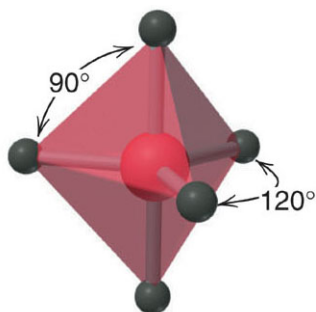
*trigonal planar*



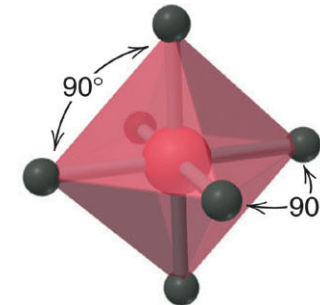
*tetrahedral*



*trigonal  
bipyramidal*



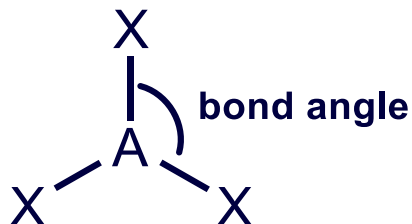
*octahedral*



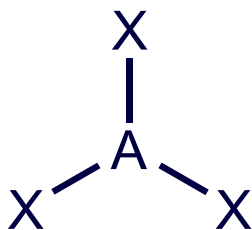


# Bond Angle

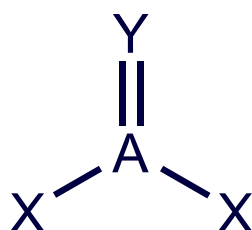
The **bond angle** is the angle formed by the nuclei of two surrounding atoms with the nucleus of the central atom.



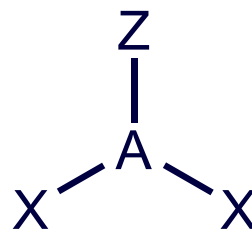
The angles shown in Figure 10.2 are **ideal** bond angles, determined by basic geometry alone. Real bond angles deviate from the ideal value in many cases.



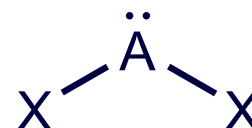
real = ideal



real  $\neq$  ideal



real  $\neq$  ideal



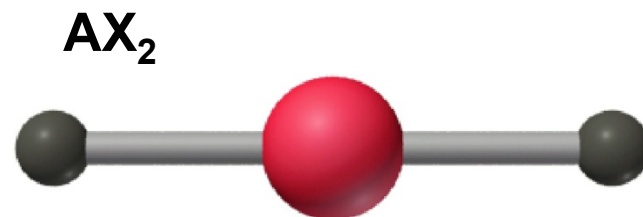
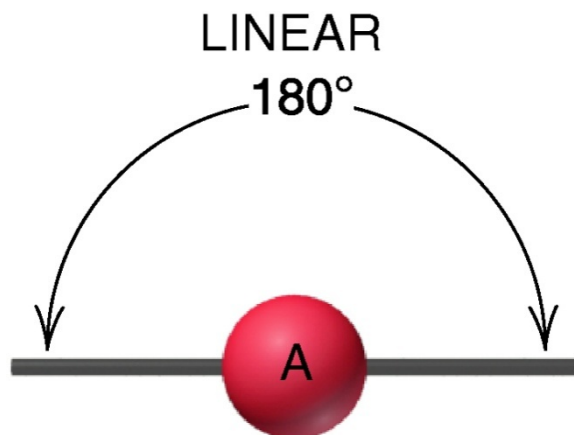
real  $\neq$  ideal



Figure 9.3

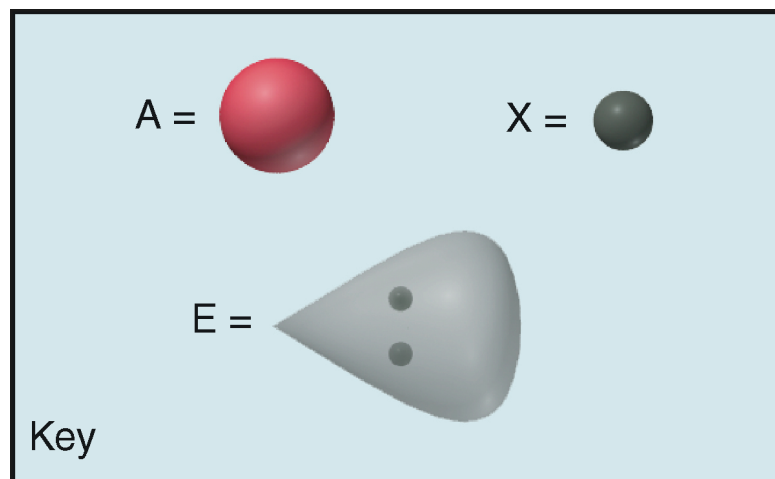
## The single molecular shape of the linear electron-group arrangement.

Copyright © The McGraw-Hill Companies, Inc. Permission required for reproduction or display.



Linear

Examples:  
 $CS_2$ ,  $HCN$ ,  $BeF_2$



This key refers to Figures 9.3 through 9.8.

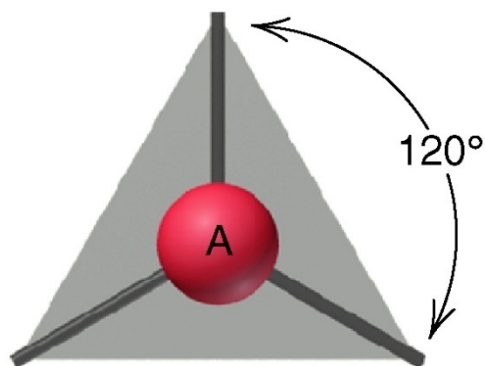


Figure 9.4

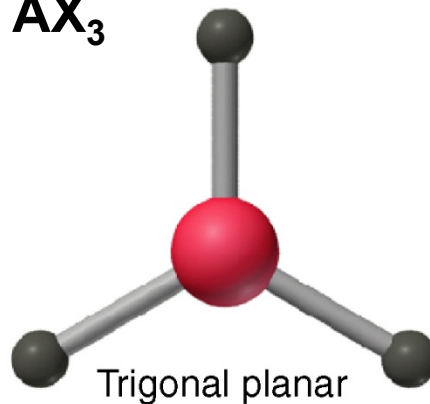
## The two molecular shapes of the trigonal planar electron-group arrangement.

Copyright © The McGraw-Hill Companies, Inc. Permission required for reproduction or display.

TRIGONAL PLANAR

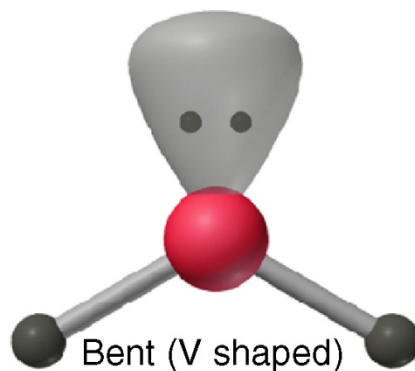


$AX_3$



Examples:  
 $SO_3$ ,  $BF_3$ ,  $NO_3^-$ ,  $CO_3^{2-}$

$AX_2E$

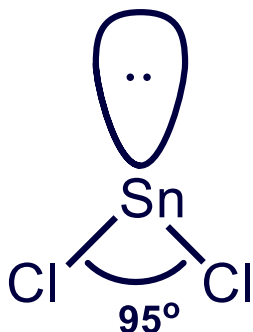


Examples:  
 $SO_2$ ,  $O_3$ ,  $PbCl_2$ ,  $SnBr_2$



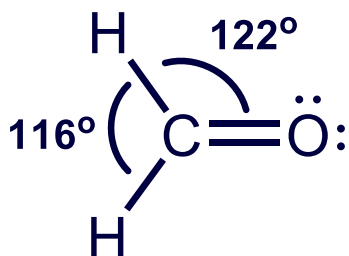
# Factors Affecting Bond Angles

## Nonbonding (Lone) Pairs



A lone pair repels bonding pairs more strongly than bonding pairs repel each other. This decreases the angle between the bonding pairs.

## Double Bonds



The ideal angle is 120°.

A double bond has greater electron density than a single bond, and repels the single bond electrons more than they repel each other.

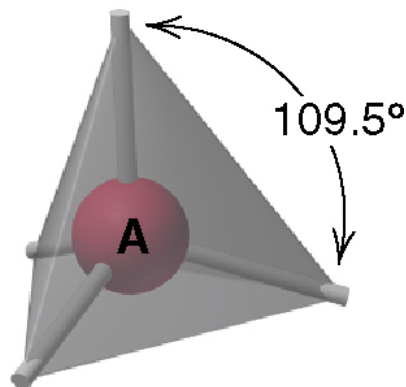


Figure 9.5

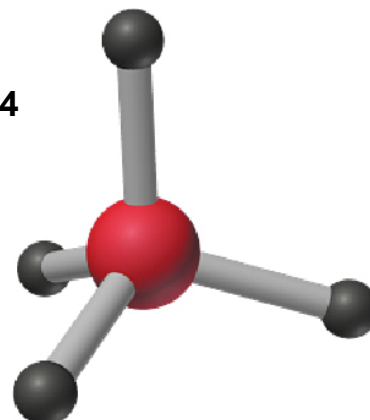
## The three molecular shapes of the tetrahedral electron-group arrangement.

Copyright © The McGraw-Hill Companies, Inc. Permission required for reproduction or display.

TETRAHEDRAL



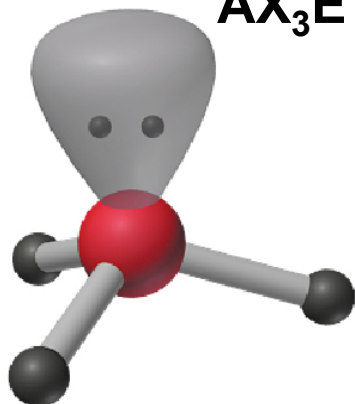
$AX_4$



Tetrahedral

Examples:  
 $CH_4$ ,  $SiCl_4$ ,  
 $SO_4^{2-}$ ,  $ClO_4^-$

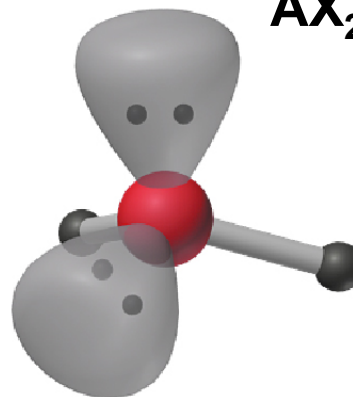
$AX_3E$



Trigonal pyramidal

Examples:  
 $NH_3$ ,  $PF_3$   
 $ClO_3^-$ ,  $H_3O^+$

$AX_2E_2$



Bent (V shaped)

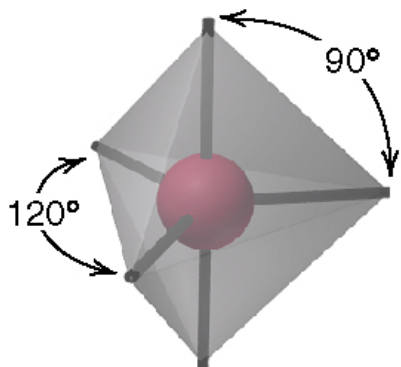
Examples:  
 $H_2O$ ,  $OF_2$ ,  $SCl_2$



## Figure 9.7 The four molecular shapes of the trigonal bipyramidal electron-group arrangement.

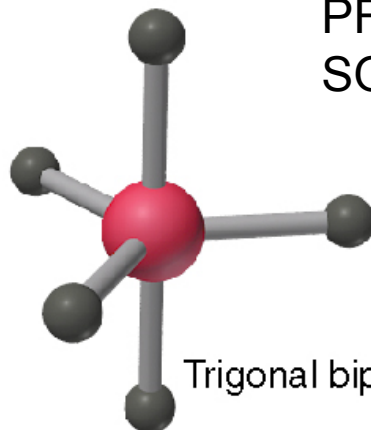
Copyright © The McGraw-Hill Companies, Inc. Permission required for reproduction or display.

TRIGONAL BIPYRAMIDAL



**AX<sub>5</sub>**

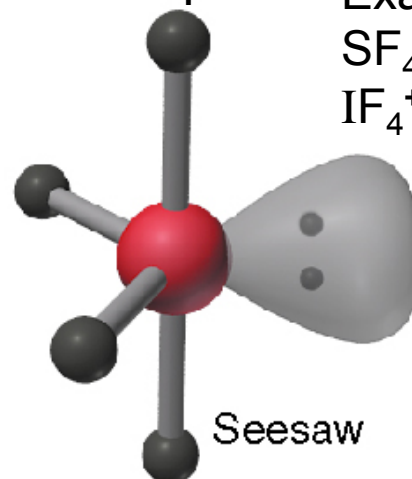
Examples:  
PF<sub>5</sub>, AsF<sub>5</sub>,  
SOF<sub>4</sub>



Trigonal bipyramidal

**AX<sub>4</sub>E**

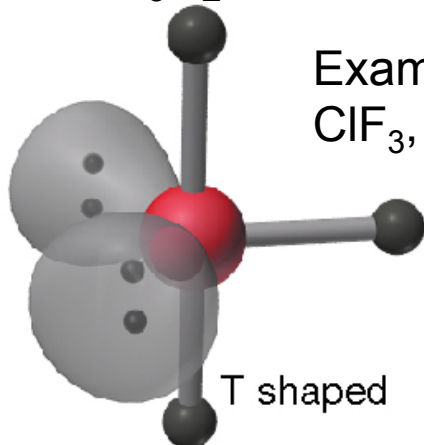
Examples:  
SF<sub>4</sub>, XeO<sub>2</sub>F<sub>2</sub>  
IF<sub>4</sub><sup>+</sup>, IO<sub>2</sub>F<sub>2</sub><sup>-</sup>



Seesaw

**AX<sub>3</sub>E<sub>2</sub>**

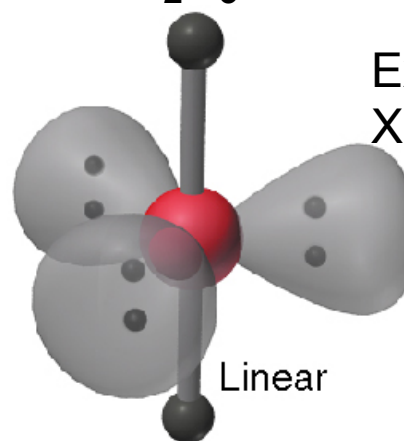
Examples:  
ClF<sub>3</sub>, BrF<sub>3</sub>



T shaped

**AX<sub>2</sub>E<sub>3</sub>**

Examples:  
XeF<sub>2</sub>, I<sub>3</sub><sup>-</sup>, IF<sub>2</sub><sup>-</sup>

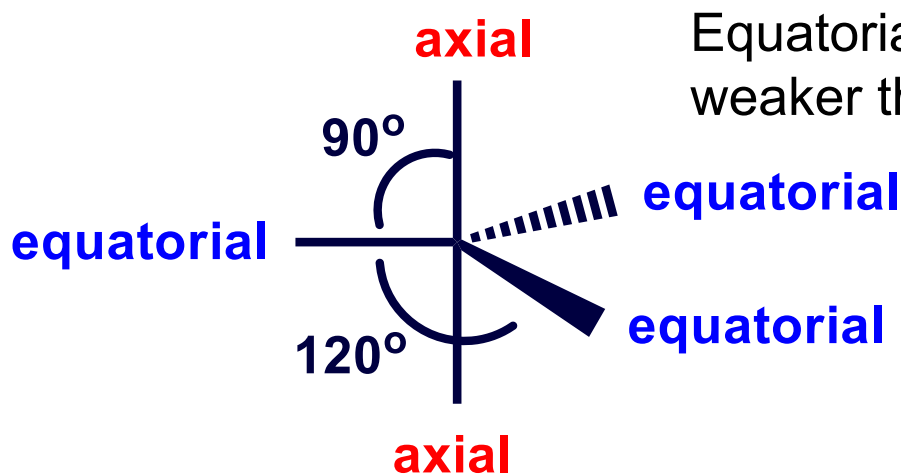


Linear



# Axial and Equatorial Positions

A five electron-group system has two different positions for electron groups, and two ideal bond angles.



Equatorial-equatorial repulsions are weaker than axial-equatorial repulsions.

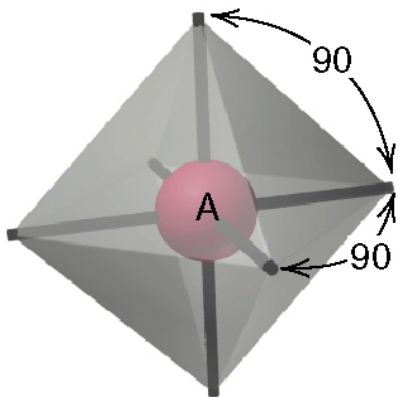
Where possible, lone pairs in a five electron-group system occupy ***equatorial*** positions.



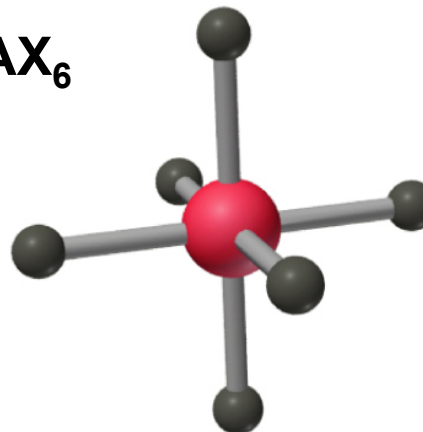
## Figure 9.8 The three molecular shapes of the octahedral electron-group arrangement.

Copyright © The McGraw-Hill Companies, Inc. Permission required for reproduction or display.

OCTAHEDRAL



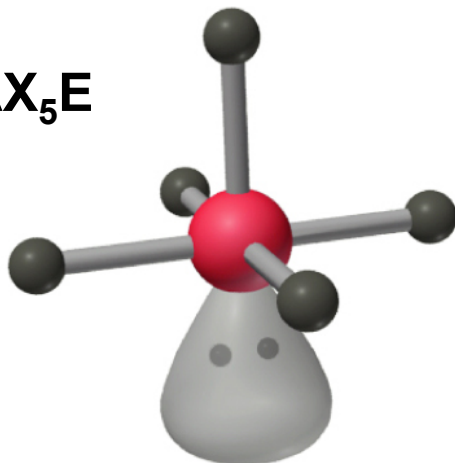
$AX_6$



Octahedral

Examples:  
 $SF_6$ ,  $IOF_5$

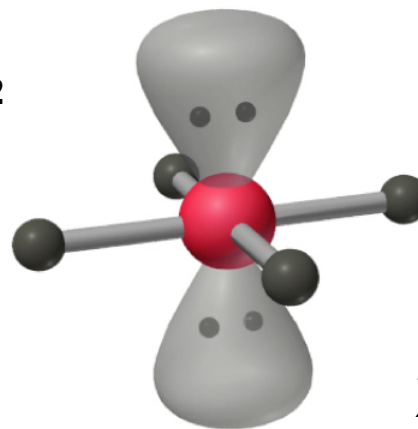
$AX_5E$



Square pyramidal

Examples:  
 $BrF_5$ ,  $TeF_5^-$ ,  
 $XeOF_4$

$AX_4E_2$



Square planar

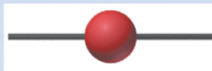
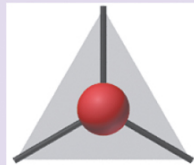
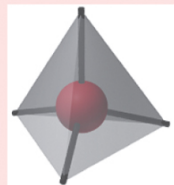

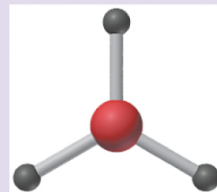
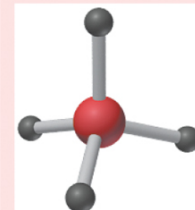
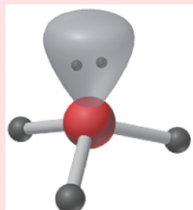
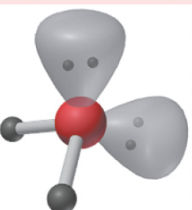
Examples:  
 $XeF_4$ ,  $ICl_4^-$





# Figure 9.10 A summary of common molecular shapes with two to six electron groups.

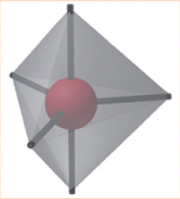
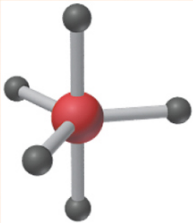
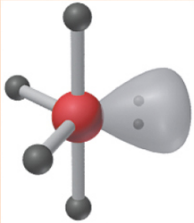
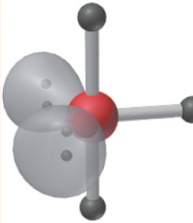
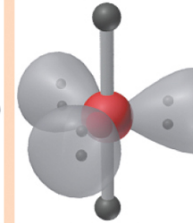
Copyright © The McGraw-Hill Companies, Inc. Permission required for reproduction or display.

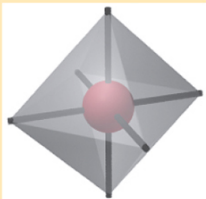
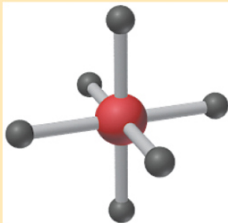
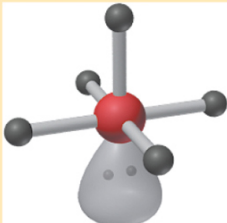
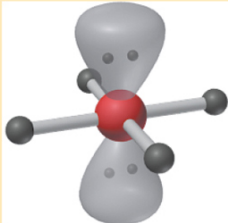
e <sup>-</sup> Group arrangement (no. of groups)	 Linear (2)		 Trigonal planar (3)		 Tetrahedral (4)				
Molecular shape (class)	 Linear (AX <sub>2</sub> )		 Trigonal planar (AX <sub>3</sub> )		 Tetrahedral (AX <sub>4</sub> )			 Trigonal pyramidal (AX <sub>3</sub> E)	 V shaped or bent (AX <sub>2</sub> E <sub>2</sub> )
No. of bonding groups	2		3		4			3	2
Bond angle	180°		120°		109.5°			<109.5°	<109.5°



# Figure 9.10 continued

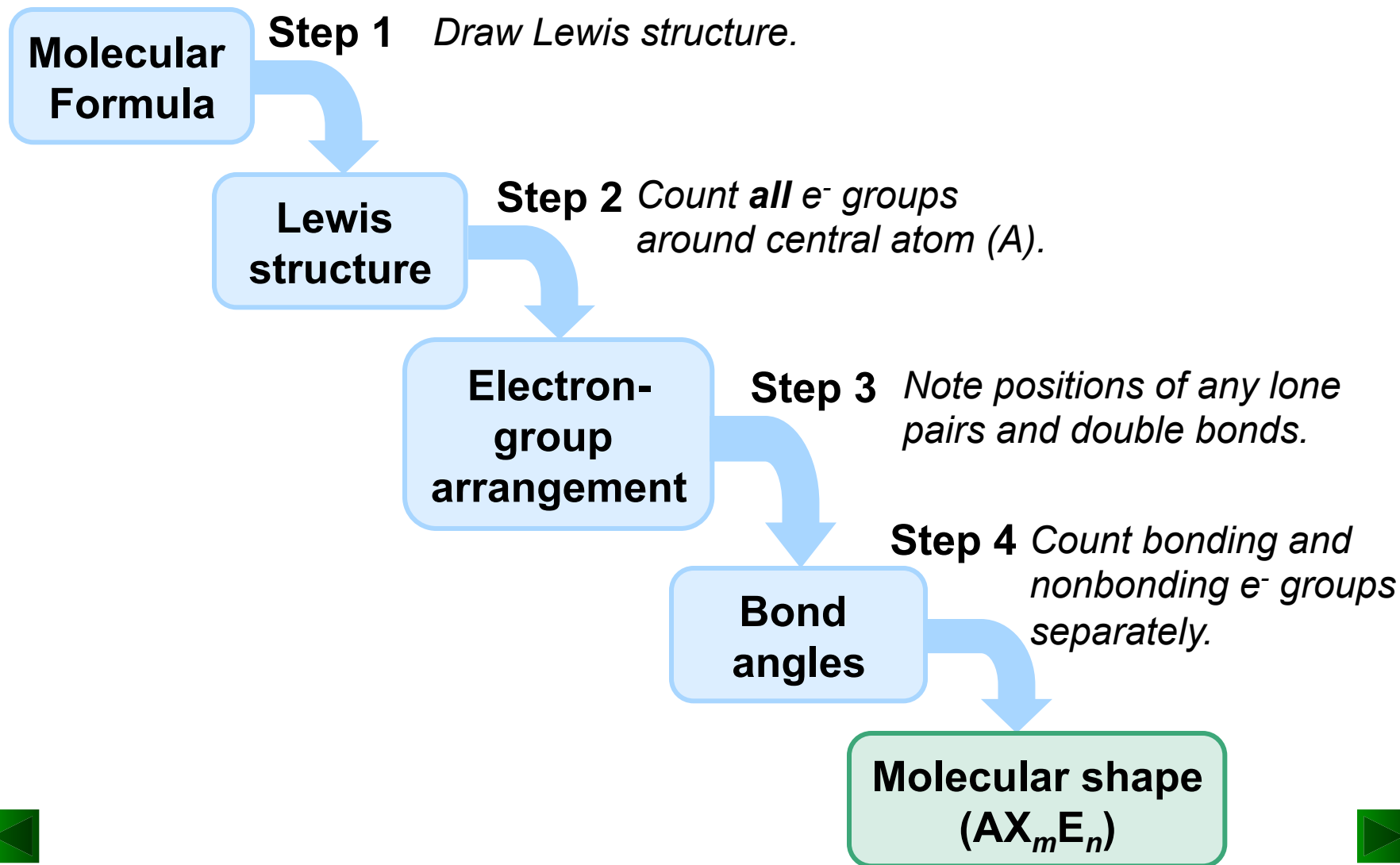
Copyright © The McGraw-Hill Companies, Inc. Permission required for reproduction or display.

e <sup>-</sup> Group arrangement (no. of groups)	 Trigonal bipyramidal (5)			
Molecular shape (class)	 Trigonal bipyramidal (AX <sub>5</sub> )	 Seesaw (AX <sub>4</sub> E)	 T shaped (AX <sub>3</sub> E <sub>2</sub> )	 Linear (AX <sub>2</sub> E <sub>3</sub> )
No. of bonding groups	5	4	3	2
Bond angle	90° (ax) 120° (eq)	<90° (ax) <120° (eq)	<90° (ax)	180°

e <sup>-</sup> Group arrangement (no. of groups)	 Octahedral (6)		
Molecular shape (class)	 Octahedral (AX <sub>6</sub> )	 Square pyramidal (AX <sub>5</sub> E)	 Square planar (AX <sub>4</sub> E <sub>2</sub> )
No. of bonding groups	6	5	4
Bond angle	90°	<90°	90°



**Figure 9.11**     **The four steps in converting a molecular formula to a molecular shape**



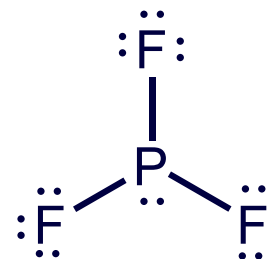
### Sample Problem 9.1

### Examining Shapes with Two, Three, or Four Electron Groups

**PROBLEM:** Draw the molecular shape and predict the bond angles (relative to the ideal bond angles) of **(a)**  $\text{PF}_3$  and **(b)**  $\text{COCl}_2$ .

### SOLUTION:

**(a)** For  $\text{PF}_3$ , there are 26 valence electrons.  
The Lewis structure is



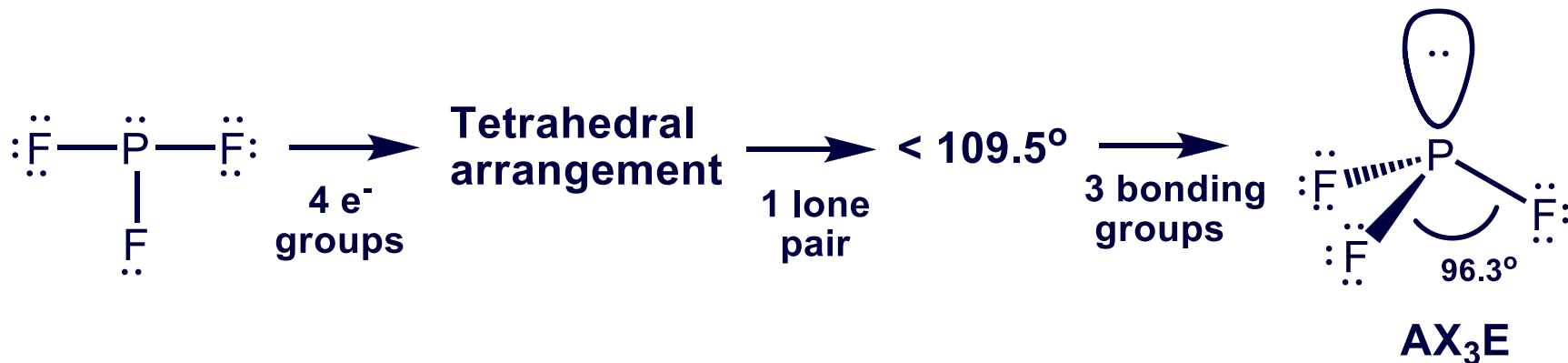
There are four electron groups around P, giving a tetrahedral electron-group arrangement. **The ideal bond angle is therefore  $109.5^\circ$ .**

There is one lone pair and three bonding pairs, so the actual bond angle will be **less than  $109.5^\circ$ .**



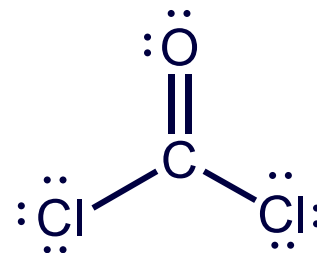
## Sample Problem 9.1

The molecular shape for  $\text{PF}_3$  is **trigonal pyramidal** ( $\text{AX}_3\text{E}$ ).

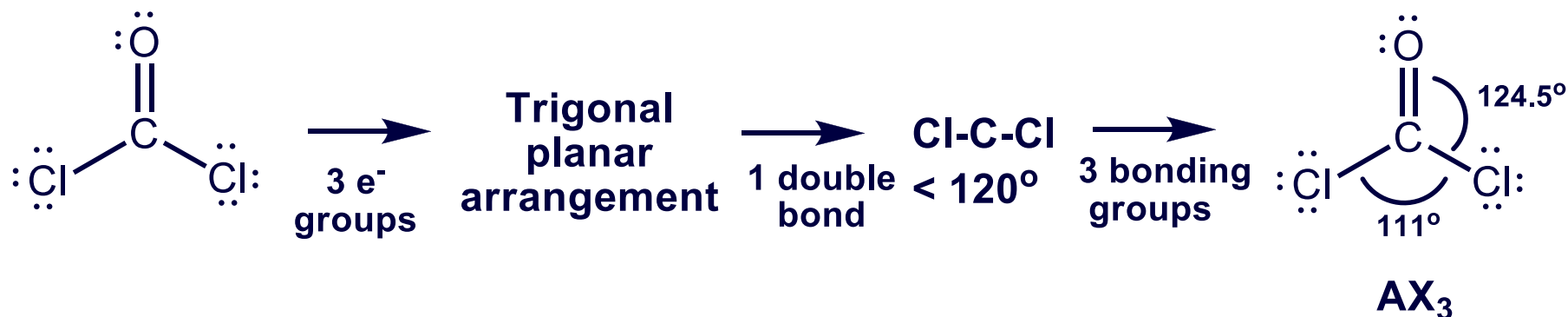


## Sample Problem 9.1

(b) For  $\text{COCl}_2$  there are 24 valence  $e^-$ . The Lewis structure is



There are three electron groups around C, giving a trigonal planar electron-group arrangement. **The ideal bond angle is  $120^\circ$** , but the double bond will compress the Cl-C-Cl angle to **less than  $120^\circ$** .



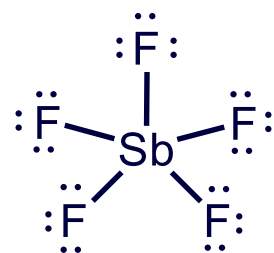
## Sample Problem 9.2

## Examining Shapes with Five or Six Electron Groups

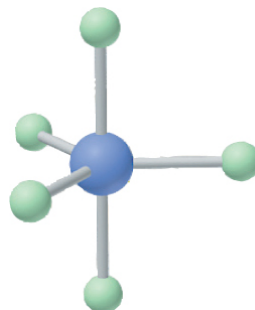
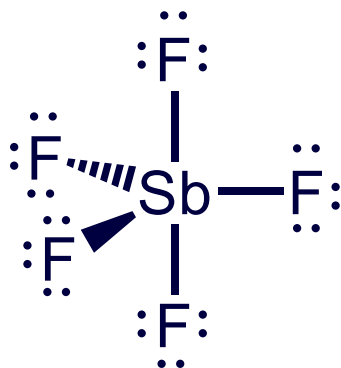
**PROBLEM:** Draw the molecular shapes and predict the bond angles (relative to the ideal bond angles) of **(a)**  $\text{SbF}_5$  and **(b)**  $\text{BrF}_5$ .

### SOLUTION:

**(a)**  $\text{SbF}_5$  has 40 valence  $e^-$ .  
The Lewis structure is

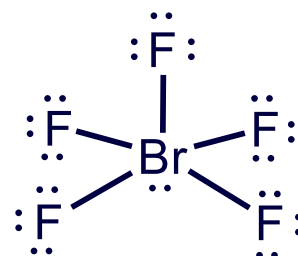


There are five electron groups around Sb, giving a trigonal bipyramidal electron-group arrangement. **The ideal bond angles are  $120^\circ$  between equatorial groups and  $90^\circ$  between axial groups.**

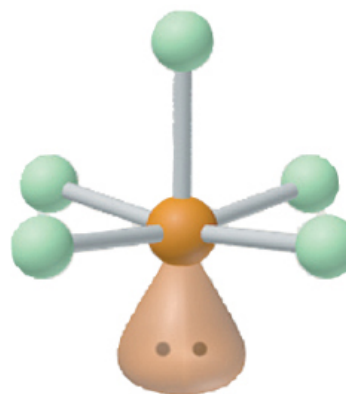
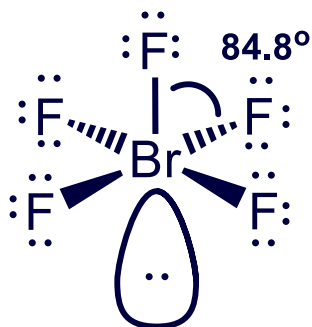


## Sample Problem 9.2

- (b)  $\text{BrF}_5$  has 42 valence  $e^-$ .  
The Lewis structure is



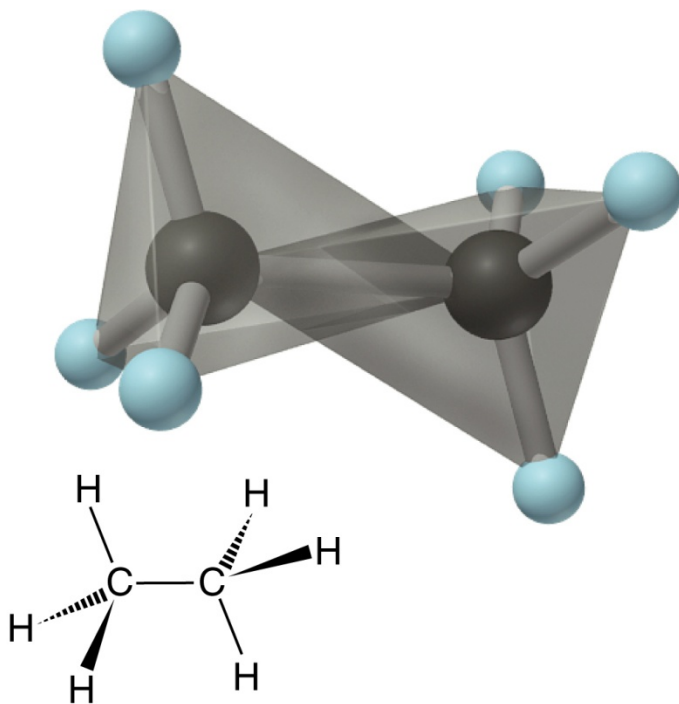
There are six electron groups around Br, giving an octahedral electron-group arrangement. **The ideal bond angles are  $90^\circ$ .** There is one lone pair, so the bond angles will be **less than  $90^\circ$**  and the molecular shape is **square pyramidal**.





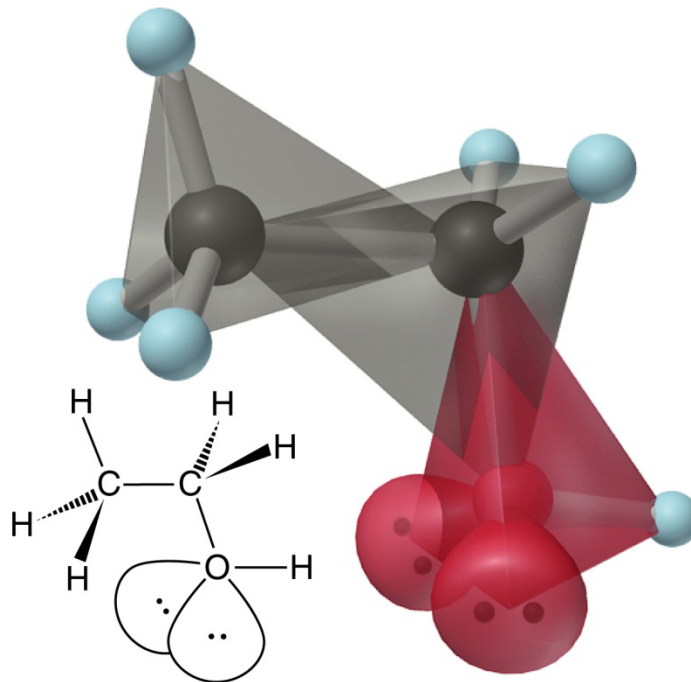
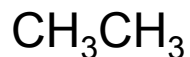
**Figure 9.12** The tetrahedral shapes around the central atoms and the overall shapes of ethane (A) and ethanol (B).

Copyright © The McGraw-Hill Companies, Inc. Permission required for reproduction or display.



**A**

ethane



**B**

ethanol



### Sample Problem 9.3

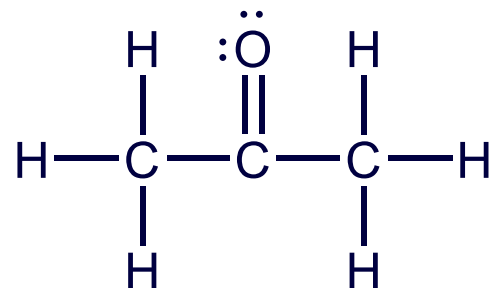
## Predicting Molecular Shapes with More Than One Central Atom

**PROBLEM:** Determine the shape around each of the central atoms in acetone,  $(\text{CH}_3)_2\text{CO}$ .

**PLAN:** There are three central C atoms, two of which are in  $\text{CH}_3$ – groups. We determine the shape around one central atom at a time.

**SOLUTION:**

Step 1: The Lewis structure is



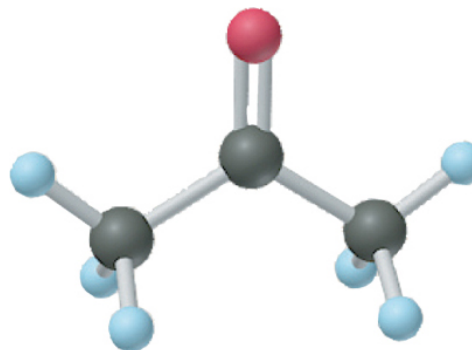
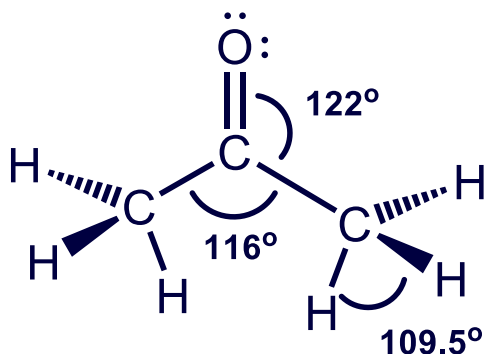
Step 2: Each  $\text{CH}_3$ – group has four electron groups around its central C, so the electron-group arrangement is *tetrahedral*. The third C atom has three electron groups around it, with a *trigonal planar* arrangement.



### Sample Problem 9.3

*Step 3:* The H-C-H bond angle in each CH<sub>3</sub>– group should be near the ideal value of 109.5°. The C=O double bond will compress the C-C-C angle to less than the ideal angle of 120°.

*Step 4:* The shape around the C in each CH<sub>3</sub>– group is **tetrahedral (AX<sub>4</sub>)**. The shape around the middle C is **trigonal planar (AX<sub>3</sub>)**.



Copyright © The McGraw-Hill Companies, Inc. Permission required for reproduction or display.



## 9.2 Molecular Shape and Molecular Polarity

Overall ***molecular polarity*** depends on both ***shape*** and ***bond polarity***.

The polarity of a molecule is measured by its ***dipole moment*** ( $\mu$ ), which is given in the unit *debye* (D).

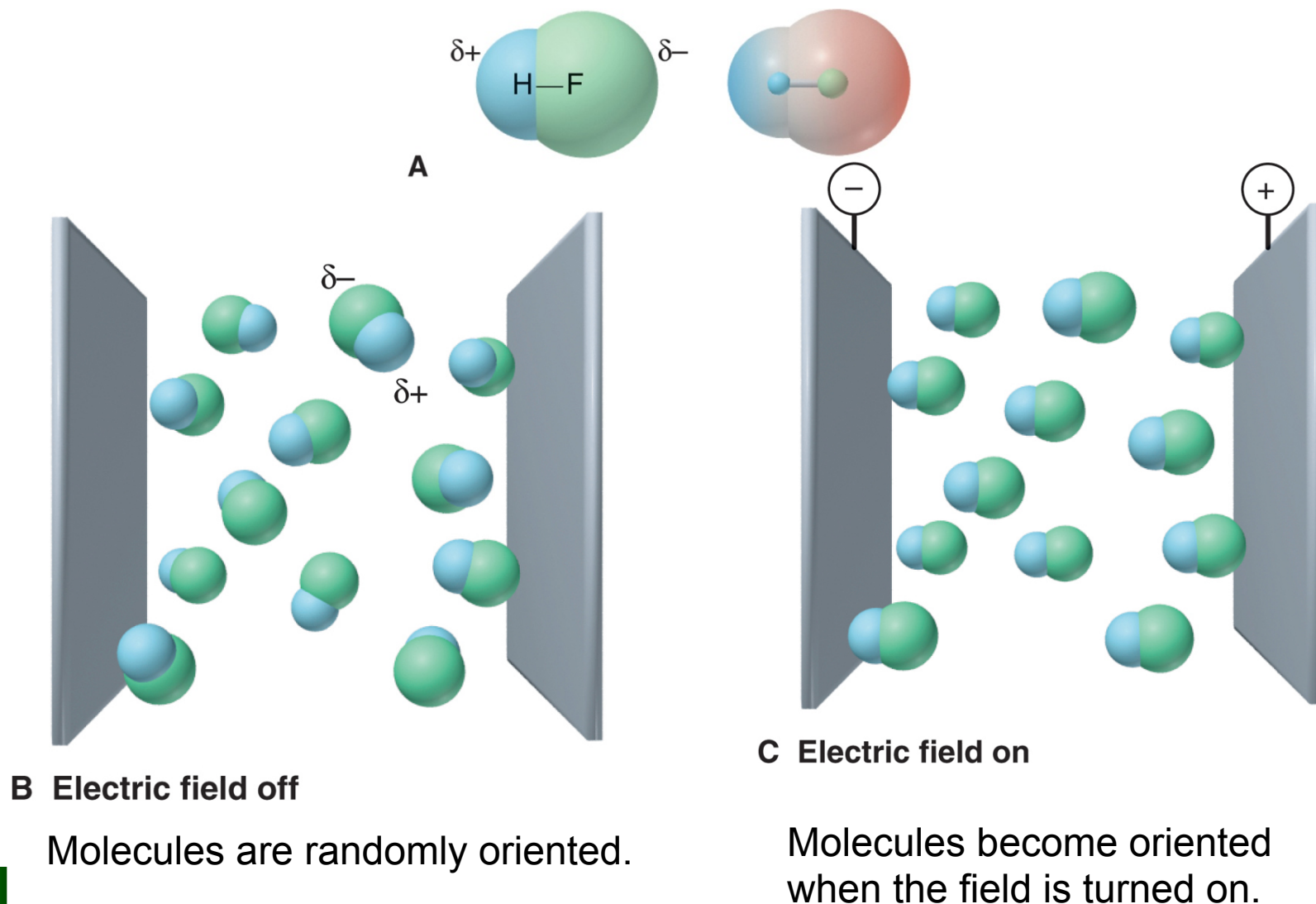
A molecule is polar if

- it contains one or more ***polar bonds*** and
- the individual bond dipoles ***do not cancel***.



## Figure 9.13 The orientation of polar molecules in an electric field.

Copyright © The McGraw-Hill Companies, Inc. Permission required for reproduction or display.

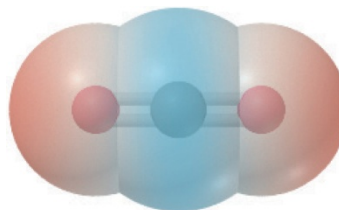
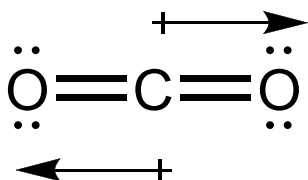


# Bond Polarity, Bond Angle, and Dipole Moment

Example: CO<sub>2</sub>

The  $\Delta\text{EN}$  between C (EN = 2.5) and O (EN = 3.5) makes each C=O bond polar.

Copyright © The McGraw-Hill Companies, Inc. Permission required for reproduction or display.



CO<sub>2</sub> is linear, the bond angle is 180°, and the individual bond polarities therefore cancel. The molecule has ***no net dipole moment*** ( $\mu = 0 \text{ D}$ ).

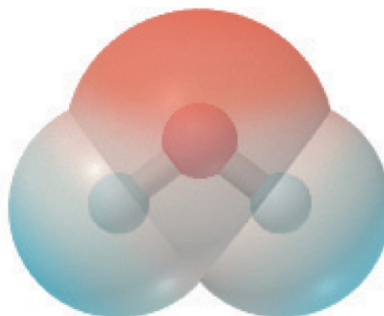
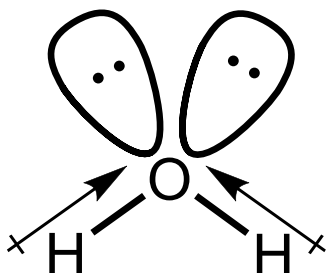


# Bond Polarity, Bond Angle, and Dipole Moment

Example:  $\text{H}_2\text{O}$

The  $\Delta\text{EN}$  between H (EN = 2.1) and O (EN = 3.5) makes each H-O bond polar.

Copyright © The McGraw-Hill Companies, Inc. Permission required for reproduction or display.

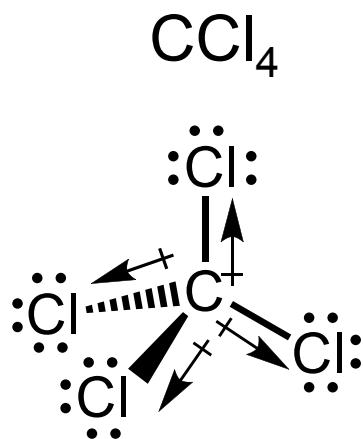


$\text{H}_2\text{O}$  has a V shaped geometry and the individual bond polarities do **not** cancel. This molecule has an ***overall molecular polarity***. The O is partially negative while the H atoms are partially positive.

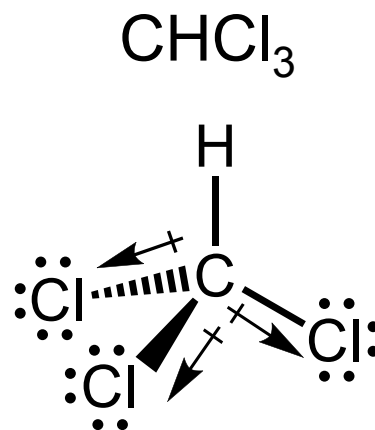


# Bond Polarity, Bond Angle, and Dipole Moment

Molecules with the same shape may have different polarities.



Bonds are polar, but individual bond polarities cancel.



Bond polarities do not cancel. This molecule is polar ( $\mu = 1.01 \text{ D}$ ).





## Sample Problem 9.4

## Predicting the Polarity of Molecules

**PROBLEM:** For each of the following use the molecular shape and EN values and trends (Figure 8.23) to predict the direction of bond and molecular polarity, if present.

- (a) Ammonia,  $\text{NH}_3$       (b) Boron trifluoride,  $\text{BF}_3$   
(c) Carbonyl sulfide,  $\text{COS}$  (atom sequence  $\text{SCO}$ )

**PLAN:** We draw and name the molecular shape, and mark each polar bond with a polar arrow pointing toward the atom with the higher EN. If bond polarities balance one another, the molecule is nonpolar. If they reinforce each other, we show the direction of overall molecular polarity.

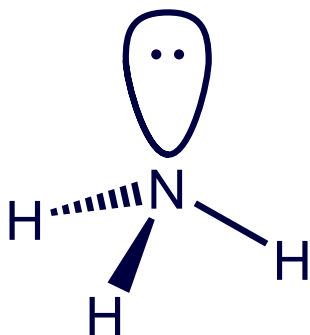


## Sample Problem 9.4

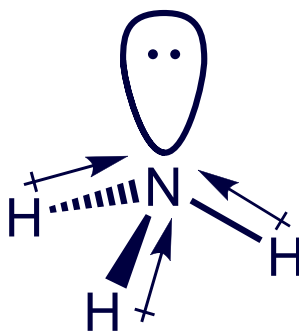
### SOLUTION:

(a)  $\text{NH}_3$  has 8 valence  $e^-$  and a trigonal pyramidal molecular shape.

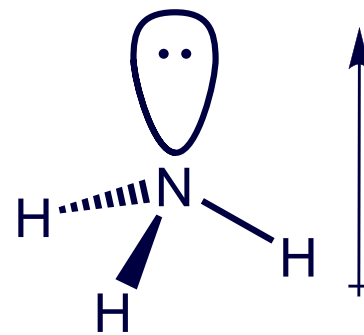
N (EN = 3.0) is more electronegative than H (EN = 2.1) so bond polarities point towards N.



molecular shape



bond polarities



molecular polarity

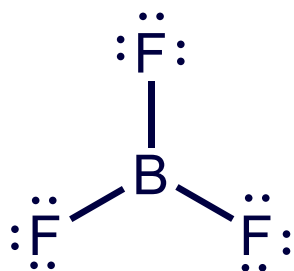
**Ammonia is polar overall.**



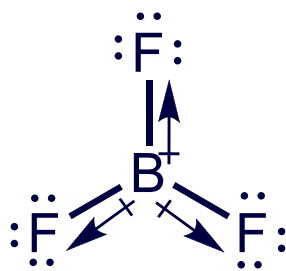
### Sample Problem 9.4

(b)  $\text{BF}_3$  has 24 valence  $e^-$  and a trigonal planar molecular shape.

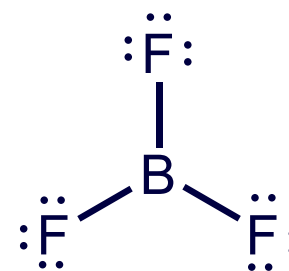
F (EN = 4.0) is more electronegative than B (EN = 2.0) so bond polarities point towards F.



**molecular shape**



**bond polarities**



**molecular polarity**

Individual bond polarities balance each other and  $\text{BF}_3$  has no molecular polarity.

**Boron trifluoride is nonpolar.**



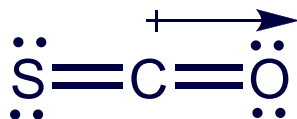
## Sample Problem 9.4

(c) COS has a linear shape.

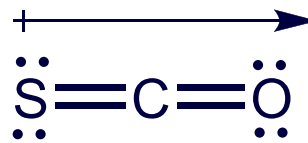
C and S have the same EN (2.5) but the C=O bond ( $\Delta\text{EN} = 1.0$ ) is quite polar.



molecular shape



bond polarities



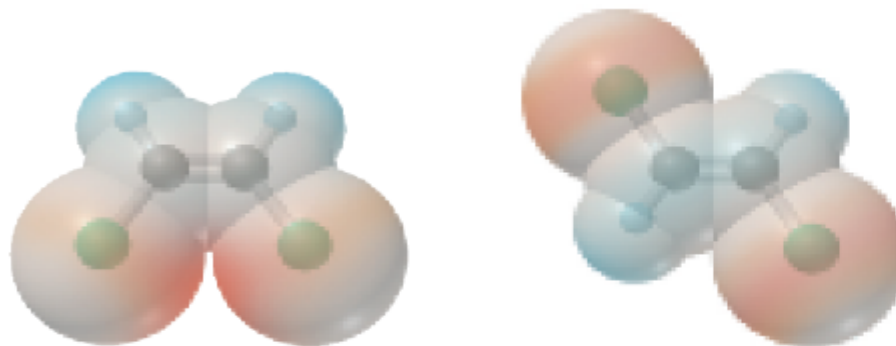
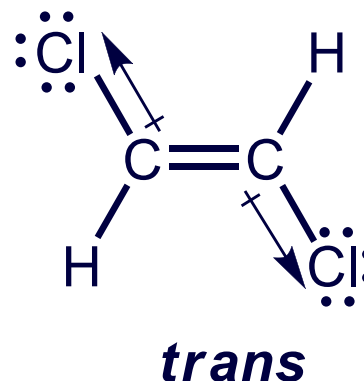
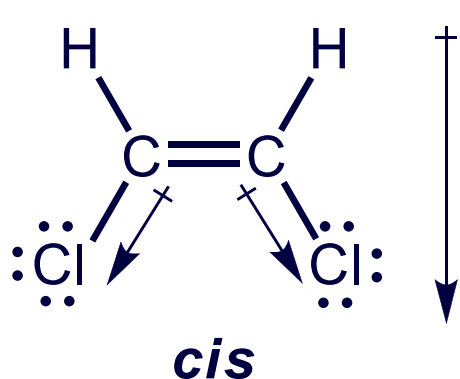
molecular polarity

**Carbonyl sulfide is polar overall.**



# The Effect of Molecular Polarity on Behavior

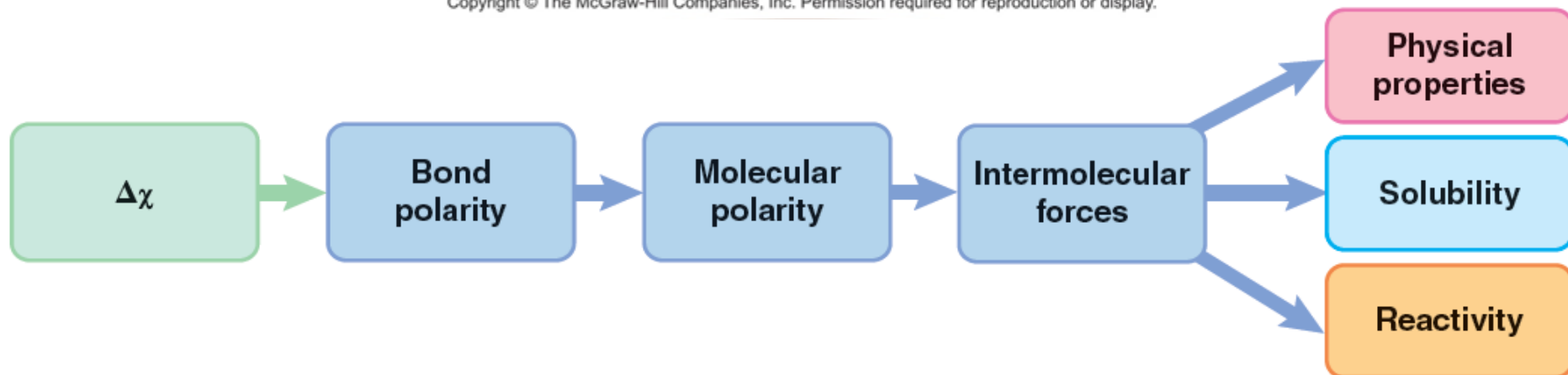
Example: The *cis* and *trans* isomers of  $C_2H_2Cl_2$



The *cis* isomer is polar while the *trans* isomer is not. The boiling point of the *cis* isomer boils is  $13^{\circ}C$  higher than that of the *trans* isomer.

**Figure 9.14**      **The influence of atomic properties on macroscopic behavior.**

Copyright © The McGraw-Hill Companies, Inc. Permission required for reproduction or display.



## **Chapter 10: Theories of Covalent Bonding**

- 10.1 Valence Bond (VB) Theory and Orbital Hybridization**
- 10.2 Modes of Orbital Overlap and the Types of Covalent Bonds**
- 10.3 Molecular Orbital (MO) Theory and Electron Delocalization**



## 10.1

# Valence Bond (VB) Theory

The basic principle of VB theory:

A covalent bond forms when the orbitals of two atoms ***overlap*** and a pair of electrons occupy the overlap region.

The space formed by the overlapping orbitals can accommodate a ***maximum of two electrons*** and these electrons must have ***opposite (paired) spins***.

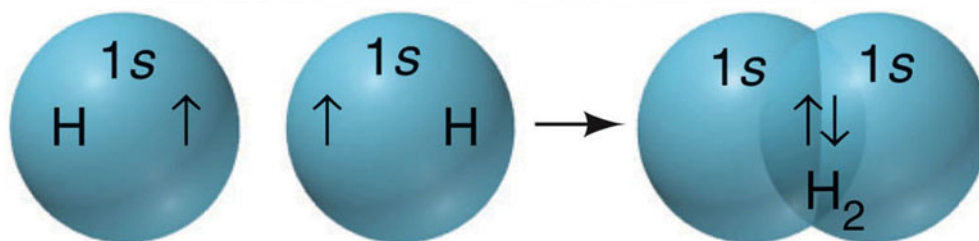
The greater the orbital overlap, the stronger the bond.

Extent of orbital overlap depends on orbital shape and direction.





**Figure 10.1      Orbital overlap and spin pairing in H<sub>2</sub>.**



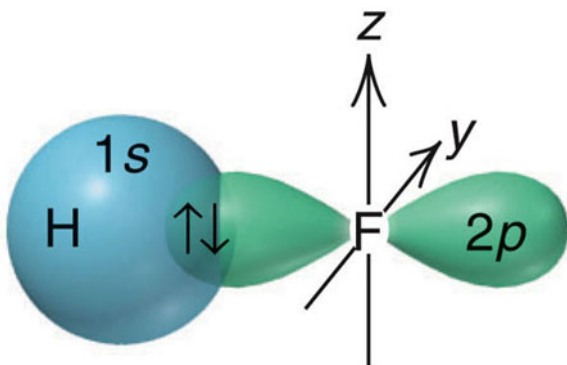
**A covalent bond results from the overlap of orbitals from two atoms.**

**The shared space is occupied by two electrons, which have opposite spins.**

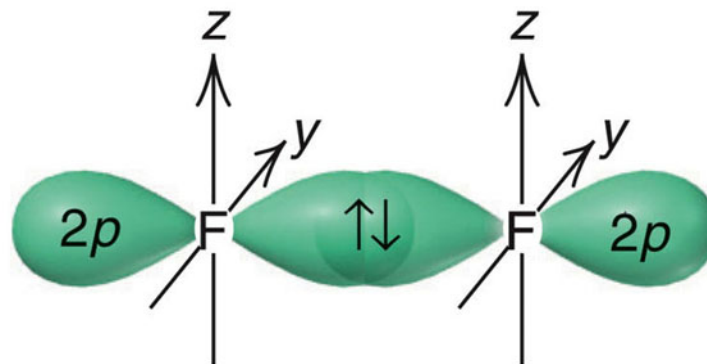


**Figure 10.2**

**Orbital orientation and maximum overlap.**



Hydrogen fluoride, HF.



Fluorine,  $F_2$ .

**The greater the extent of orbital overlap, the stronger the bond.**



# VB Theory and Orbital Hybridization

The orbitals that form when bonding occurs are ***different*** from the atomic orbitals in the isolated atoms.

If no change occurred, we could not account for the molecular shapes that are observed.

Atomic orbitals “mix” or ***hybridize*** when bonding occurs to form ***hybrid orbitals***.

The spatial orientation of these hybrid orbitals correspond with observed molecular shapes.



# Features of Hybrid Orbitals

The ***number*** of hybrid orbitals formed ***equals*** the number of atomic orbitals mixed.

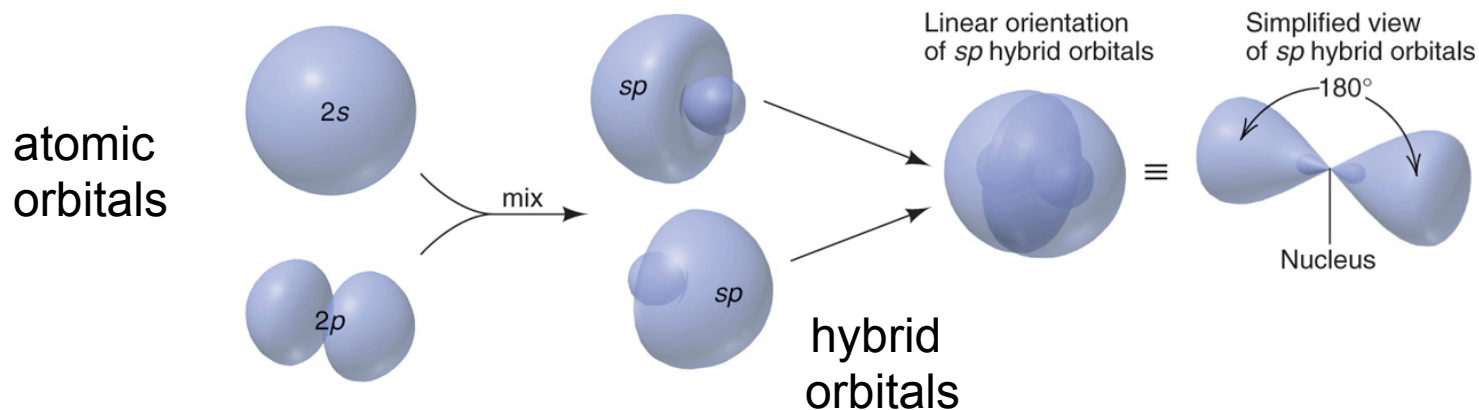
The ***type*** of hybrid orbitals formed ***varies*** with the types of atomic orbitals mixed.

The ***shape*** and ***orientation*** of a hybrid orbital ***maximizes*** overlap with the other atom in the bond.

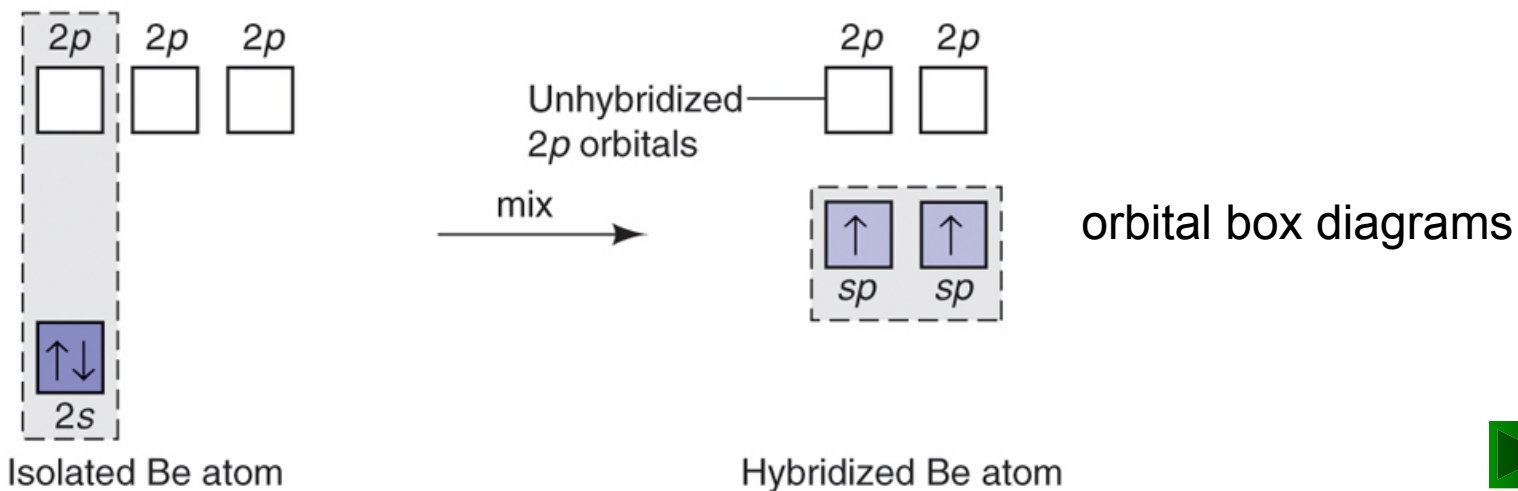


# Figure 10.3 Formation and orientation of $sp$ hybrid orbitals and the bonding in $\text{BeCl}_2$ .

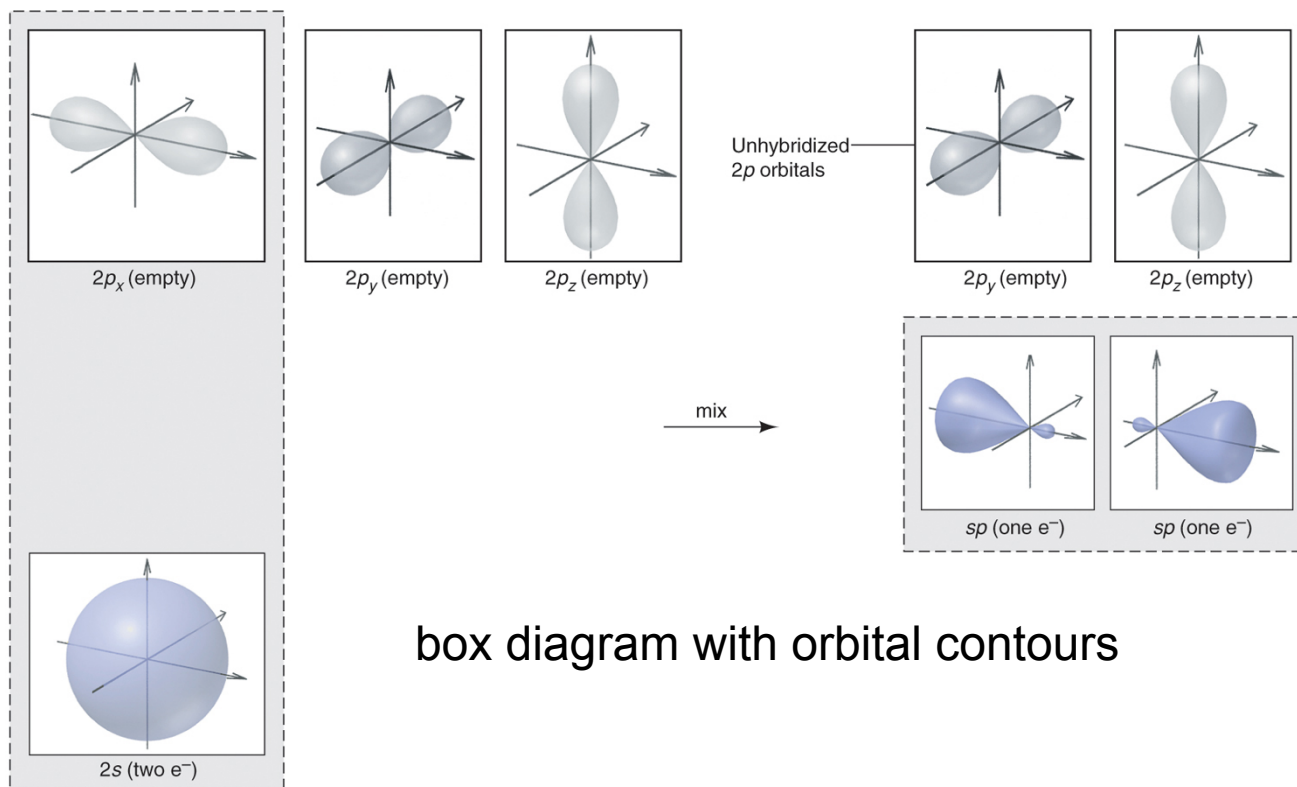
Copyright © The McGraw-Hill Companies, Inc. Permission required for reproduction or display.



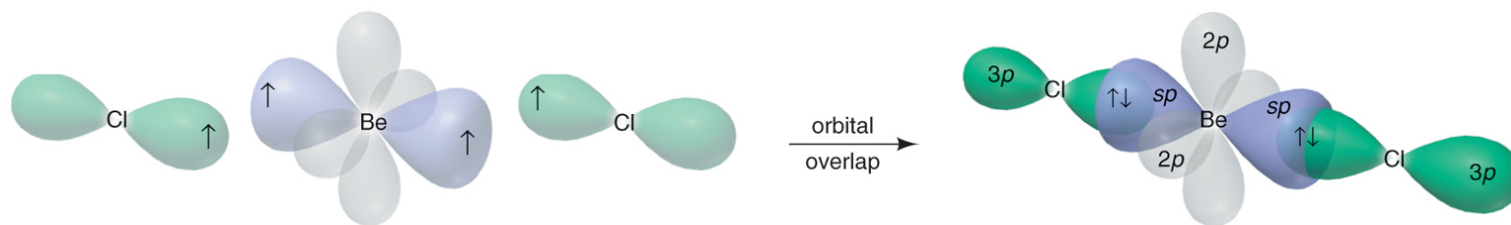
One  $2s$  and one  $2p$  atomic orbital mix to form two  $sp$  hybrid orbitals.



# Figure 10.3 continued



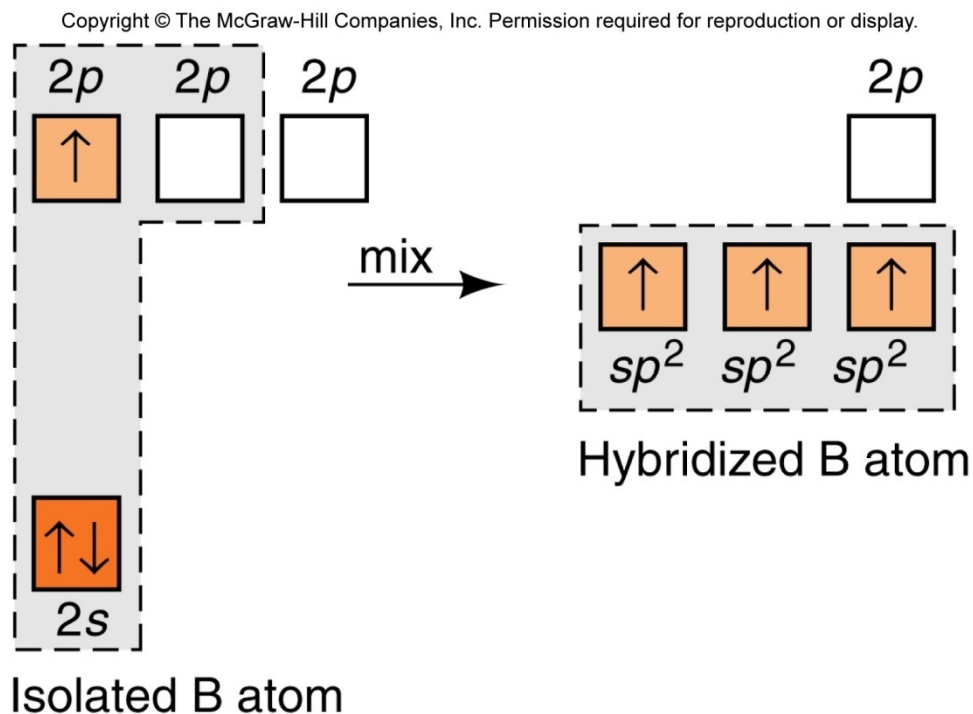
box diagram with orbital contours



Overlap of Be and Cl orbitals to form  $\text{BeCl}_2$ .

Figure 10.4

## The $sp^2$ hybrid orbitals in $\text{BF}_3$ .

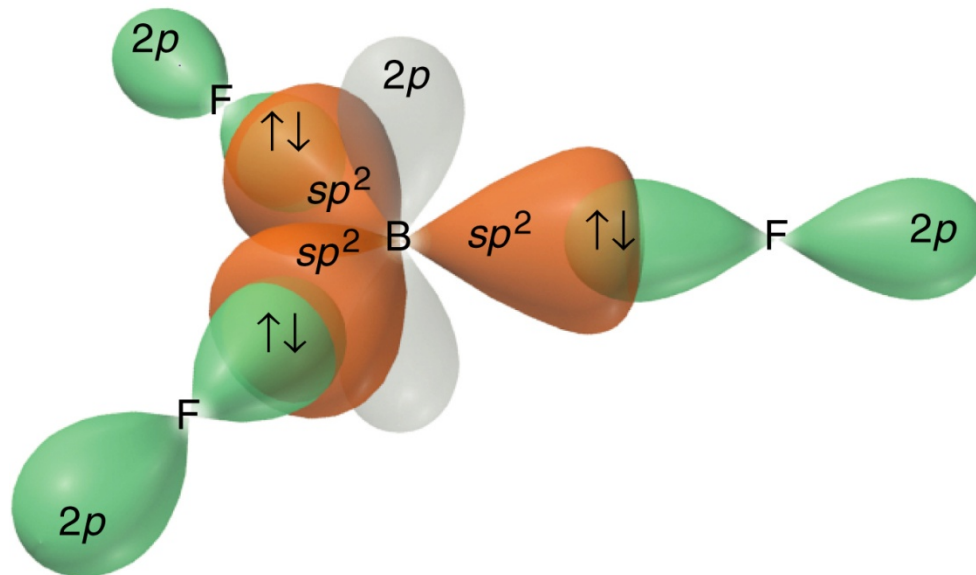


Mixing one  $s$  and two  $p$  orbitals gives three  $sp^2$  hybrid orbitals. The third  $2p$  orbital remains unhybridized.



## Figure 10.4 continued

Copyright © The McGraw-Hill Companies, Inc. Permission required for reproduction or display.



**The three  $sp^2$  orbitals point to the corners of an equilateral triangle, their axes  $120^\circ$  apart.**

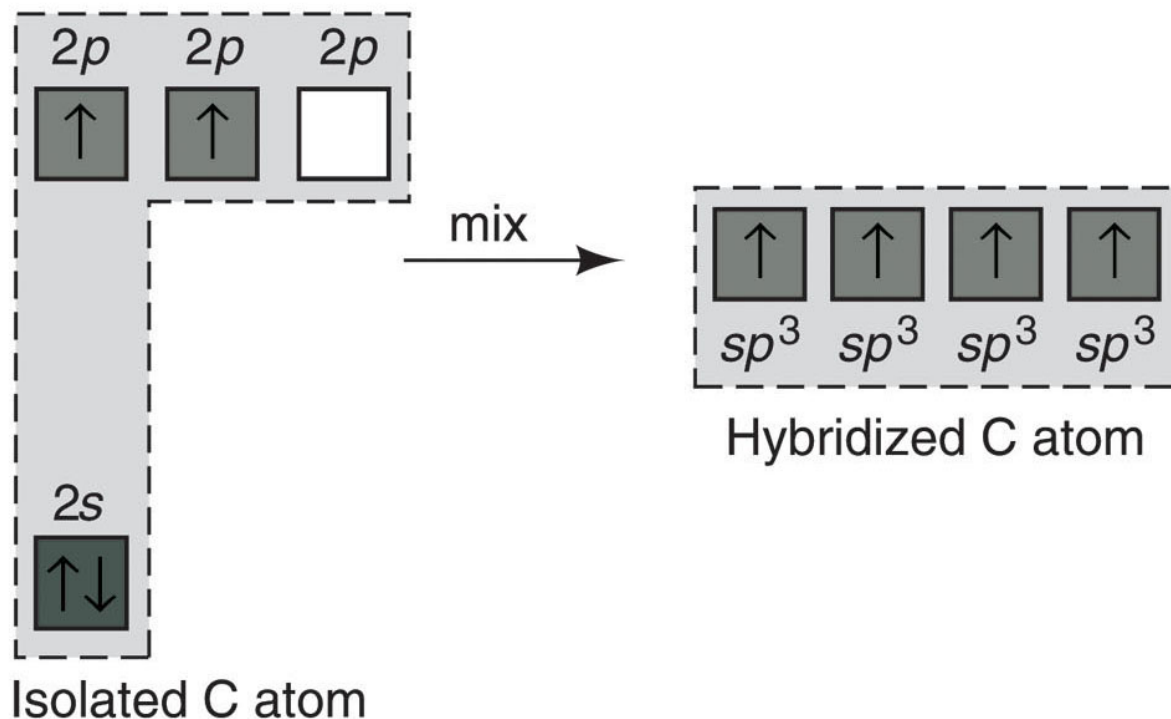
**Each half-filled  $sp^2$  orbital overlaps with the half-filled  $2p$  orbital of a F atom.**





**Figure 10.5**

**The  $sp^3$  hybrid orbitals in  $\text{CH}_4$ .**



**The four  $sp^3$  orbitals adopt a tetrahedral shape.**

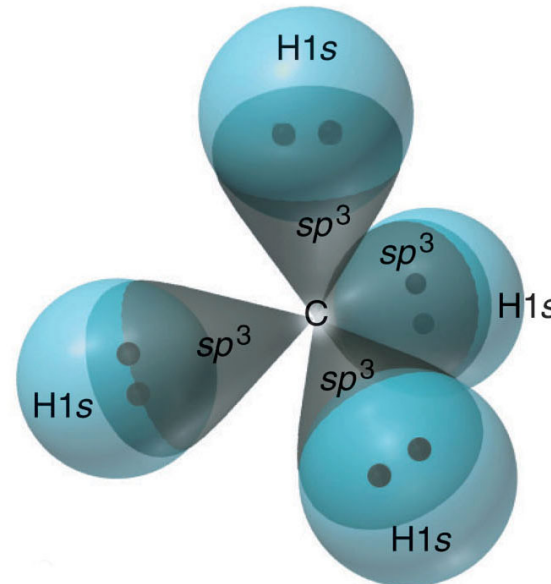
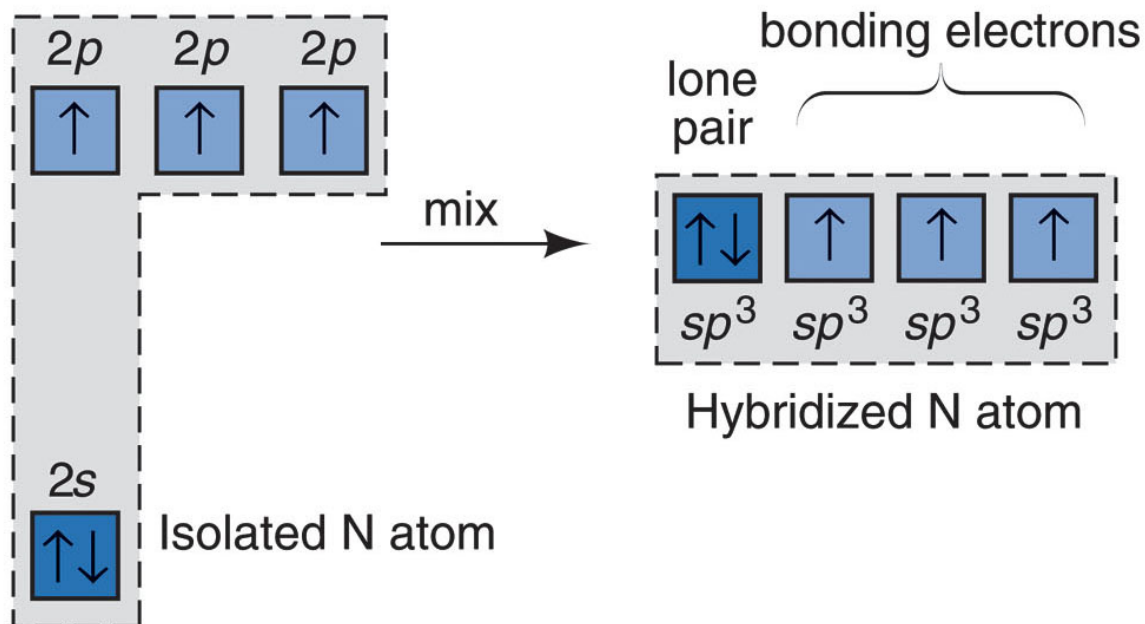


Figure 10.6

The  $sp^3$  hybrid orbitals in  $\text{NH}_3$ .



The N lone pair occupies an  $sp^3$  hybrid orbital, giving a trigonal pyramidal shape.

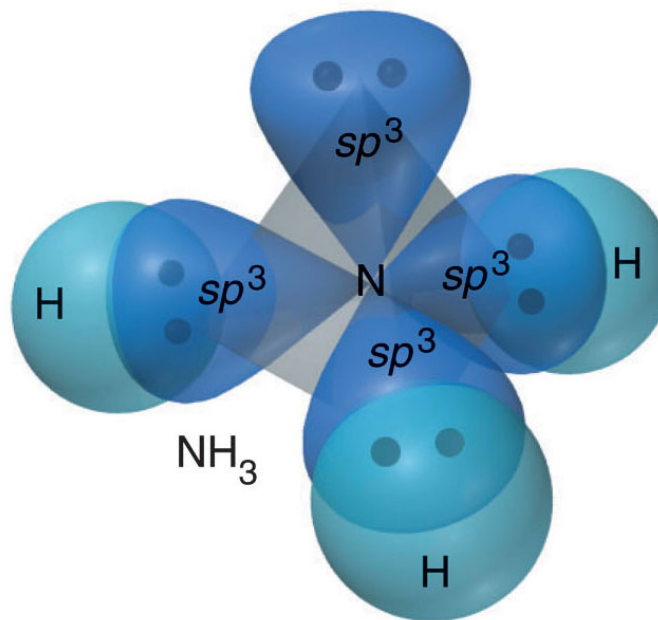
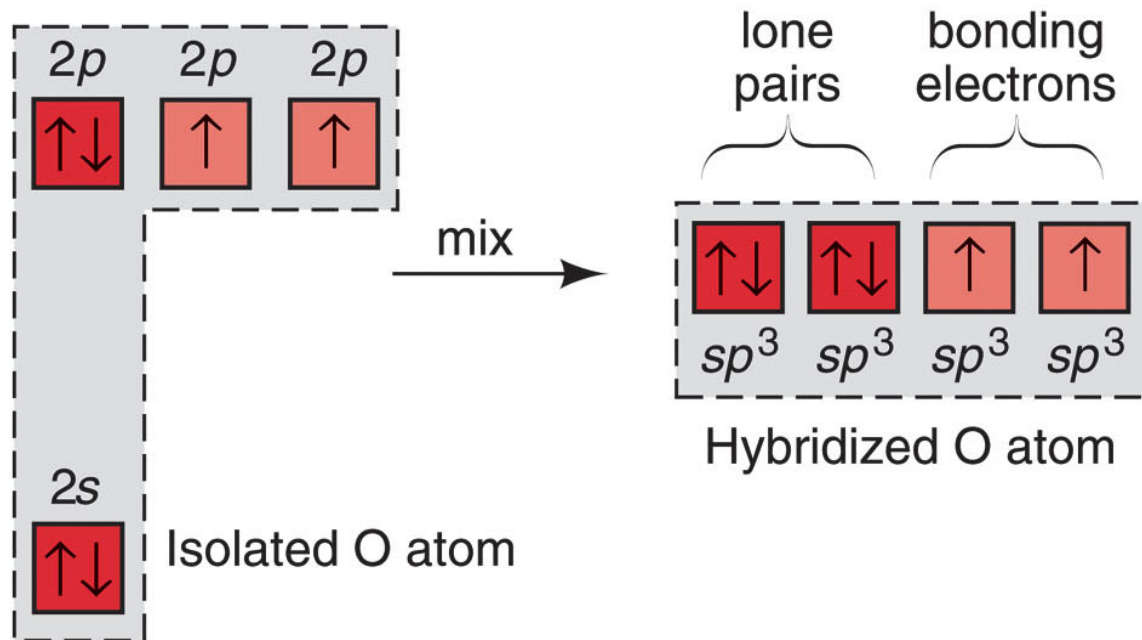
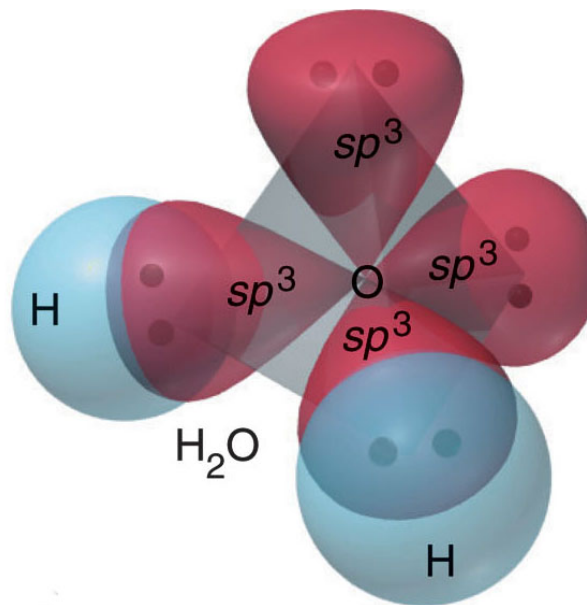


Figure 10.6 continued

## The $sp^3$ hybrid orbitals in $H_2O$ .



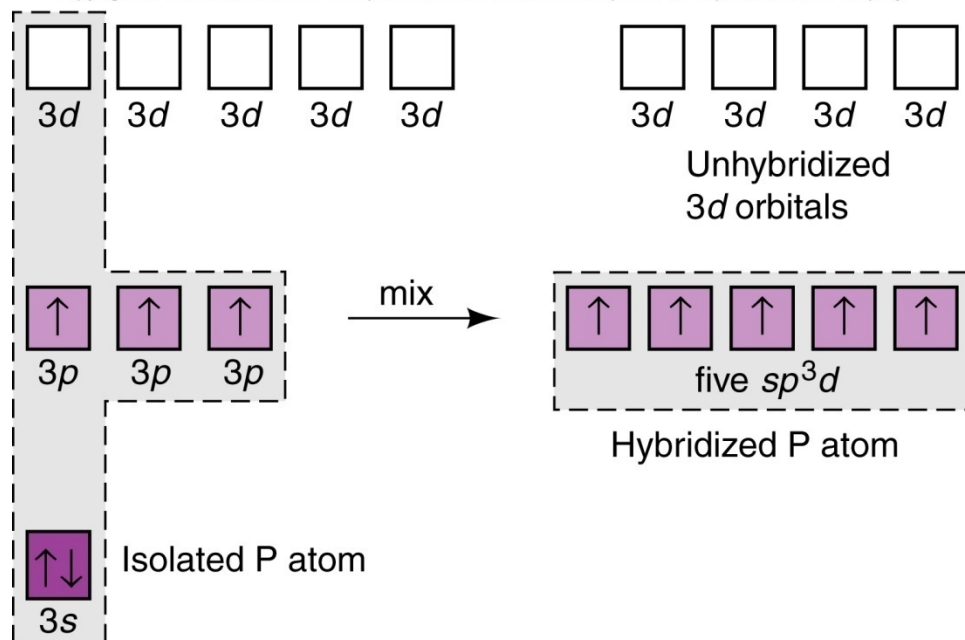
The O lone pairs occupy  $sp^3$  hybrid orbitals, giving a bent shape.



**Figure 10.7**

# **The $sp^3d$ hybrid orbitals in $\text{PCl}_5$ .**

Copyright © The McGraw-Hill Companies, Inc. Permission required for reproduction or display.



**A**

**The formation of more than four bonding orbitals requires  $d$  orbital involvement in hybridization.**

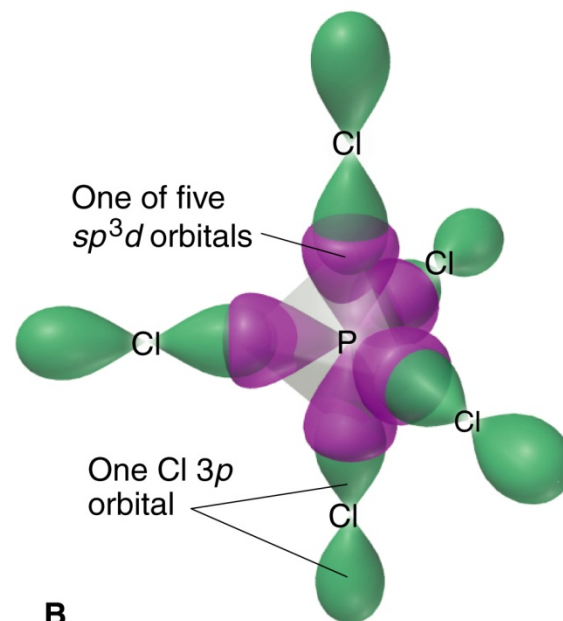
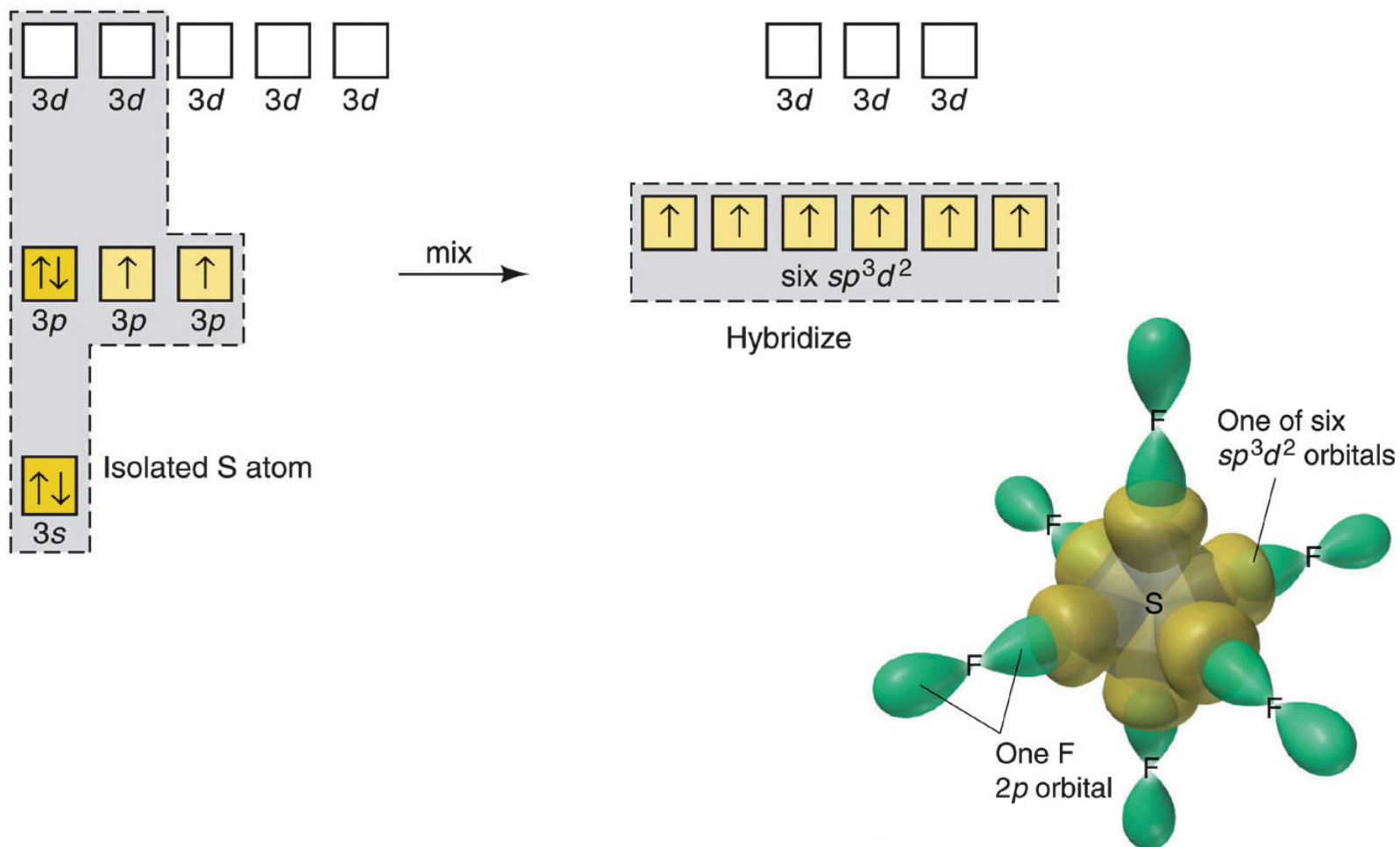
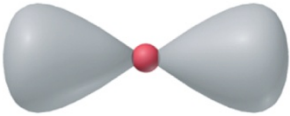
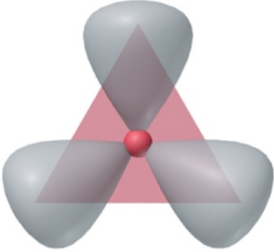
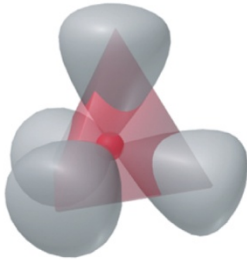
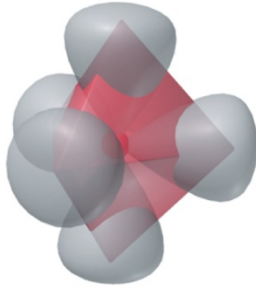
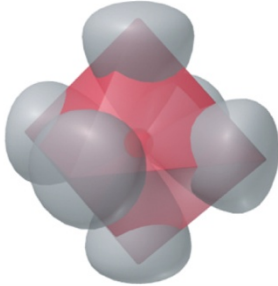


Figure 10.8

# The $sp^3d^2$ hybrid orbitals in $SF_6$ .

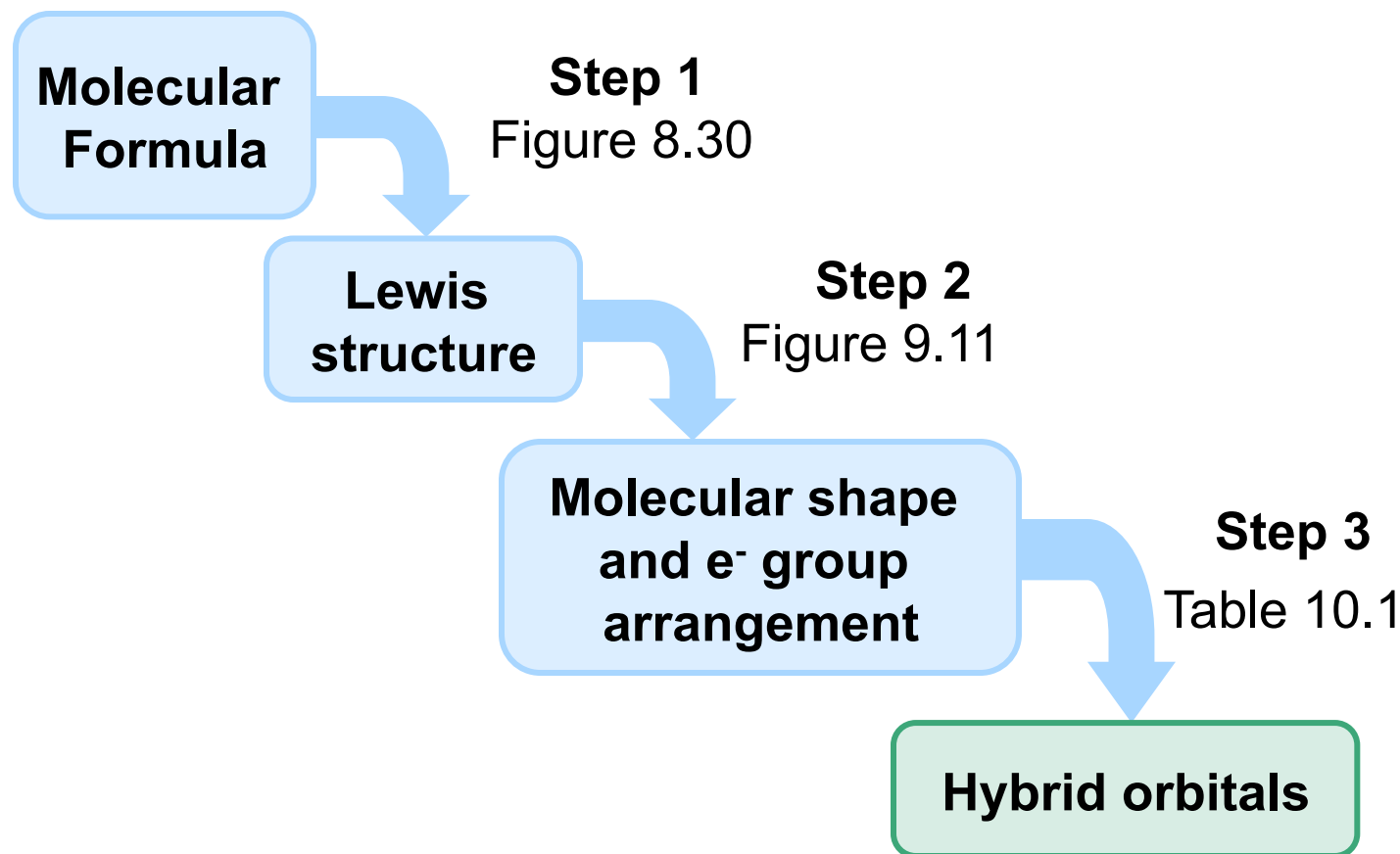


# Table 10.1 Composition and Orientation of Hybrid Orbitals

	Linear	Trigonal Planar	Tetrahedral	Trigonal Bipyramidal	Octahedral
Atomic orbitals mixed	one $s$ one $p$	one $s$ two $p$	one $s$ three $p$	one $s$ three $p$ one $d$	one $s$ three $p$ two $d$
Hybrid orbitals formed	two $p$	three $sp^2$	four $sp^3$	five $sp^3d$	six $sp^3d^2$
Unhybridized orbitals remaining	two $p$	one $p$	none	four $d$	three $d$
Orientation					



**Figure 10.9 From molecular formula to hybrid orbitals.**



## Sample Problem 10.1

## Postulating Hybrid Orbitals in a Molecule

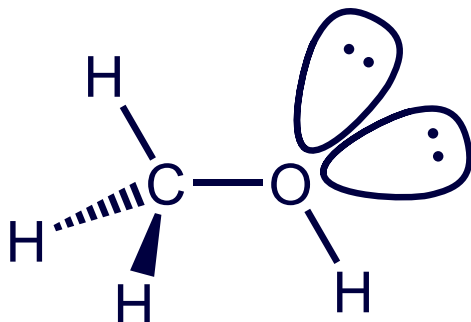
**PROBLEM:** Use partial orbital diagrams to describe how mixing of the atomic orbitals of the central atom(s) leads to hybrid orbitals in each of the following:

(a) Methanol,  $\text{CH}_3\text{OH}$       (b) Sulfur tetrafluoride,  $\text{SF}_4$

**PLAN:** We use the molecular formula to draw the Lewis structure and determine the electron-group arrangement around each central atom. We then postulate the type of hybrid orbitals required and write a partial orbital diagram.

**SOLUTION:**

(a)  $\text{CH}_3\text{OH}$

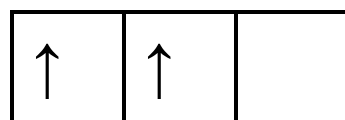


The electron-group arrangement is tetrahedral around both the C and the O atom.

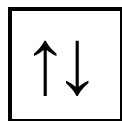




### Sample Problem 10.1

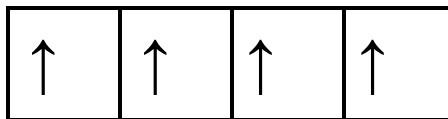


2p



2s

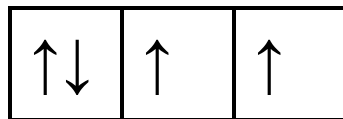
isolated C atom



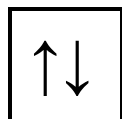
$sp^3$

hybridized C atom

C has four half-filled  $sp^3$  orbitals.

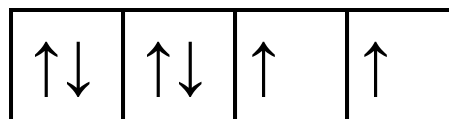


2p



2s

isolated O atom



$sp^3$

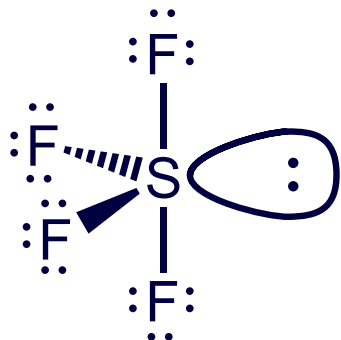
hybridized O atom

The O atom has two half-filled  $sp^3$  orbitals and two filled with lone pairs.

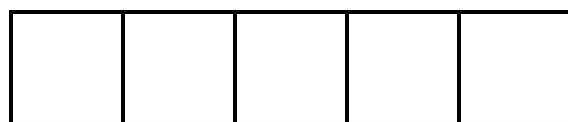


## Sample Problem 10.1

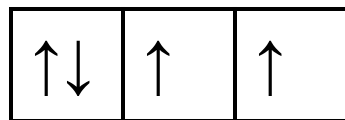
(b)  $\text{SF}_4$



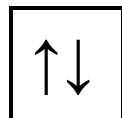
The electron-group arrangement is trigonal bipyramidal, so the central S atom is  $sp^3d$  hybridized.



$3d$

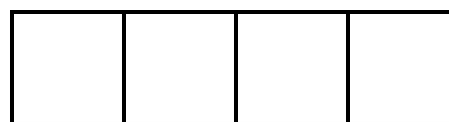


$3p$

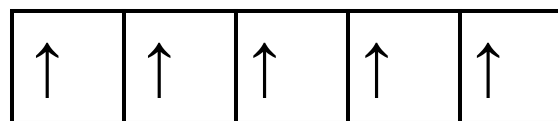


$3s$

isolated S atom



$3d$



$sp^3d$

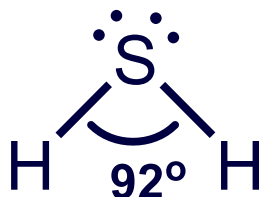
hybridized S atom



# Limitations of the Hybridization Model

Hybridization is not always consistent with observed molecular shapes.

This is particularly true for the bonding of larger atoms.



The bond angle in H<sub>2</sub>S is closer to the angle between unhybridized *p* orbitals.

*d*-Orbitals do not hybridize effectively with *s* and *p* orbitals, which are much lower in energy and more stable.



## 10.2

# Types of Covalent Bonds

A ***sigma*** ( $\sigma$ ) bond is formed by ***end-to-end*** overlap of orbitals.

***All single bonds are  $\sigma$  bonds.***

A ***pi*** ( $\pi$ ) bond is formed by ***sideways*** overlap of orbitals.

A  $\pi$  bond is weaker than a  $\sigma$  bond because sideways overlap is less effective than end-to-end overlap.

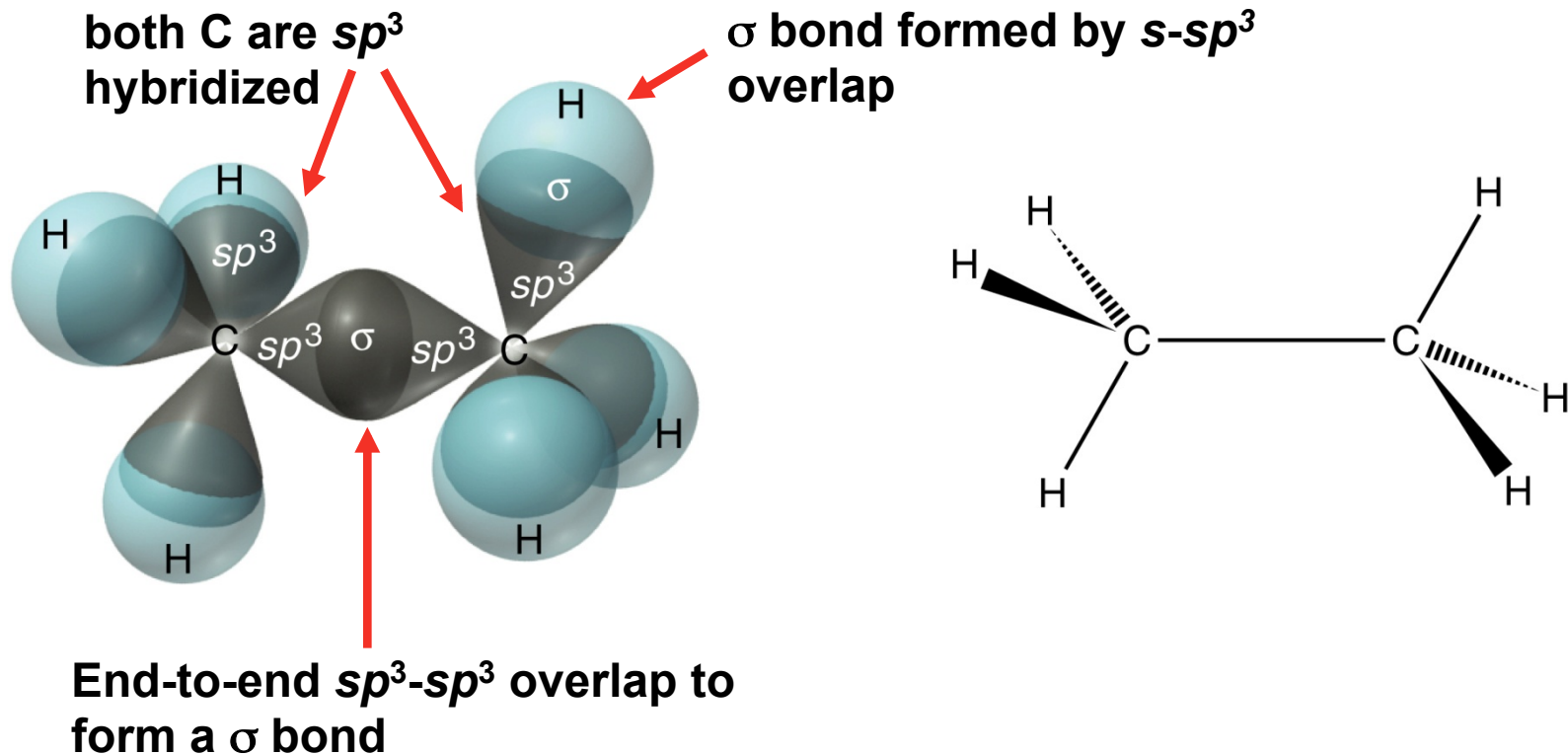
A double bond consists of one  $\sigma$  bond and one  $\pi$  bond



**Figure 10.10**

## The $\sigma$ bonds in ethane ( $\text{C}_2\text{H}_6$ ).

Copyright © The McGraw-Hill Companies, Inc. Permission required for reproduction or display.

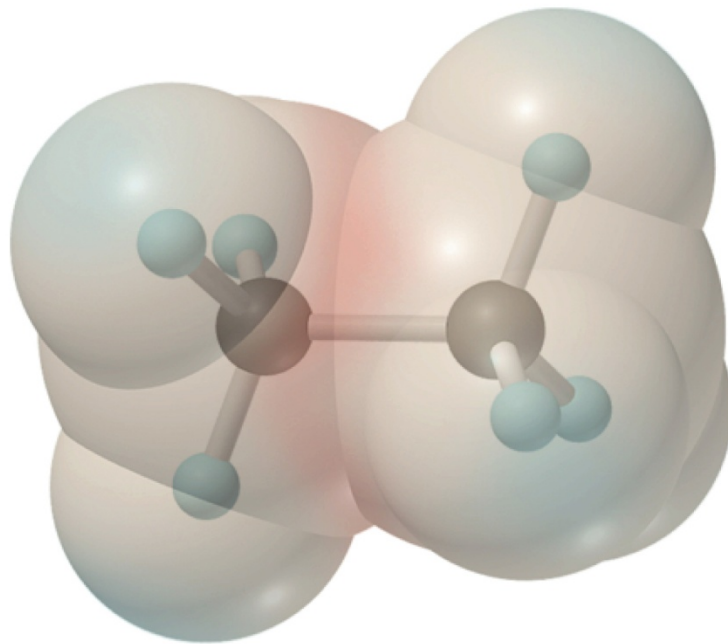


A  $\sigma$  bond is cylindrically symmetrical, with its highest electron density along the bond axis.



## Figure 10.10 continued

Copyright © The McGraw-Hill Companies, Inc. Permission required for reproduction or display.



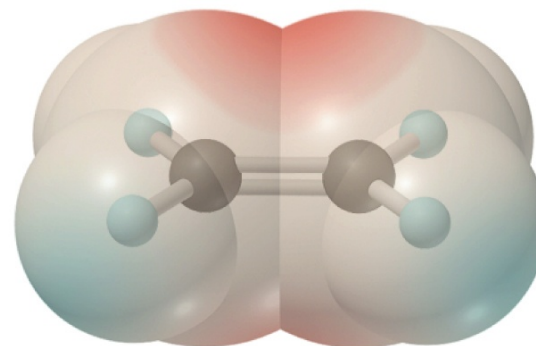
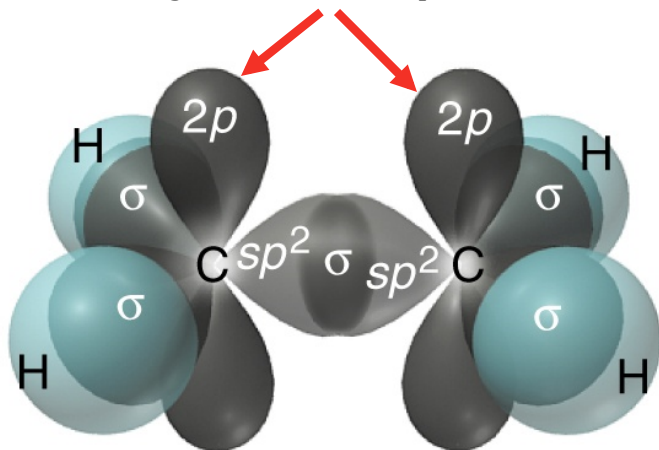
**There is relatively even distribution of electron density over all  $\sigma$  bonds.**



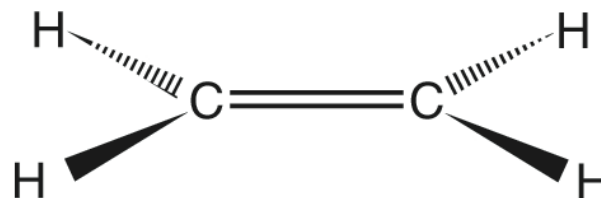
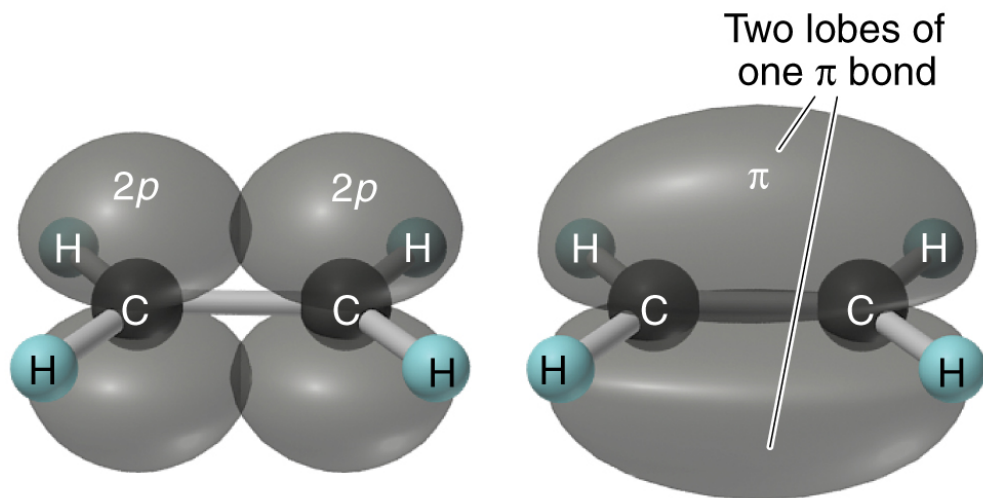
## Figure 10.11 The $\sigma$ and $\pi$ bonds in ethylene ( $\text{C}_2\text{H}_4$ ).

Copyright © The McGraw-Hill Companies, Inc. Permission required for reproduction or display.

unhybridized  $2p$  orbitals

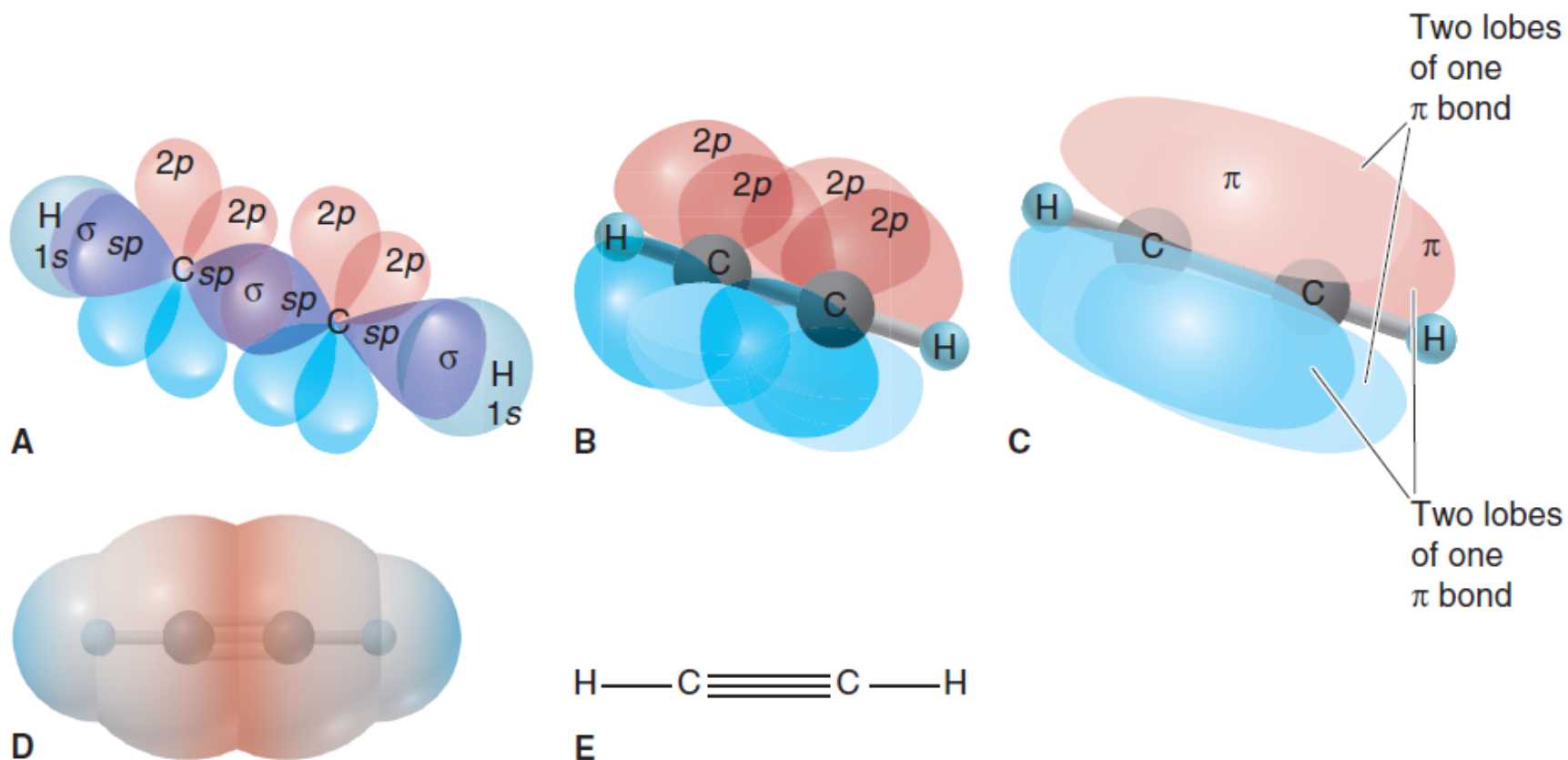


A  $\pi$  bond has two regions of electron density.



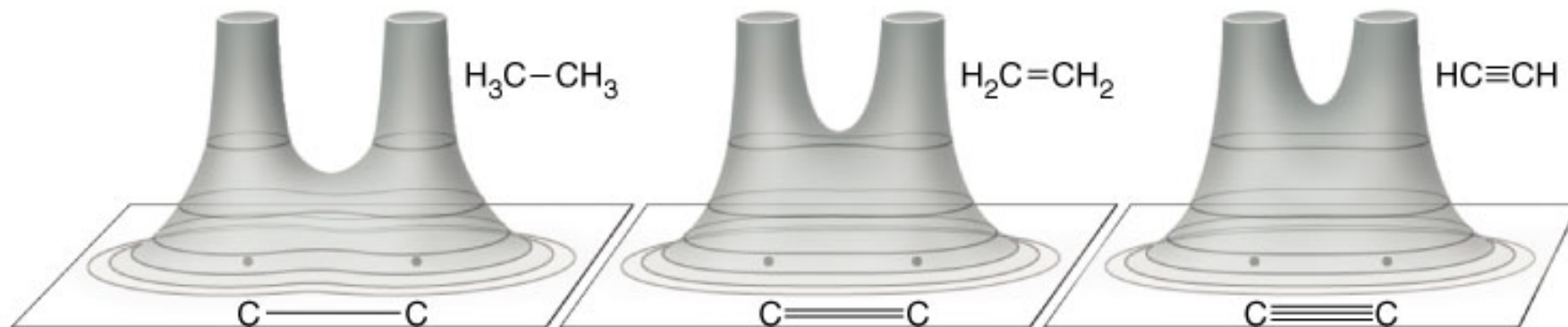
# Figure 10.12 The $\sigma$ and $\pi$ bonds in ethyne ( $\text{C}_2\text{H}_2$ ).

Copyright © The McGraw-Hill Companies, Inc. Permission required for reproduction or display.





**Figure 10.13**      **Electron density and bond order in ethane, ethylene, and acetylene.**



**A double bond is less than twice as strong as a single bond, because a  $\pi$  bond is weaker than a  $\sigma$  bond.**

**However, in terms of bond order, a single bond has  $\text{BO} = 1$ , a double bond has  $\text{BO} = 2$ , and a triple bond has  $\text{BO} = 3$ .**



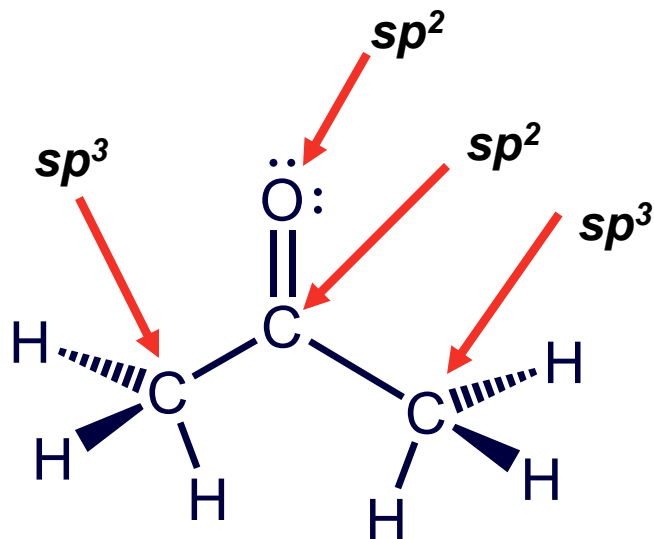
## Sample Problem 10.2

## Describing the Types of Bonds in Molecules

**PROBLEM:** Describe the types of bonds and orbitals in propanone (acetone,  $(\text{CH}_3)_2\text{CO}$ .)

**PLAN:** We use the Lewis structures to determine the arrangement of groups and shape at each central atom. We postulate the hybrid orbitals, taking note of the multiple bonds present.

**SOLUTION:**

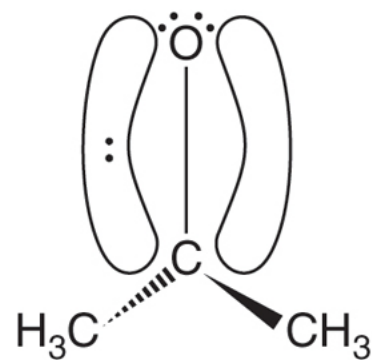
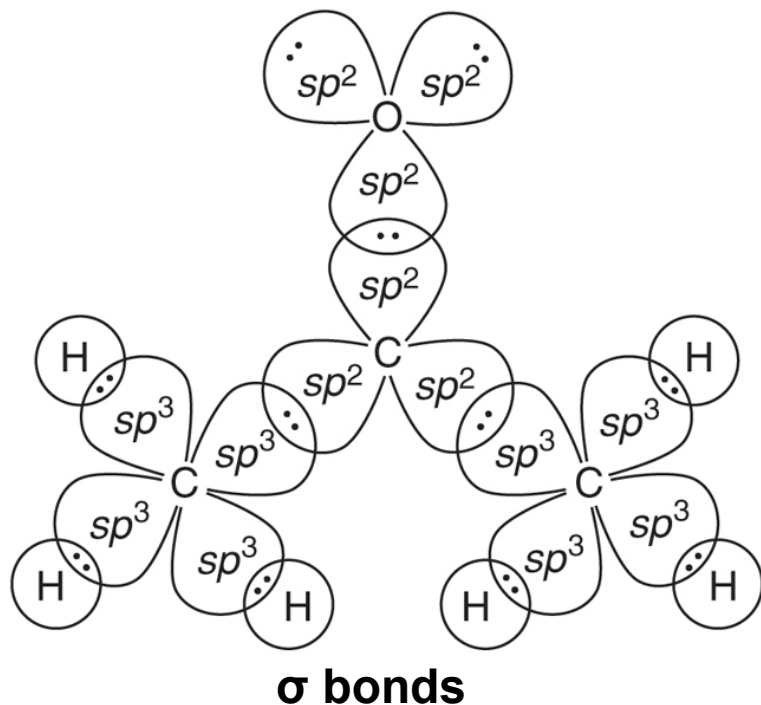


## Sample Problem 10.2

The  $sp^3$  hybridized C atoms form  $\sigma$  bonds using  $sp^3$  hybrid orbitals.

The  $sp^2$  hybridized C and O atoms form  $\sigma$  bonds using  $sp^2$  hybrid orbitals, and the  $\pi$  bond of the C=O double bond is formed using  $p$  orbitals.

Copyright © The McGraw-Hill Companies, Inc. Permission required for reproduction or display.

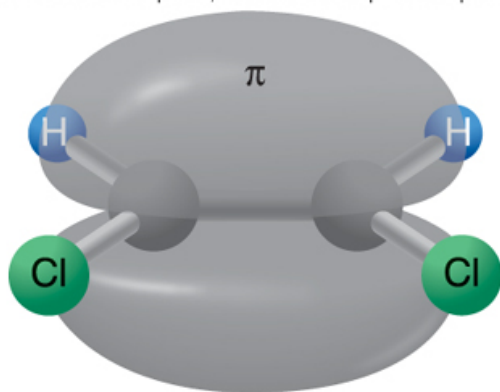


**$\pi$  bond (shown with molecule rotated 90°).**



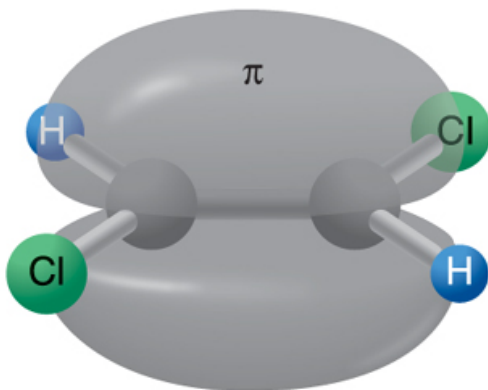
## Figure 10.14      Restricted rotation around a $\pi$ bond.

Copyright © The McGraw-Hill Companies, Inc. Permission required for reproduction or display.



**A**

***cis*-1,2-Dichloroethene**



**B**

***trans*-1,2-Dichloroethene**



## 10.3

# Molecular Orbital (MO) Theory

The combination of orbitals to form bonds is viewed as the combination of ***wave functions***.

***Atomic*** wave functions (AOs) combine to form ***molecular*** wave functions (MOs).

***Addition*** of AOs forms a ***bonding MO***, which has a region of ***high*** electron density between the nuclei.

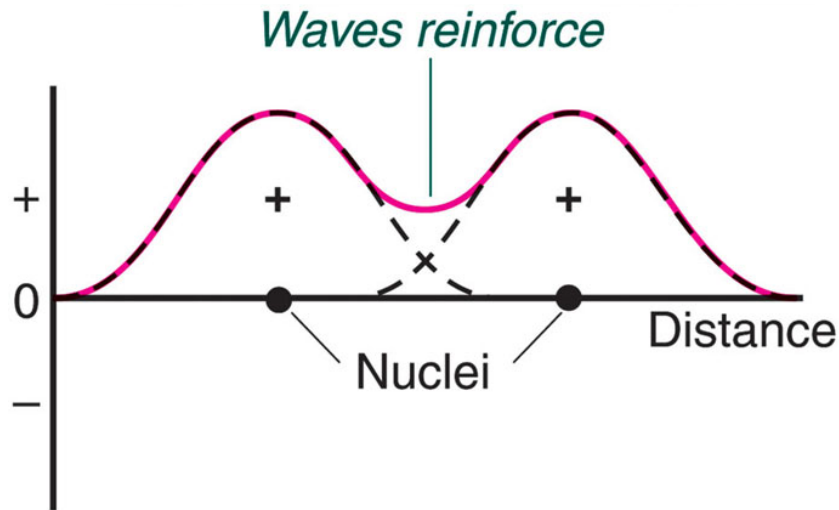
***Subtraction*** of AOs forms an ***antibonding MO***, which has a ***node***, or region of ***zero*** electron density, between the nuclei.



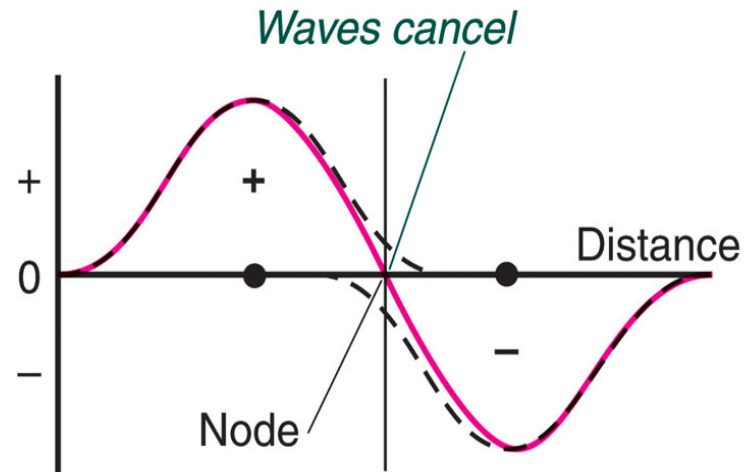
**Figure 10.16**

**An analogy between light waves and atomic wave functions.**

Copyright © The McGraw-Hill Companies, Inc. Permission required for reproduction or display.



**Amplitudes of wave functions added**

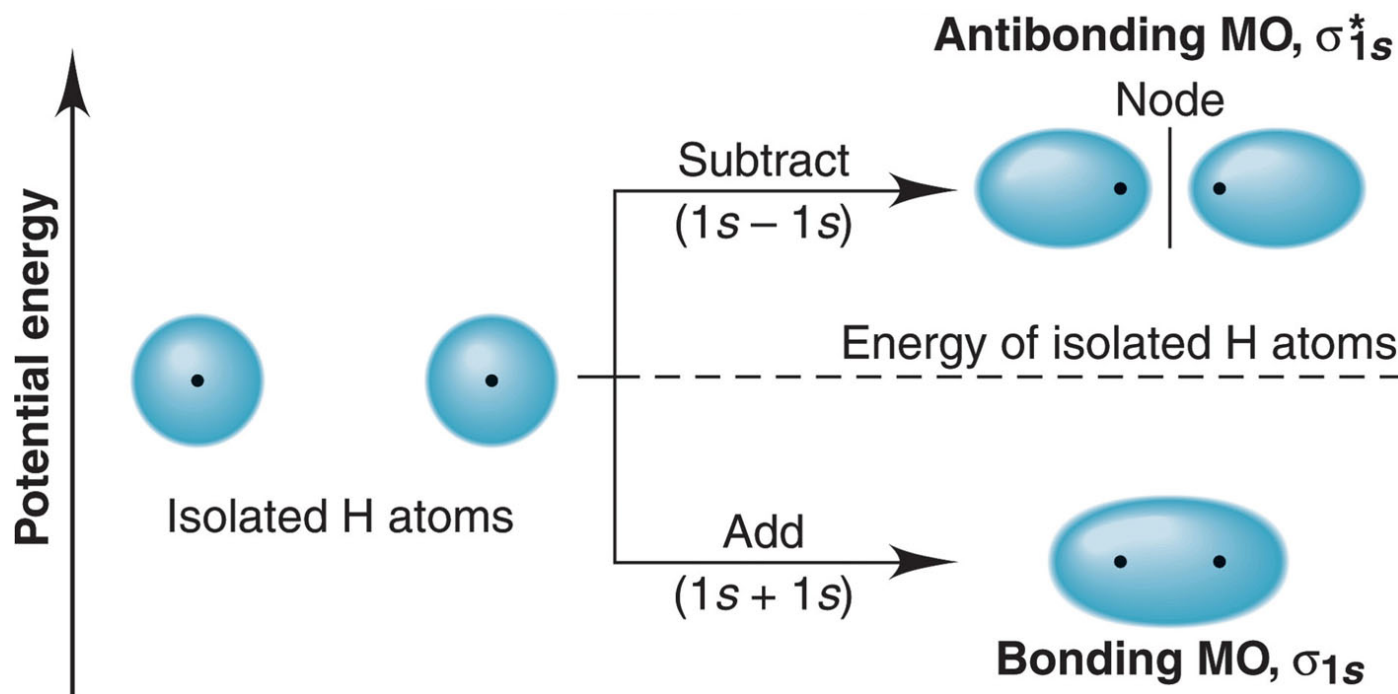


**Amplitudes of wave functions subtracted**



## Figure 10.17      Contours and energies of $\text{H}_2$ bonding and antibonding MOs.

Copyright © The McGraw-Hill Companies, Inc. Permission required for reproduction or display.



The bonding MO is lower in energy and the antibonding MO is higher in energy than the AOs that combined to form them.



# Molecular Orbital Diagrams

An **MO diagram**, just like an atomic orbital diagram, shows the relative energy and number of electrons in each MO.

The MO diagram also shows the AOs from which each MO is formed.

Bond order is calculated as follows:

$$\frac{1}{2}[(\text{\# of } e^- \text{ in bonding MO}) - (\text{\# of } e^- \text{ in antibonding MO})]$$

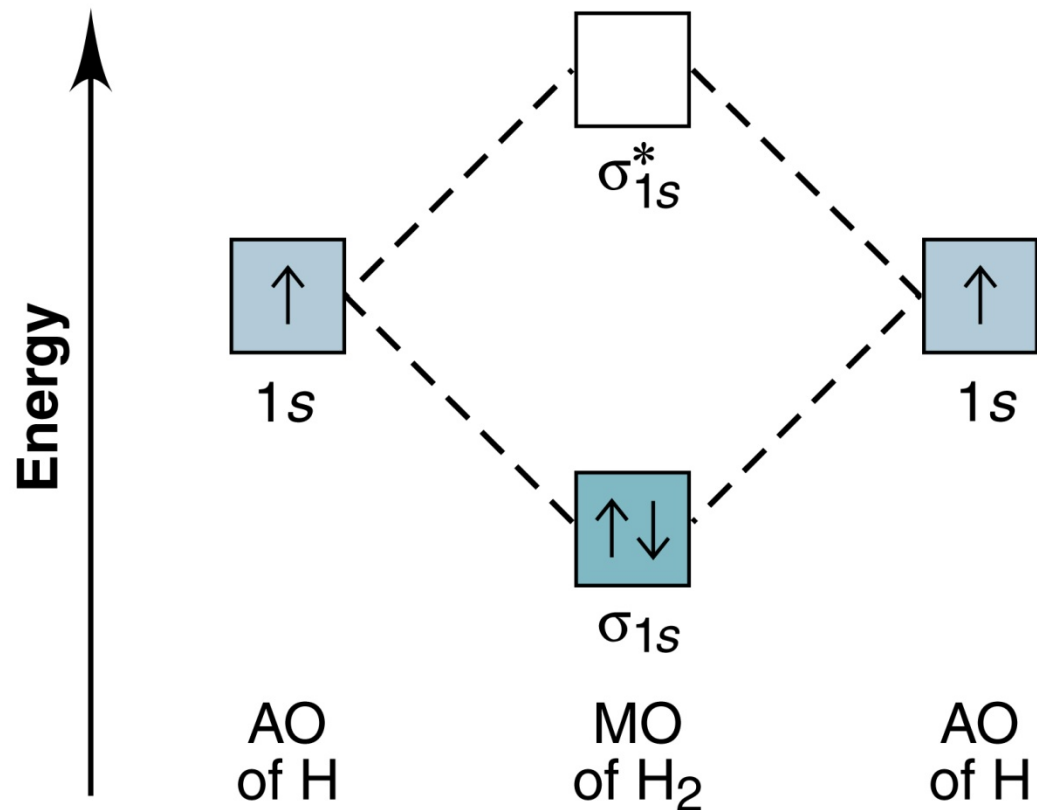




Figure 10.18

MO diagram for H<sub>2</sub>.

Copyright © The McGraw-Hill Companies, Inc. Permission required for reproduction or display.



$$\text{H}_2 \text{ bond order} = \frac{1}{2} (2 - 0) = 1$$



# Electrons in Molecular Orbitals

Electrons are placed in MOs just as they are in AOs.

- MOs are filled in order of increasing energy.
- An MO can hold a maximum of 2 e<sup>-</sup> with opposite spins.
- Orbitals of equal energy are half-filled, with spins parallel, before pairing spins.

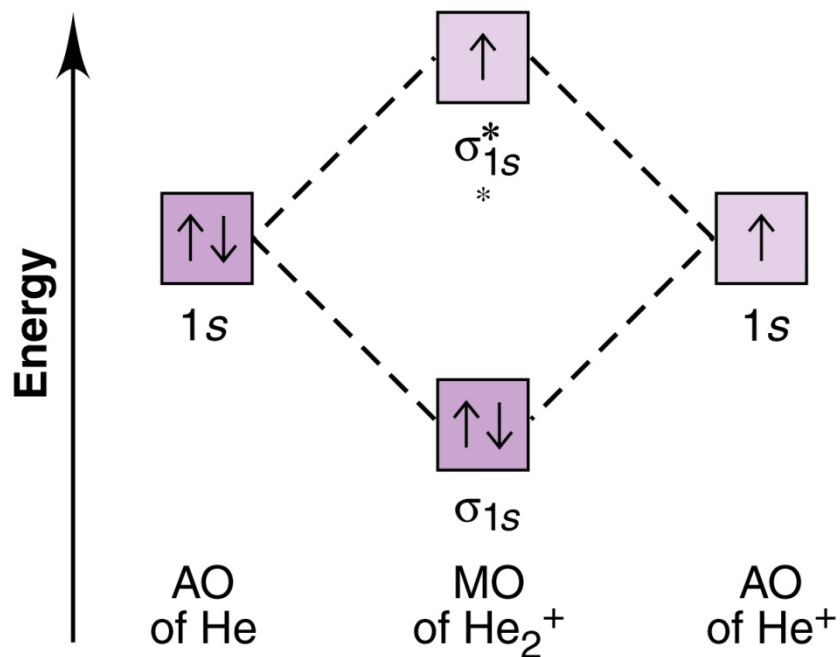
A molecular electron configuration shows the type of MO and the number of e<sup>-</sup> each contains. For H<sub>2</sub> the configuration is  $(\sigma_{1s})^2$ .



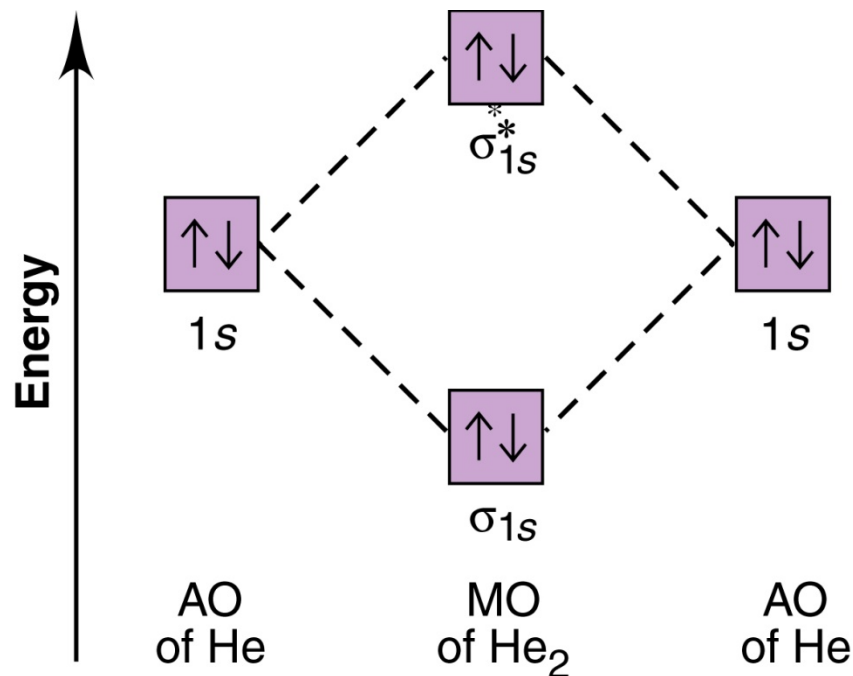
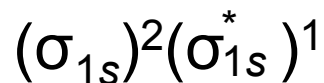
Figure 10.19

# MO diagram for $\text{He}_2^+$ and $\text{He}_2$ .

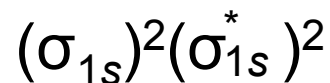
Copyright © The McGraw-Hill Companies, Inc. Permission required for reproduction or display.



$\text{He}_2^+$  bond order =  $\frac{1}{2}$



$\text{He}_2$  bond order = 0



### Sample Problem 10.3

## Predicting Stability of Species Using MO Diagrams

**PROBLEM:** Use MO diagrams to find bond orders and predict whether (a)  $\text{H}_2^+$  and (b)  $\text{H}_2^-$  exist. If either exists, write its electron configuration.

**PLAN:** Since the 1s AOs form the MOs, the MO diagrams are similar to the one for  $\text{H}_2$ . We find the number of electrons in each species and distribute them one at a time to the MOs following the rules for orbital filling. We calculate the bond order and predict stability.

**SOLUTION:**

(a)  $\text{H}_2^+$  has one electron to place in its MOs while  $\text{H}_2^-$  has three electrons to place.

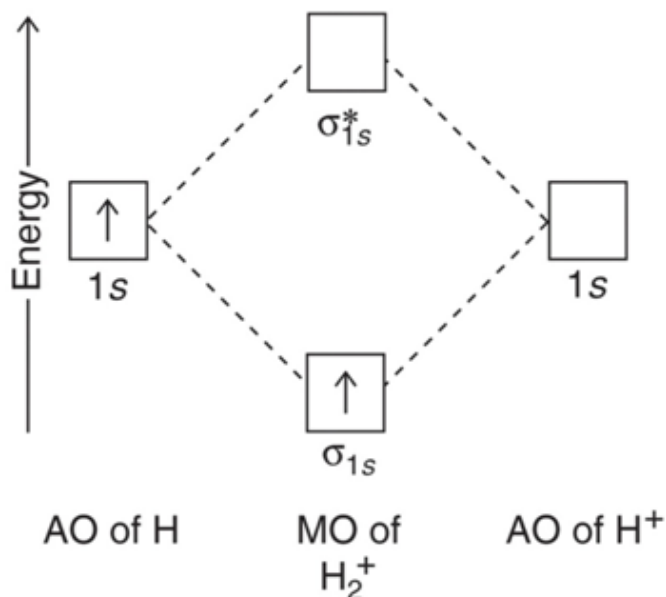


## Sample Problem 10.3

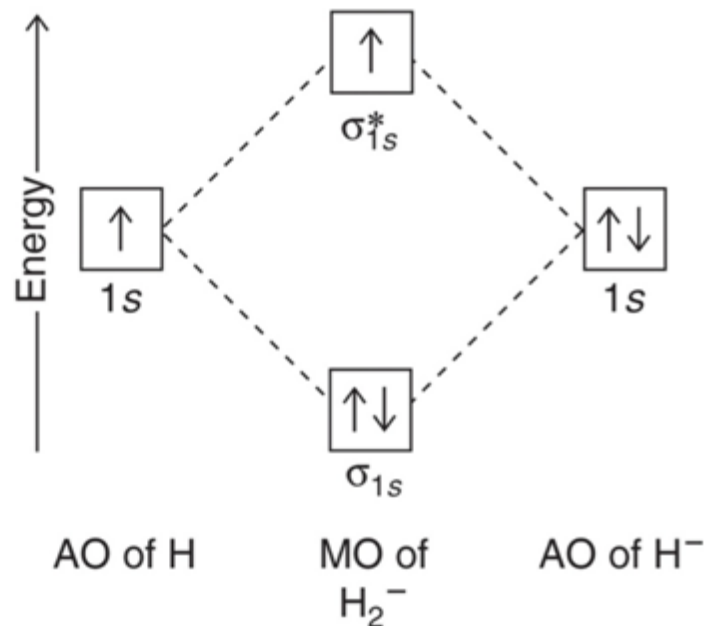
(b)

Copyright © The McGraw-Hill Companies, Inc. Permission required for reproduction or display.

(a)



For  $\text{H}_2^+$ , the bond order is  
 $\frac{1}{2}(1 - 0) = \frac{1}{2}$ ;  
 so we predict that  $\text{H}_2^+$  exists.  
 The configuration is  $(\sigma_{1s})^1$ .

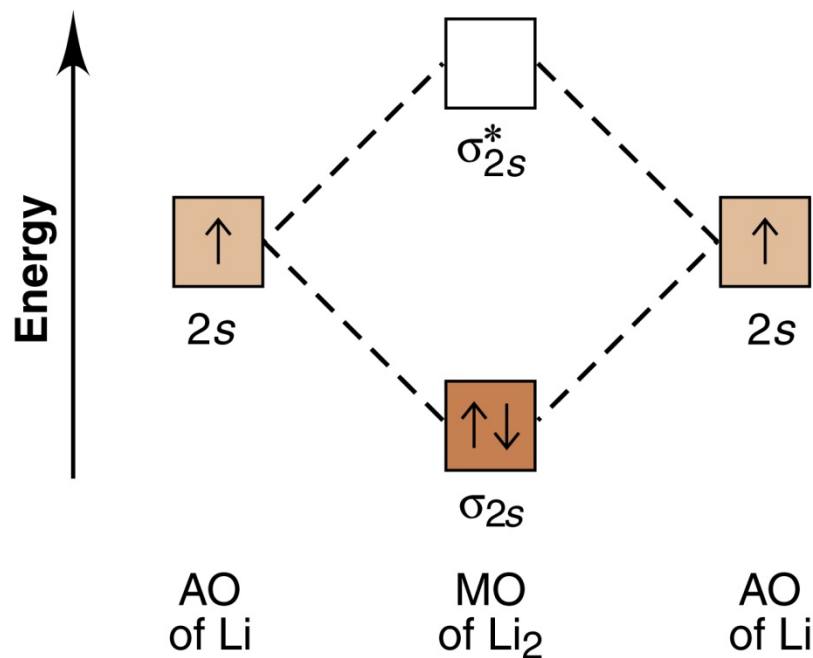


For  $\text{H}_2^-$ , the bond order is  
 $\frac{1}{2}(2 - 1) = \frac{1}{2}$ ;  
 so we predict that  $\text{H}_2^-$  exists.  
 The configuration is  $(\sigma_{1s})^2(\sigma_{1s}^*)^1$ .

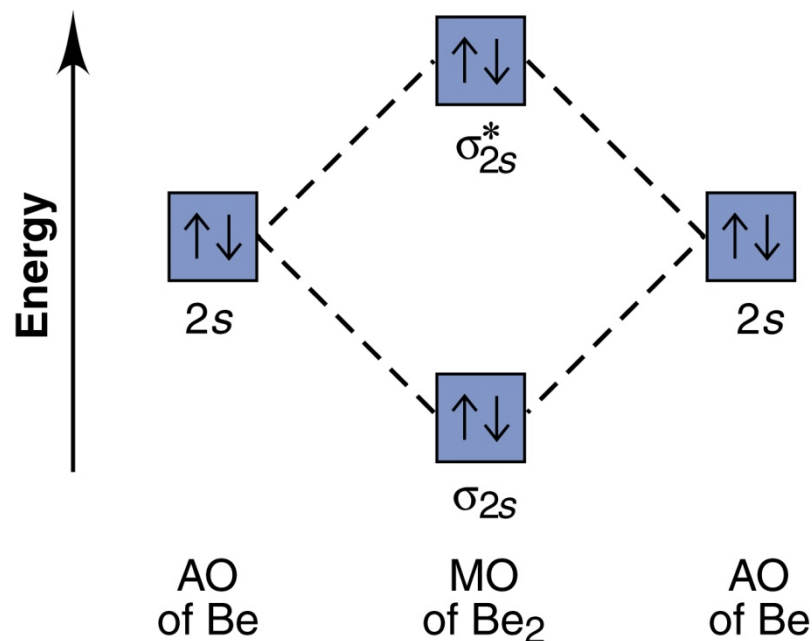


## Figure 10.20 Bonding in s-block homonuclear diatomic molecules.

Copyright © The McGraw-Hill Companies, Inc. Permission required for reproduction or display.



$\text{Li}_2$  bond order = 1

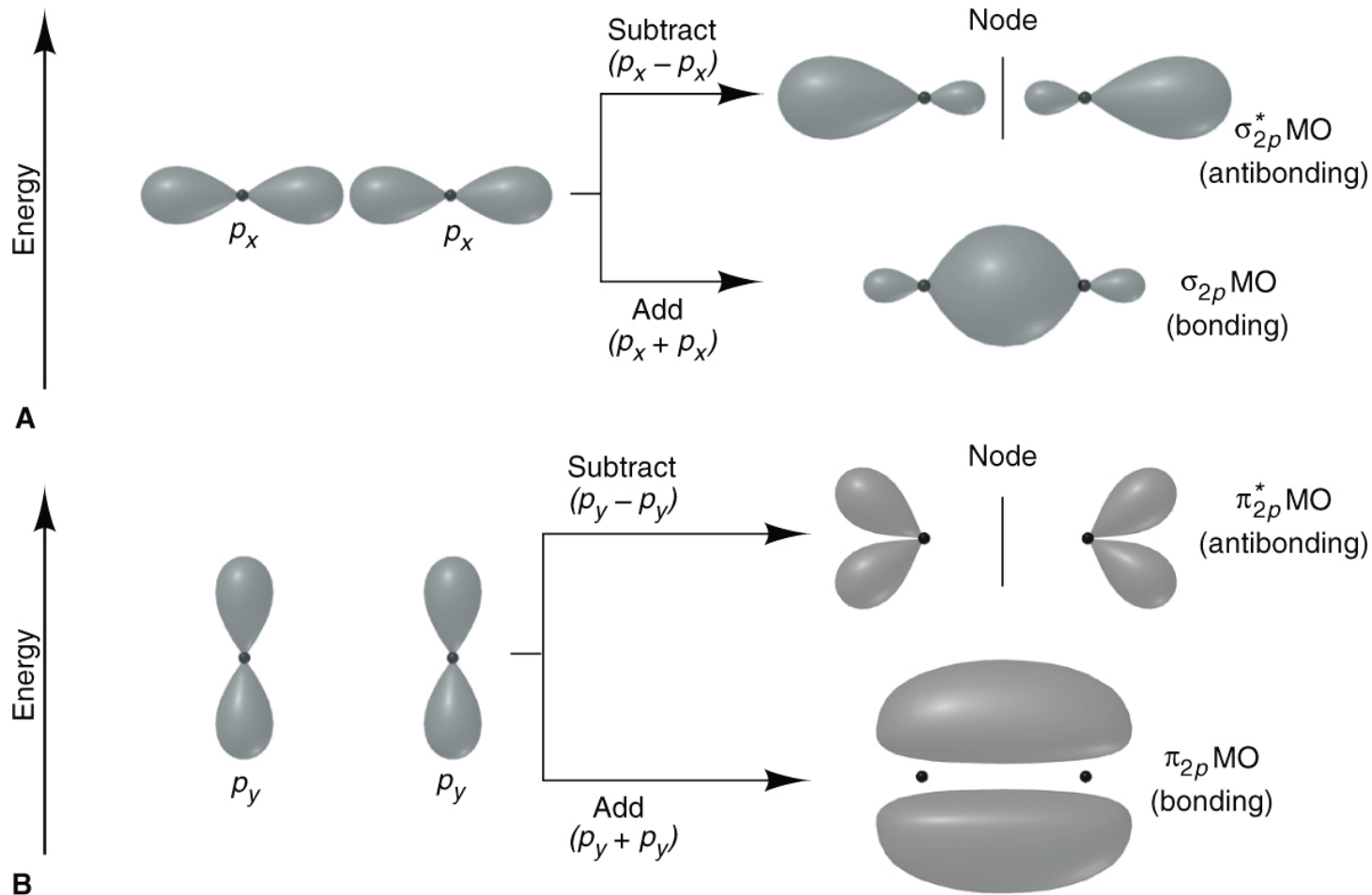


$\text{Be}_2$  bond order = 0



## Figure 10.21 Shapes and energies of $\sigma$ and $\pi$ MOs from combinations of $2p$ atomic orbitals.

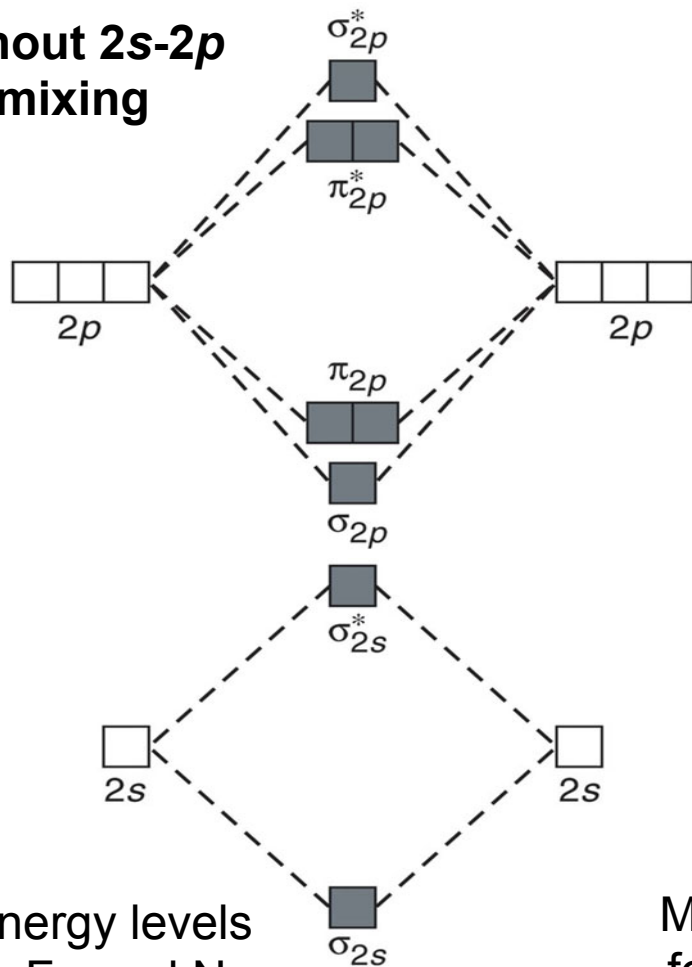
Copyright © The McGraw-Hill Companies, Inc. Permission required for reproduction or display.



**Figure 10.22 Relative MO energy levels for Period 2 homonuclear diatomic molecules.**

Copyright © The McGraw-Hill Companies, Inc. Permission required for reproduction or display.

**without 2s-2p mixing**



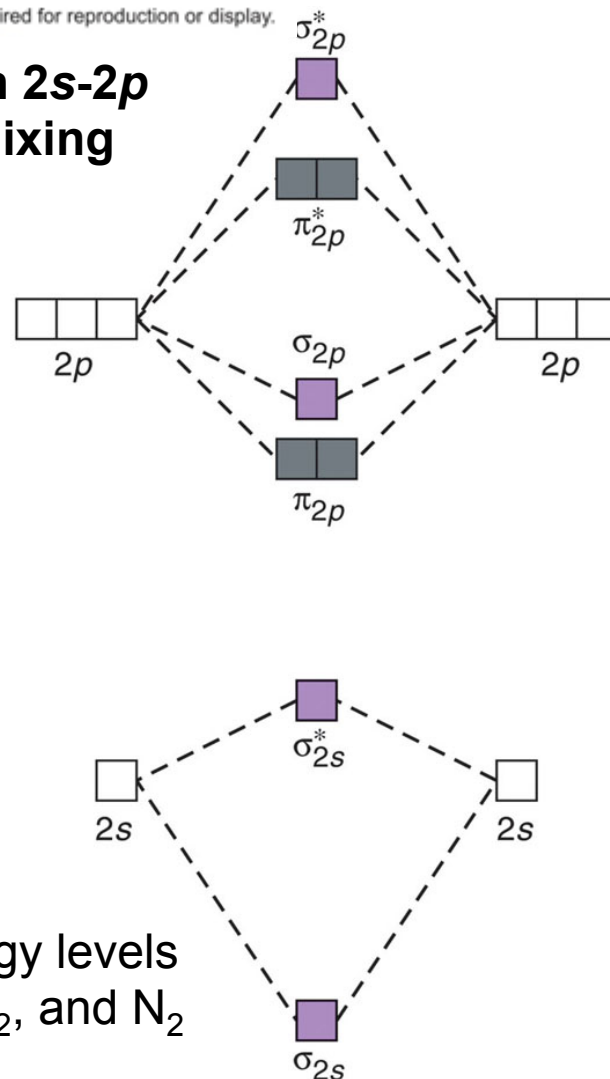
MO energy levels  
for  $O_2$ ,  $F_2$ , and  $Ne_2$

AO

MO

AO

**with 2s-2p mixing**



MO energy levels  
for  $B_2$ ,  $C_2$ , and  $N_2$

AO

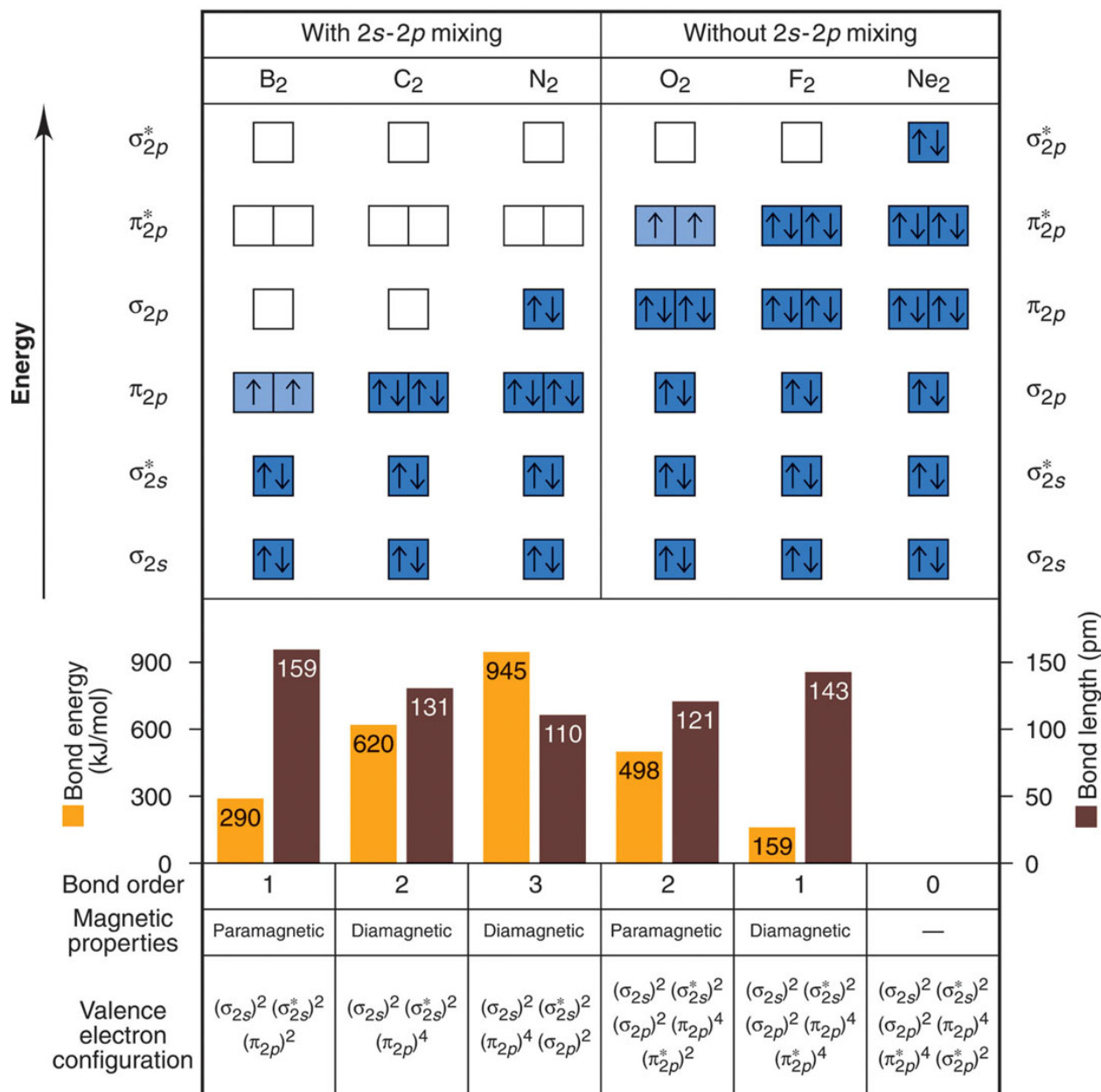
MO

AO



Figure 10.23

**MO occupancy and some properties of homonuclear diatomic molecular properties for B<sub>2</sub> through Ne<sub>2</sub>.**



## Figure 10.24      The paramagnetic properties of O<sub>2</sub>.

Copyright © The McGraw-Hill Companies, Inc. Permission required for reproduction or display.



© The McGraw-Hill Companies, Inc./Charles Winters Photographer

©2013 McGraw-Hill Ryerson Limited

## Sample Problem 10.4

## Using MO Theory to Explain Bond Properties

**PROBLEM:** Explain the following data with diagrams showing the occupancy of MOs:

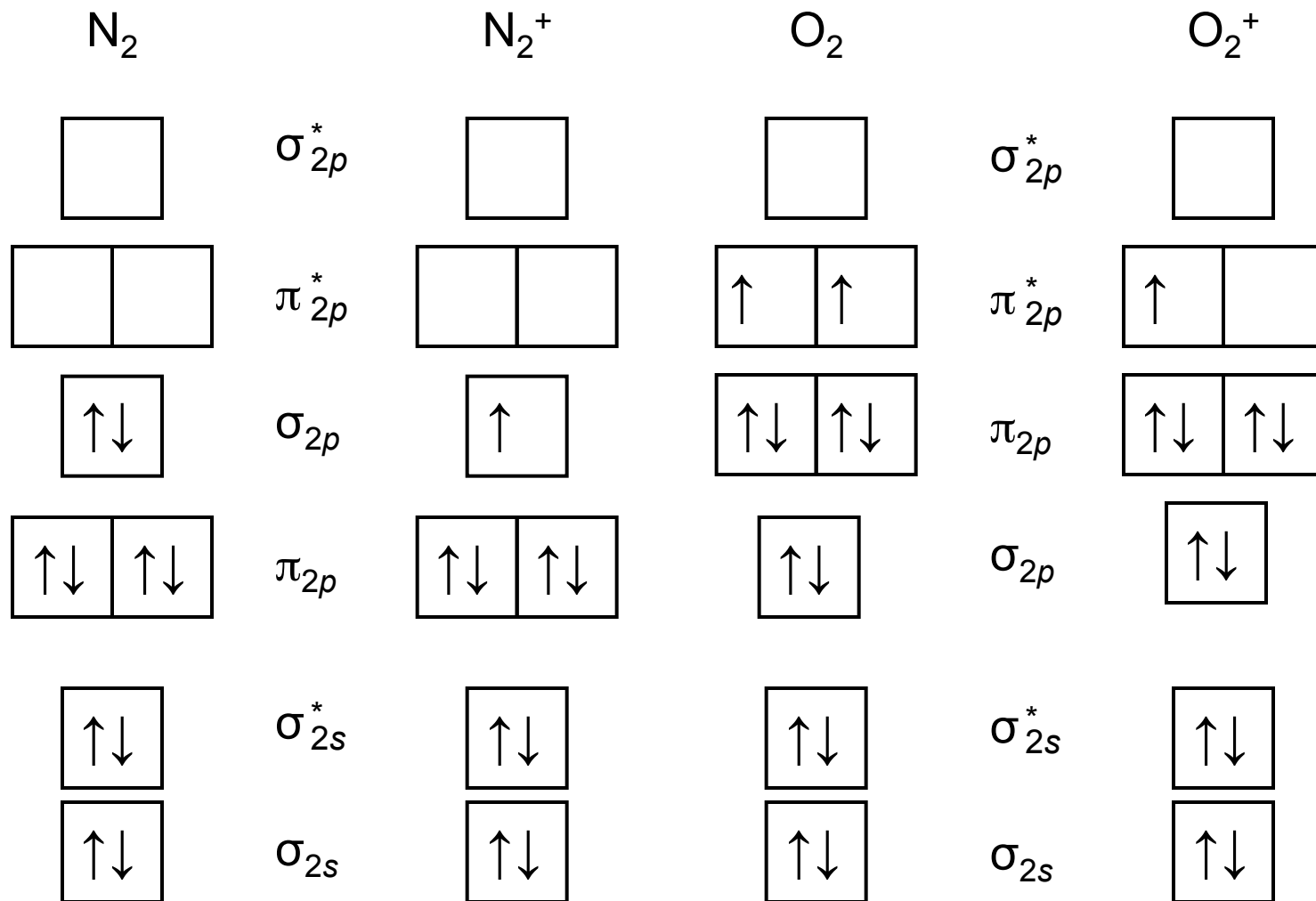
	$\text{N}_2$	$\text{N}_2^+$	$\text{O}_2$	$\text{O}_2^+$
Bond energy (kJ/mol)	945	841	498	623
Bond length (pm)	110	112	121	112

**PLAN:** The data show that removing an electron from each parent molecule has opposite effects:  $\text{N}_2^+$  has a weaker longer bond than  $\text{N}_2$ , but  $\text{O}_2^+$  has a stronger, shorter bond than  $\text{O}_2$ . We determine the valence electrons in each species, draw the sequence of MO energy levels (showing orbital mixing in  $\text{N}_2$  but not in  $\text{O}_2$ ), and fill them with electrons. We then calculate bond orders, which relate directly to bond energy and inversely to bond length.



## Sample Problem 10.4

## SOLUTION:



## Sample Problem 10.4

**Calculating bond orders:**

**For  $\text{N}_2$   $\frac{1}{2}(8 - 2) = 3$       For  $\text{N}_2^+$   $\frac{1}{2}(7 - 2) = 2.5$**

**$\text{N}_2^+$  has a longer, weaker bond than  $\text{N}_2$  because to form  $\text{N}_2^+$ , a *bonding* electron is removed and the bond order decreases.**

**For  $\text{O}_2$   $\frac{1}{2}(8 - 4) = 2$       For  $\text{O}_2^+$   $\frac{1}{2}(8 - 3) = 2.5$**

**$\text{O}_2^+$  has a shorter, stronger bond than  $\text{O}_2$  because to form  $\text{O}_2^+$ , an *antibonding* electron is removed and the bond order increases.**

