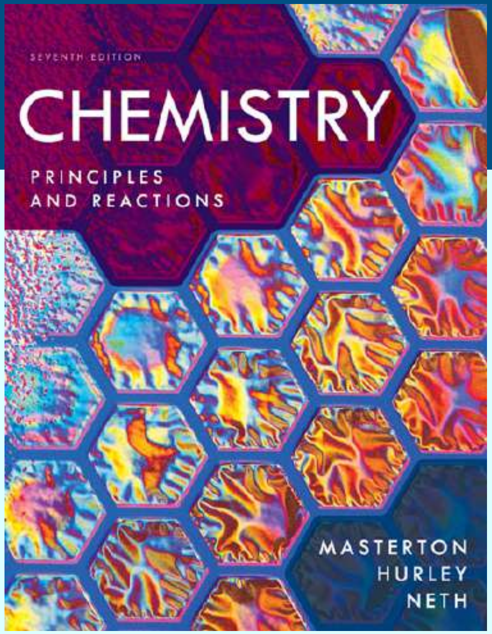


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# *Chapter 7*
# *Covalent Bonding*

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# Outline

1. Lewis Structures; the Octet Rule
2. Molecular Geometry
3. Molecular Polarity
4. Atomic Orbitals; Hybridization

# Covalent Bonding Introduction

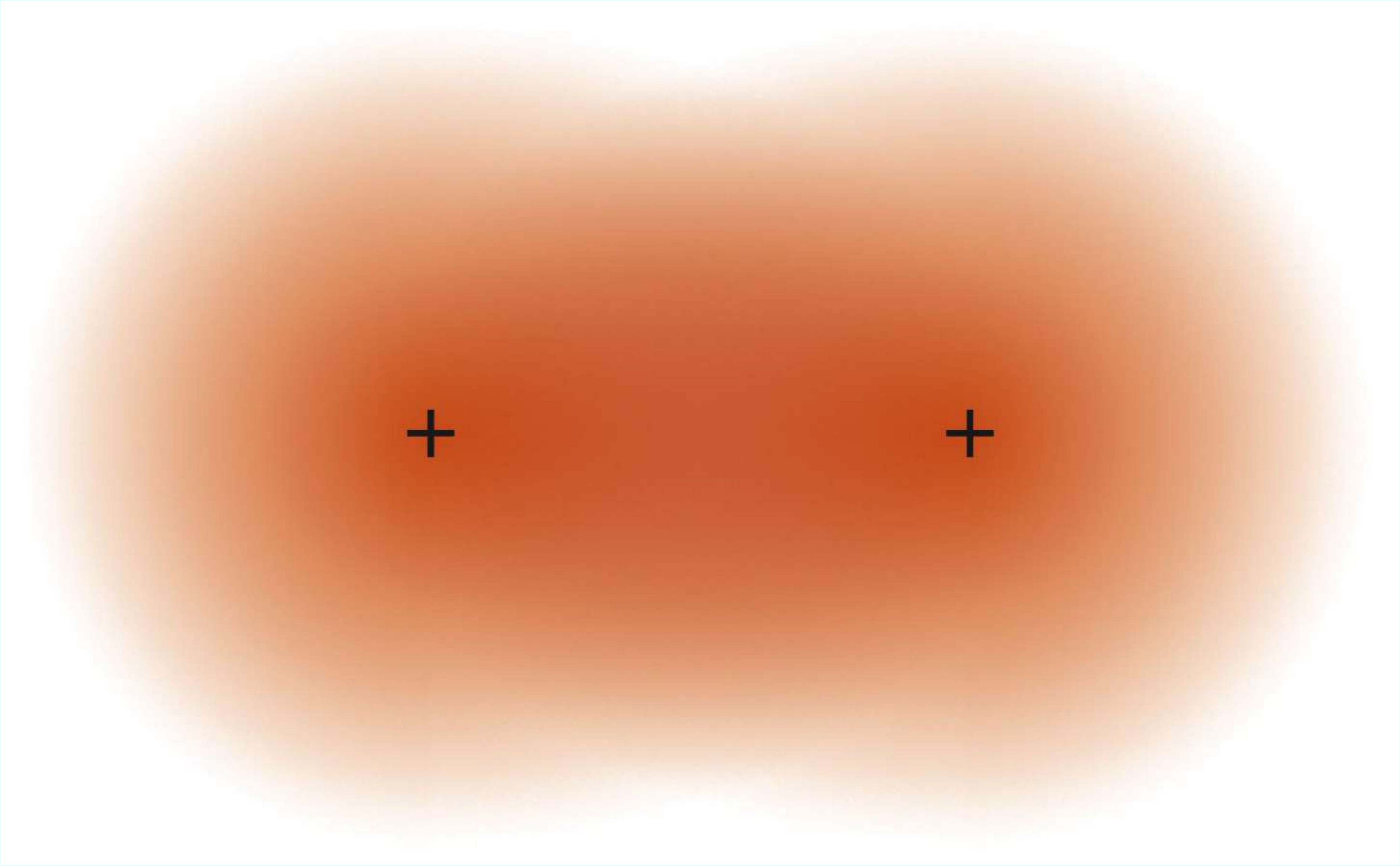
- Recall that electrons in atoms are placed into atomic orbitals according to the Aufbau principle and Hund's Rule

- In this section of the course, we will look at the location of electrons in molecules containing covalent bonds

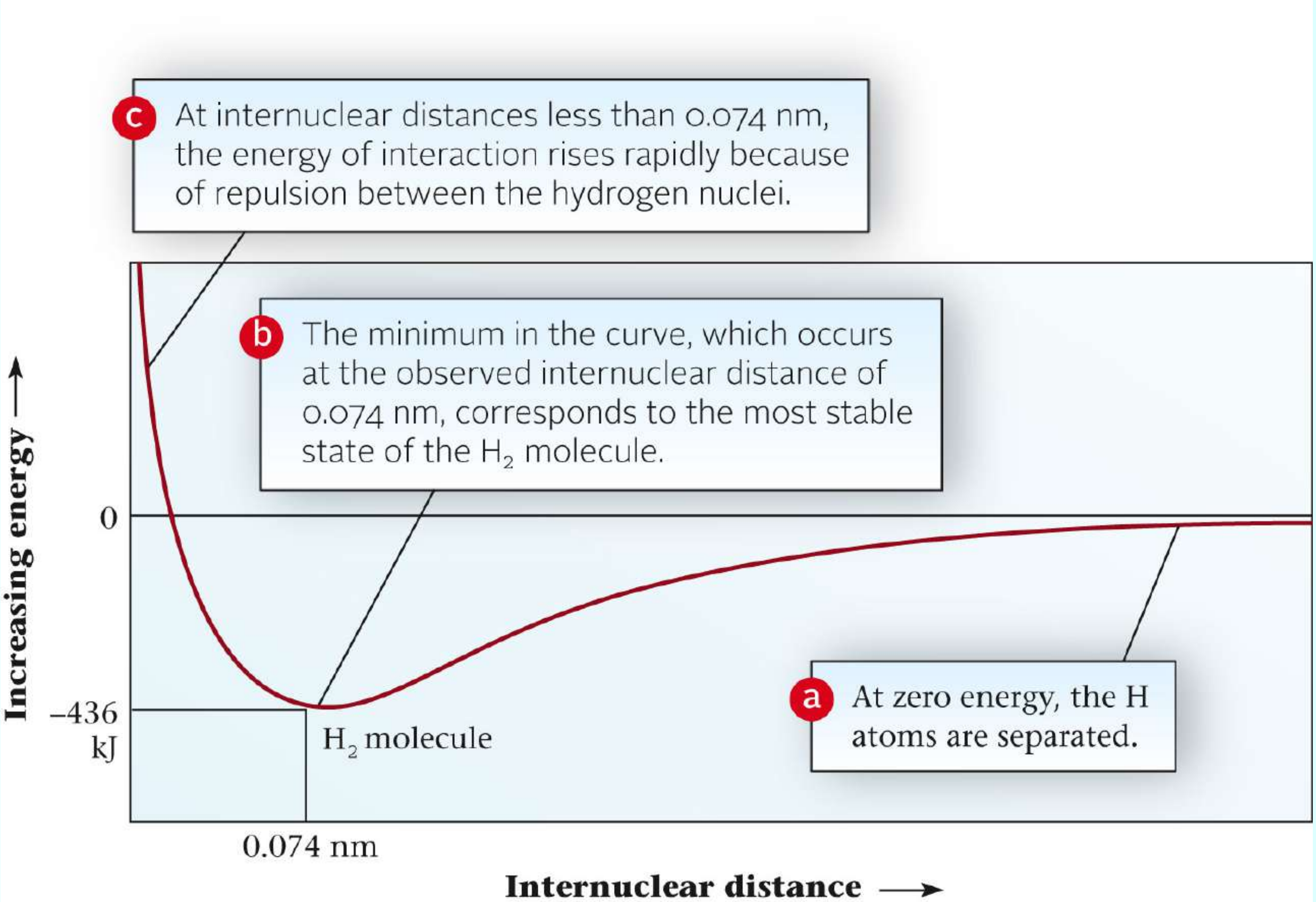
# Covalent Bonding Introduction, Cont'd

- **Electron density**
  - Electrons are located between nuclei
    - Electrostatic energy of the system is lowered
    - When two hydrogen atoms come together, electron density is spread over the entire molecule
  - Study of the covalent bond as it exists in molecules and polyatomic ions

# Figure 7.1 – The Hydrogen Molecule



# Figure 7.2


c At internuclear distances less than 0.074 nm, the energy of interaction rises rapidly because of repulsion between the hydrogen nuclei.
b The minimum in the curve, which occurs at the observed internuclear distance of 0.074 nm, corresponds to the most stable state of the $H_2$ molecule.
a At zero energy, the H atoms are separated.
Increasing energy
0
–436 kJ
$H_2$ molecule
0.074 nm
Internuclear distance

# Lewis Structures

- Recall that atoms may form ions that are isoelectronic with the nearest noble gas
  - Na forms $Na^+$ $1s^2 2s^2 2p^6 3s^1 \rightarrow 1s^2 2s^2 2p^6$
  - F forms $F^-$ $1s^2 2s^2 2p^5 \rightarrow 1s^2 2s^2 2p^6$
- Some atoms share electrons rather than ionize
  - Sharing results in atoms becoming isoelectronic with the nearest noble gas, as they do in forming ions

# Valence

- Outermost electrons are called valence electrons
  - Consider F
    - $1s^2 2s^2 2p^5$
    - 1s are *core* electrons
    - 2s and 2p are *valence* electrons
  - Consider HF 

    - Hydrogen contributes a 1s electron to form a covalent bond
    - F contributes seven electrons and shares one more
    - Total of eight valence electrons
    - F in HF now has a total of eight valence electrons; H has two

# Tools

- Lewis structures
  - Distribute electron pairs in a molecule such that each atom achieves an octed (hydrogen a duet)
- Molecular geometry
  - Location of both shared and unshared electron pairs leads to VSEPR geometry

# Table 1.1

**TABLE 7.1 Lewis Structures of Atoms Commonly Forming Covalent Bonds**

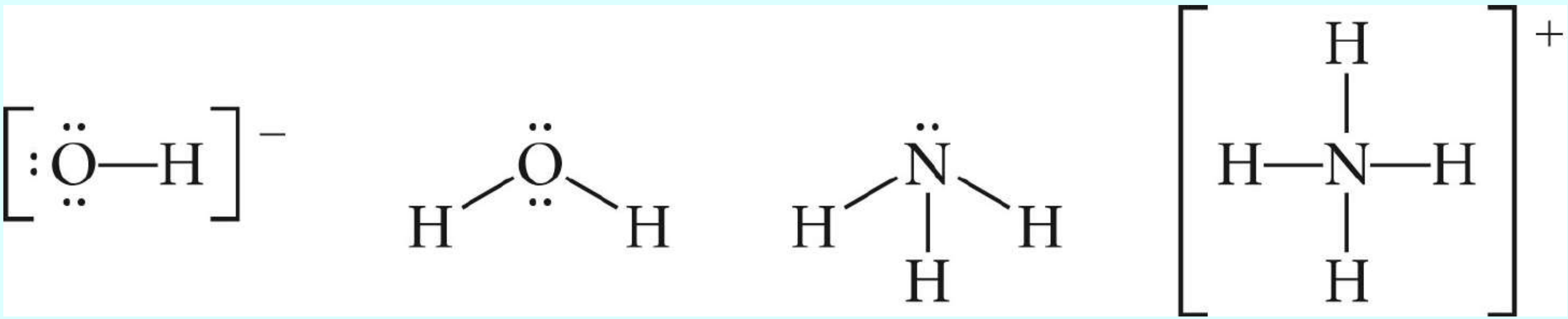
| Group: | 1 | 2 | 13 | 14 | 15 | 16 | 17 | 18 |
|---|---|---|---|---|---|---|---|---|
| No. of valence $e^-$: | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
| | H· | | | | | | | |
| | | ·Be· | ·B· | ·C· | ·N· | ·O· | :F· | |
| | | | | ·Si· | ·P· | ·S· | :Cl· | |
| | | | | ·Ge· | ·As· | ·Se· | :Br· | :Kr: |
| | | | | | ·Sb· | ·Te· | :I· | :Xe: |

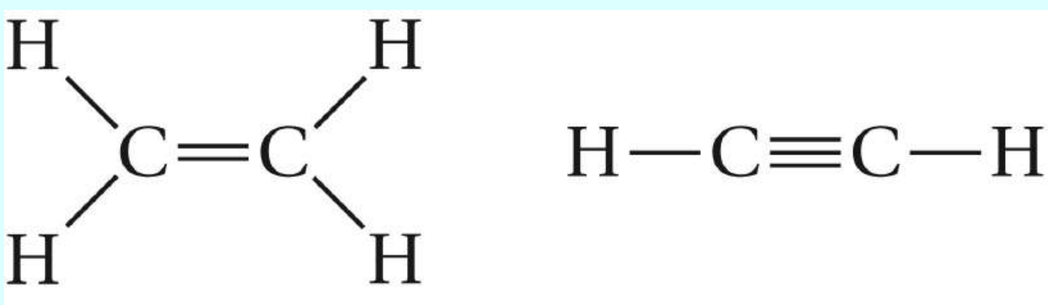
# Electron Ownership

- An atom owns
  - All lone electrons
    - Shown as lone pairs
  - Half the number of bonding electrons
    - A bond pair is shown as a line
    - Multiple bonds are possible
      - Double bonds are two pairs
      - Triple bonds are three pairs

# Examples of Lewis Structures

- $OH^-$, $H_2O$, $NH_3$, $NH_4^+$, $C_2H_4$, $C_2H_2$





# The Octet Rule

- Main group elements seek to attain an octet of electrons
  - Recall that an $s^2p^6$ configuration is isoelectronic with a noble gas
  - Closed electron shells
  - Exception: H
    - The duet rule

# Writing Lewis Structures*

1. Draw a skeleton structure for the species, joining the atoms by single bonds
2. Count the number of valence electrons (VE)
3. Determine the number of valence electrons still available for distribution (AE)
4. Determine the number of valence electrons required to complete an octet for each atom (except H) in the structure (this is NE, needed electrons)
   - If AE = NE, the skeleton is correct
   - If AE < NE, place double or triple bonds as needed

*see p. 193 of the text

# 1. Drawing the Skeleton Structure

- One atom must be central
  - This is usually the first one written in the formula
  - Less electronegative elements are usually central
  - Atoms that are usually terminal,  not central
    - Hydrogen (must be terminal)
    - Halogens
    - Oxygen

# 2. Counting the Valence Electrons (VE)

- Total the valence electrons for each atom present in the molecule or ion.
  - For an anion, add one electron for each unit of negative  charge
  - For a cation, subtract one electron for each unit of positive charge

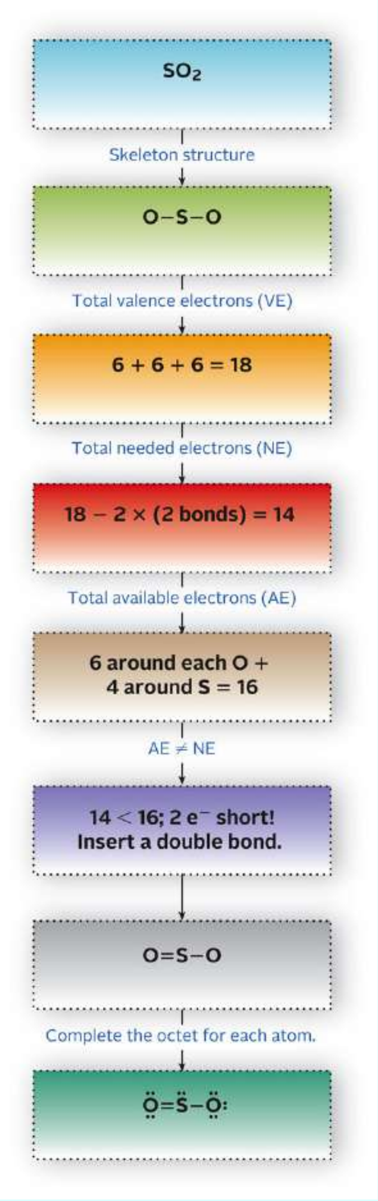
# 3. Determining the Number of Available Electrons, AE

- Each bond represents a pair of electrons
- AE = VE – (2 x number of bonds)

# 4. Completing the Octets

- Distribute the remaining electrons to complete the octet for each element
  - If AE = NE, the structure is correct
  - If AE < NE, use double or triple bonds as needed
- Some elements never participate in multiple bonds:  hydrogen and halogens

# Figure 7.3: Lewis Structure Flowchart



# Example 7.1

## EXAMPLE 7.1

Draw Lewis structures of

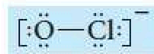
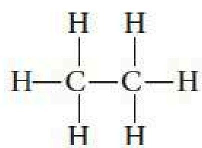
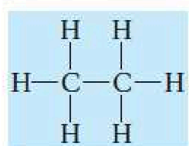
(a) the hypochlorite ion, $OCl^-$ (b) ethane, $C_2H_6$

### STRATEGY

1. Follow the steps outlined in Figure 7.3.
2. For ethane, hydrogen must be a terminal atom since it cannot form double bonds. Carbon ordinarily forms four bonds.

# Example 7.1, (Cont'd)

SOLUTION

| | |
|---|---|
| (a) Skeleton | $[O–Cl]^-$ |
| VE | 6 (for O) + 7 (for Cl) + 1(−1 charge) = 14 |
| AE | AE = VE − 2(bonds) = 14 − 2(1 bond) = 12 |
| NE | 6 (for O to have an octet) + 6 (for Cl to have an octet) = 12 |
| AE = NE ? | Yes; distribute electrons. |
| Lewis structure |  |
| (b) Skeleton |  |
| VE | 2 × 4 (for C) + 6 × 1 (for H) = 14 |
| AE | AE = VE − 2(bonds) = 14 − 2(7 bonds) = 0 |
| NE | 0 : All the H atoms have duets and both C atoms have octets. |
| AE = NE ? | Yes; distribute electrons. |
| Lewis structure |  |

END POINT

After you have written the Lewis structure, it is a good idea to add the number of unshared electron pairs and bonding electrons. This sum must equal the number of valence electrons (VE).

# Example 7.2

EXAMPLE 7.2

Draw the Lewis structures of

(a) $NO_2^-$ (b) $N_2$

STRATEGY

Follow the steps outlined in Figure 7.3.

*continued*

# Example 7.2, (Cont'd)

SOLUTION

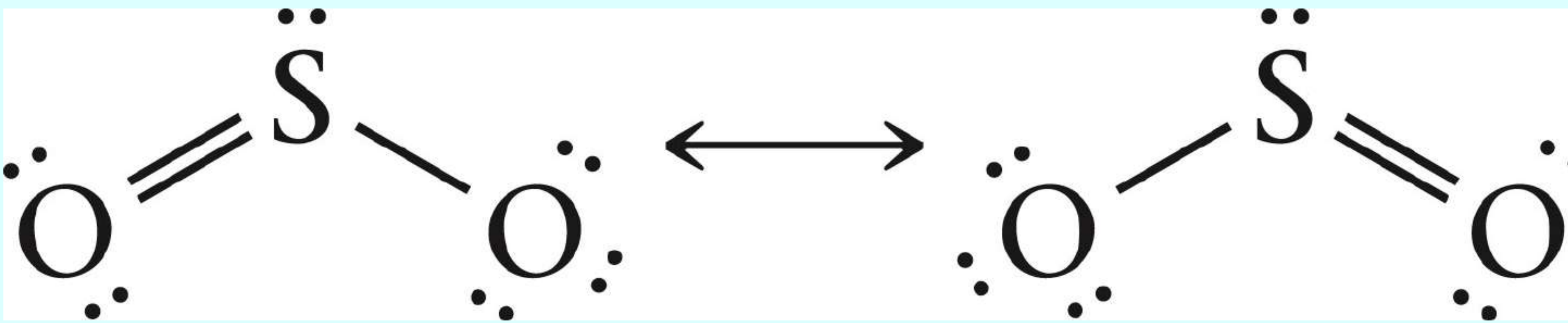
| | |
|---|---|
| (a) Skeleton | $[O–N–O]^-$ |
| VE | 2(6 (for O)) + 5 (for N) + 1(−1 charge) = 18 |
| AE | AE = VE − 2(bonds) = 18 − 2(2 bonds) = 14 |
| NE | 2(6 (for each O)) + 4 (for N) = 16 |
| AE = NE ? | No; 2 electrons short |
| | Convert a single bond to a double bond. |
| Lewis structure | $[:\ddot{\underset{..}{O}}—\ddot{N}=\ddot{O}:]^-$ |
| (b) Skeleton | N–N |
| VE | 2 (5 (for each N)) = 10 |
| AE | AE = VE − 2(bonds) = 10 − 2(1 bond) = 8 |
| NE | 2 × 6 (for each N to have an octet) = 12 |
| AE = NE ? | No; 4 electrons short |
| | Convert a single bond to a triple bond. |
| Lewis structure | $:N\equiv N:$ |

END POINT

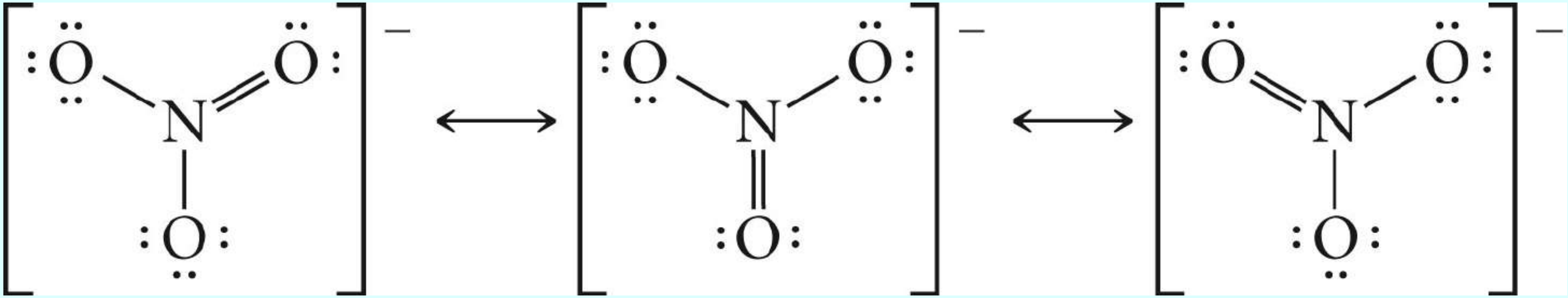
For the Lewis structure of $NO_2^-$ , it does not matter which single bond you convert to a double bond. We will talk about this in more detail when we discuss resonance forms.

# Resonance Forms

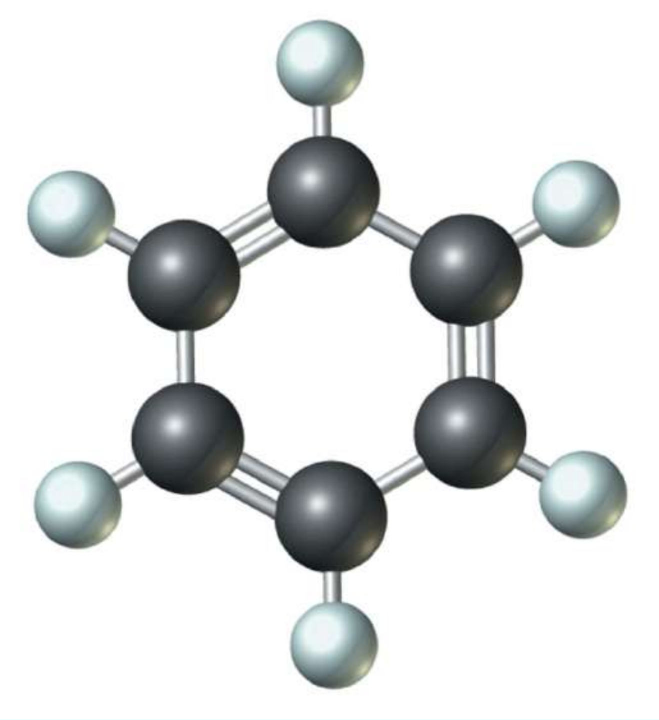
- In certain cases, Lewis structures do not represent chemical or physical reality
  - Consider $SO_2$
  - Both S-O bonds are equal in length, yet the Lewis structure indicates one double and one single bond

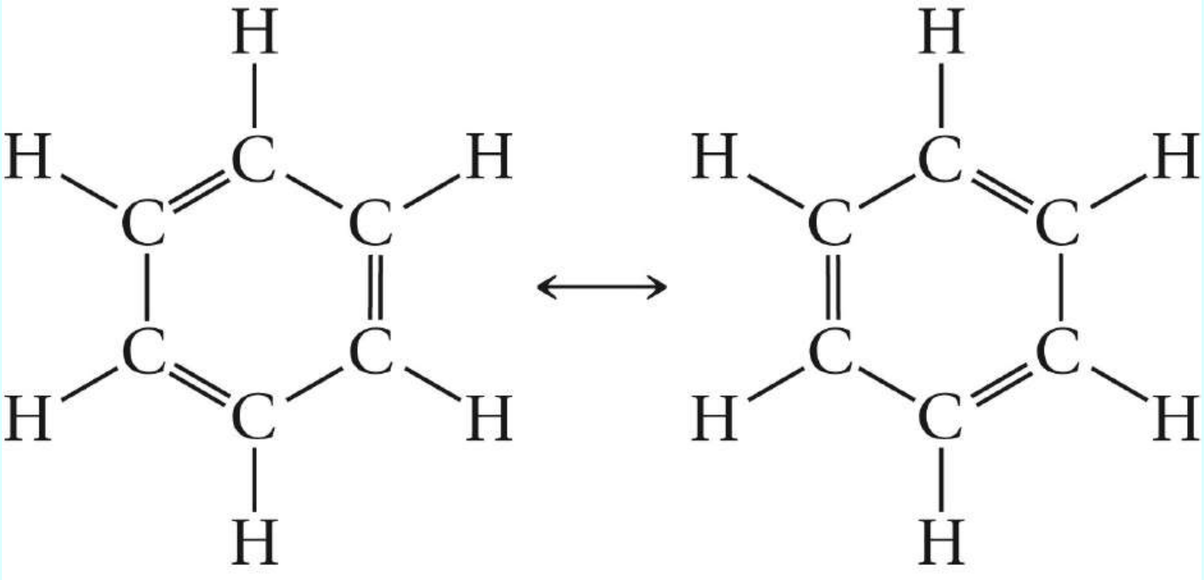


# Resonance in the Nitrate Ion



# Benzene





# Notes on Resonance Structures

1. Resonance forms are not different molecules, nor are they representations of electron shifting
2. Resonance structures arise when two Lewis structures are equally plausible
3. Only ***electrons*** can be shifted in resonance structures. Atoms ***cannot*** be moved.

# Example 7.3

## EXAMPLE 7.3

Write two resonance structures for the $NO_2^-$ ion.

### STRATEGY

1. The Lewis structure of $NO_2^-$ is derived in Example 7.2.

   [:Ö—N̈=Ö:]$^-$

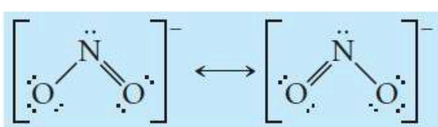
2. Change the position of the multiple bond and one of the unshared electron pairs.

3. Do not change the skeleton.

### SOLUTION

The Lewis structures of the two resonance forms are



# Formal Charges

- Formal charges  are analogous to oxidation numbers:
  - They are not actual charges
  - They keep track of electron ownership

# Formal Charges

- Formal charges are determined by totaling the number of valence electrons (X), and then subtracting the total of the number of lone electrons (Y) plus half the number of bonding electrons (Z/2)
- Since half the number of bonding electrons is the number of bonds, this relationship simplifies to:

$$\text{formal charge} = \text{VE} - \text{number of unshared electrons} - \text{number of bonds}$$

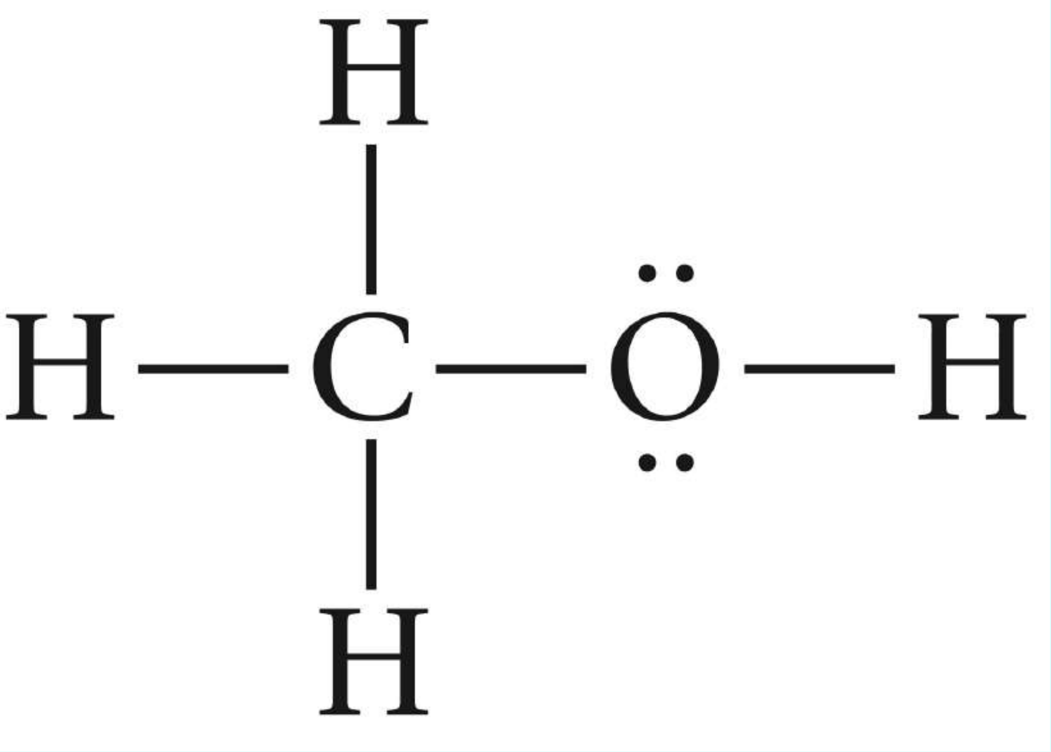
# Rules Governing Formal Charge

- The quality of a Lewis structure can be determined by the distribution of formal charge
  - Minimize charges
    - Best to have no $C_f$ or small $C_f$
  - Watch electronegativity
    - The most electronegative atoms should have the most negative formal charge
  - Minimize separation of charge

# Calculating Formal Charge on $CH_3OH$

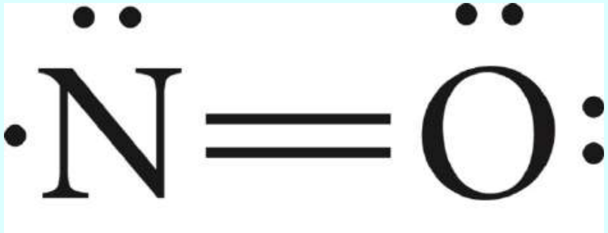
- Consider $CH_3OH$
  - The formal charge on carbon is 4 – 0 – 4 = 0
  - The formal charge on oxygen is 6 – 4 – 2 = 0

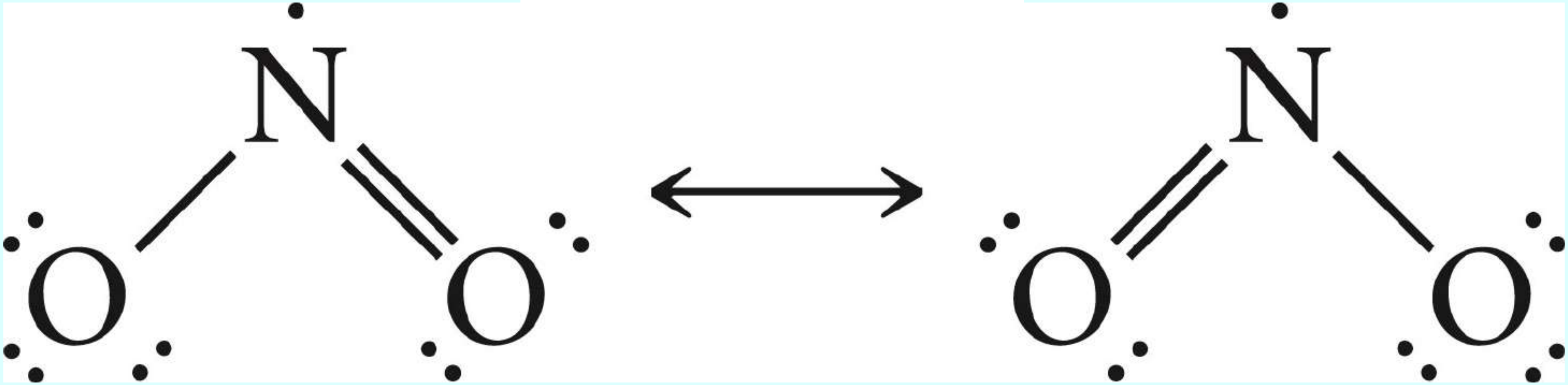
# Example



# Exceptions to the Octet Rule

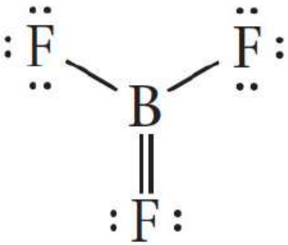
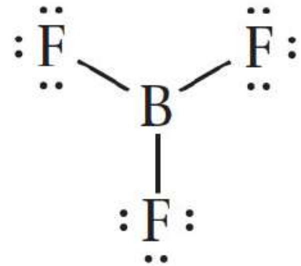
- Electron deficient molecules
  - Odd electron species (free radicals)
  - Paramagnetic
  - Examples: NO, $NO_2$





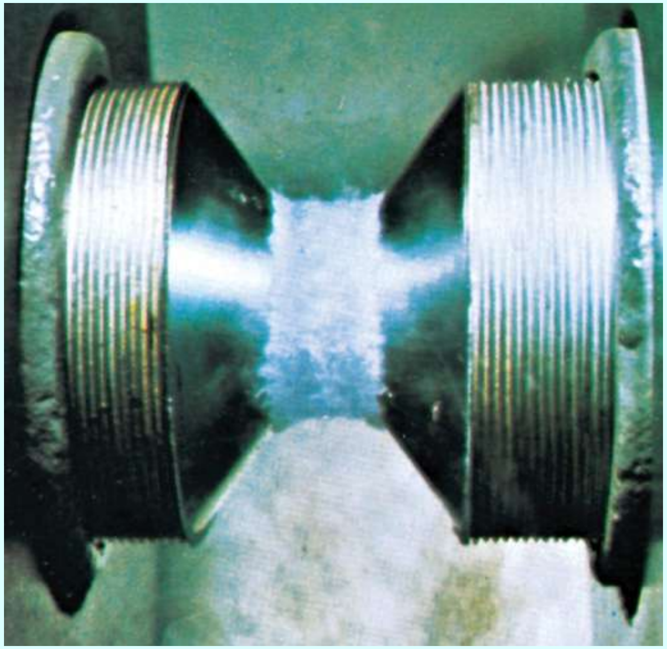
# Table 7.2 Sub-Octets: $BeF_2$ and $BF_3$

**TABLE 7.2 Possible Structures for $BeF_2$ and $BF_3$**

| Structure I | $C_f$ | Structure II | $C_f$ |
|---|---|---|---|
|  | Be = −2<br>F = +1 |  | Be = 0<br>F = 0 |
|  | B = −1<br>F = +1,0,0 |  | B = 0<br>F = 0 |

# Exceptions to the Octet Rule, (Cont'd)

- Molecular oxygen, $O_2$
- Molecular oxygen is paramagnetic
- Although it has an even number of electrons, it exists as a *diradical (two unpaired electrons)*
- Lewis structure for $O_2$ is difficult to draw

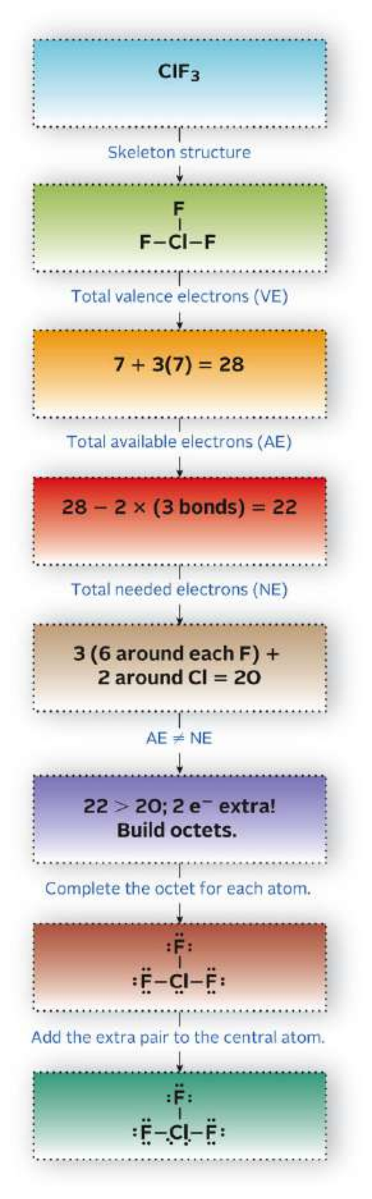


# Expanded Octets

- Some elements are capable of surrounding themselves with more than four pairs of electrons
  - Expanded octets
  - $PCl_5$, $SF_6$

| Period | Grp 15 | Grp 16 | Grp 17 | Grp 18 |
|---|---|---|---|---|
| 3 | P | S | Cl | |
| 4 | As | Se | Br | Kr |
| 5 | Sb | Te | I | Xe |

# Figure 7.6: Schema for Expanded Octets



# Example 7.4 – Expanded Octets

EXAMPLE 7.4

Draw Lewis structures of $XeF_4$.

STRATEGY

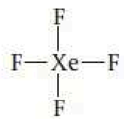
If AE < NE, follow the process described in Figure 7.3.

If AE = NE, your skeleton is correct; add electrons as unshared pairs to form octets around the atoms.

If AE > NE, follow the process described in Figure 7.6.

SOLUTION

Skeleton



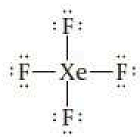
VE — 4(7 (for each F)) + 8 (for Xe) = 36

AE — AE = VE − 2(bonds) = 36 − 2(4 bonds) = 28

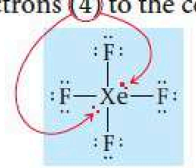
NE — 4(6 (for each F to have an octet)) + 0 (Xe has an octet) = 24

AE = NE ? — No; AE > NE. There are 4 extra electrons.

Satisfy the octet rule



Lewis structure — Add extra electrons (4) to the central atom.

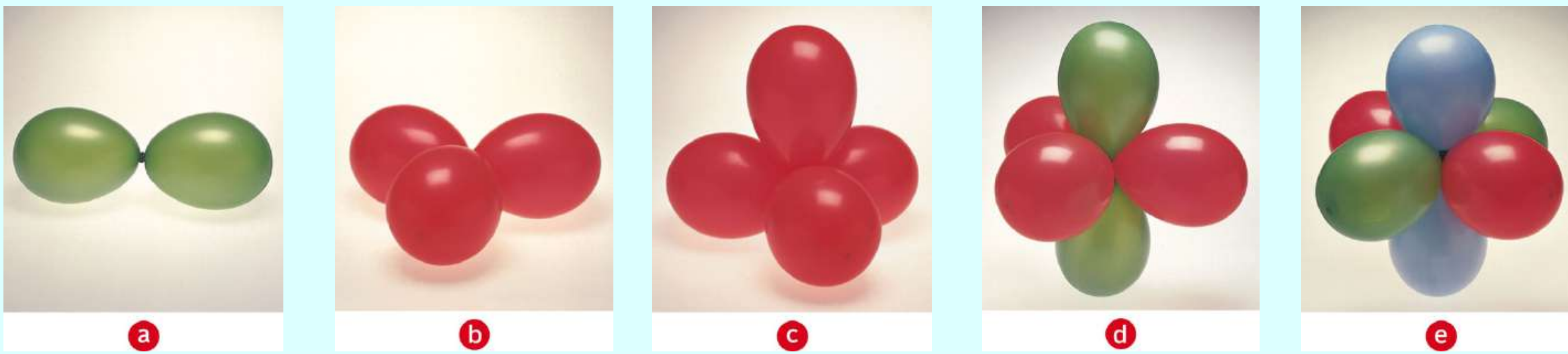


# Molecular Geometry

- Diatomic molecules are the easiest to visualize in three dimensions
  - HCl
  - $Cl_2$
- Diatomic molecules are ***linear***

# Figure 7.4 – Ideal Geometries

- There is a fundamental geometry that corresponds to the total number of electron pairs around the central atom:  2, 3, 4, 5 and 6




*linear* *trigonal planar* *tetrahedral* *trigonal bipyramidal* *octahedral*

# Valence Shell Electron Pair Repulsion Theory

- The ideal geometry of a molecule is determined by the way the electron pairs orient themselves in space
  - The orientation of electron pairs arises from electron repulsions
  - The electron pairs spread out so as to minimize repulsion

# Two electron pairs

- ***Linear***
- Bond angles
  - The bond angle in a linear molecule is always 180°

# Three electron pairs

- ***Trigonal planar***
- The electron pairs form an equilateral triangle around the central atom
- Bond angles are 120°

# Four Electron Pairs

- ***Tetrahedral***
- Bond angles are 109.5°

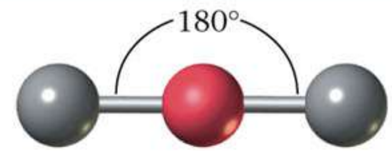
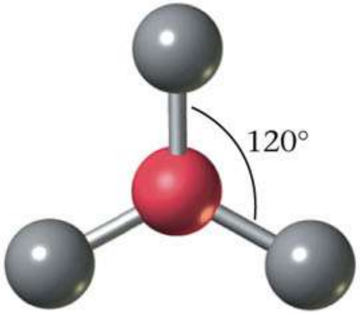
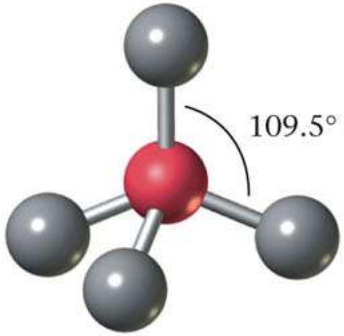
# Five Electron Pairs

- ***Trigonal bipyramid***
- Bond angles vary
  - In the trigonal plane, 120°
  - Between the plane and apexes, 90°
  - Between the central atom and both apexes, 180°

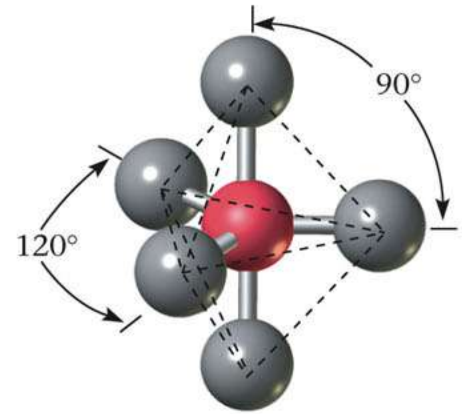
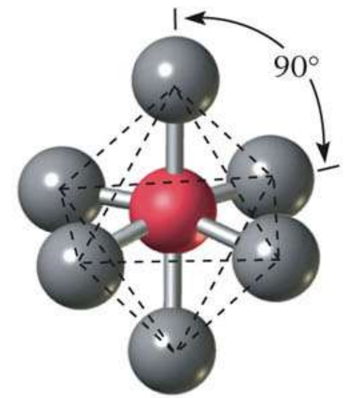
# Six Electron Pairs

- ***Octahedron***
- The octahedron is a ***square bipyramid***
- Bond angles vary
  - 90° in and out of plane
  - 180° between diametrically opposite atoms and the central atom

# Figure 7.8 - Molecular Geometry Summarized

| Species type | Orientation of electron pairs | Predicted bond angles | Example | Ball-and-stick model |
|---|---|---|---|---|
| $AX_2$ | Linear | 180° | $BeF_2$ |   |
| $AX_3$ | Trigonal planar | 120° | $BF_3$ |   |
| $AX_4$ | Tetrahedron | 109.5° | $CH_4$ |   |

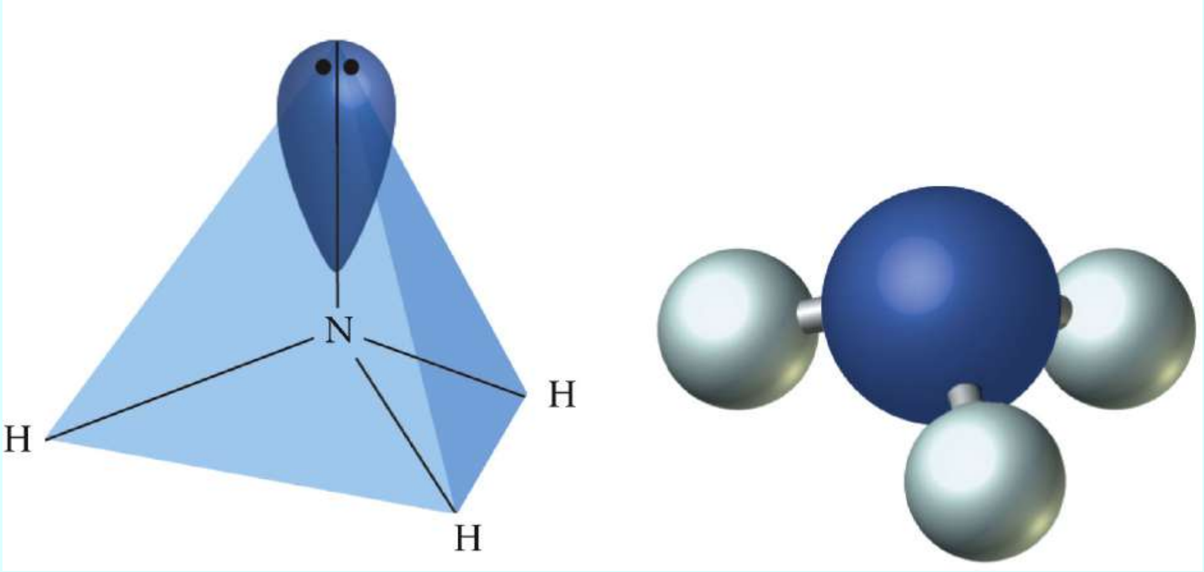
# Figure 7.8 - Molecular Geometry Summarized, (Cont'd)

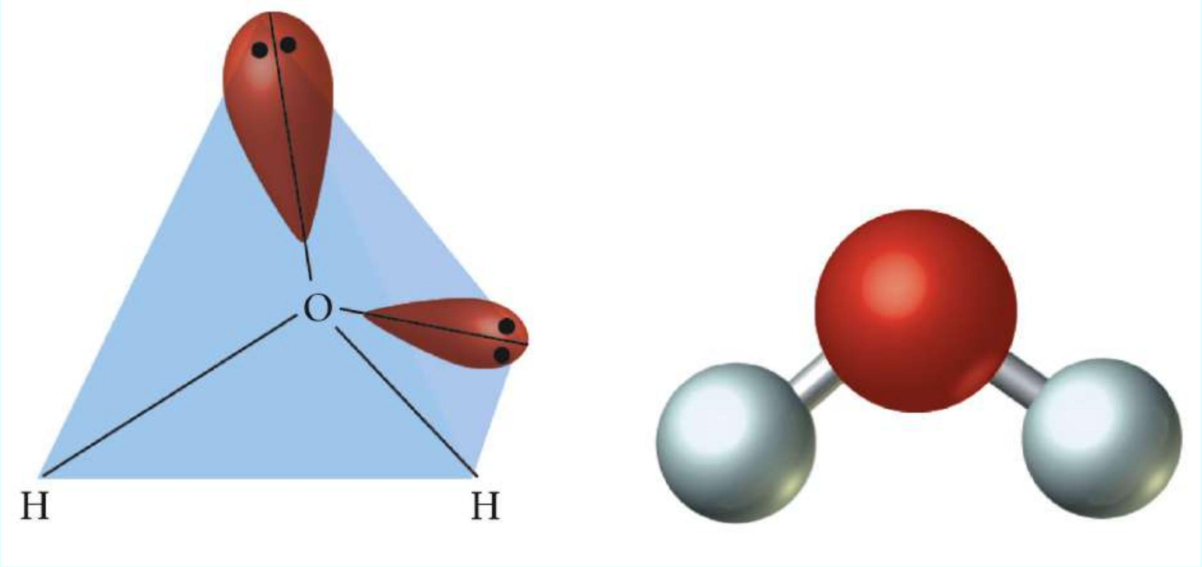
| Species type | Orientation of electron pairs | Predicted bond angles | Example | Ball-and-stick model |
|---|---|---|---|---|
| $AX_5$ | Trigonal bipyramid | 90°<br>120°<br>180° | $PF_5$ |  |
| $AX_6$ | Octahedron | 90°<br>180° | $SF_6$ |  |

# Unshared Pairs and Geometry

- Electron pair geometry
  - Consider the ***terminal atoms*** and the ***lone pairs*** around the central atom
- Molecular geometry
  - Consider only the ***terminal atoms*** around the central atom

# Figure 7.9-7.10: Ammonia and Water



# Bond Angles and Lone Pairs

- Ammonia and water show smaller bond angles than predicted from the ideal geometry
  - The lone pair is larger in volume than a bond pair
  - There is a nucleus at only one end of the bond so the electrons are free to spread out over a larger area of space

# The A-X-E Notation

- A denotes a central atom
- X denotes a terminal atom
- E denotes a lone pair
- Example
  - Water
    - $H_2O$
    - O is central
      - Two lone pairs
      - Two hydrogens
    - $AX_2E_2$

# Table 7.3 - Molecular Geometry Summary with Lone Pairs Included

**TABLE 7.3 Geometries with Two, Three, or Four Electron Pairs Around a Central Atom**

| No. of Terminal Atoms (X) + Unshared Pairs (E) | Species Type | Ideal Bond Angles* | Molecular Geometry | Examples |
|---|---|---|---|---|
| 2 | $AX_2$ | 180° | Linear | $BeF_2$, $CO_2$ |
| 3 | $AX_3$ | 120° | Trigonal planar | $BF_3$, $SO_3$ |
| | $AX_2E$ | 120°* | Bent | $GeF_2$, $SO_2$ |
| 4 | $AX_4$ | 109.5° | Tetrahedron | $CH_4$ |
| | $AX_3E$ | 109.5°* | Trigonal pyramid | $NH_3$ |
| | $AX_2E_2$ | 109.5°* | Bent | $H_2O$ |

*In these species, the observed bond angle is ordinarily somewhat less than the ideal value.

# Example 7.5

## EXAMPLE 7.5

Predict the geometry of

(a) $NH_4^+$ (b) $BF_3$ (c) $PCl_3$

### STRATEGY

1. Start by writing Lewis structures for each species.
2. Focus on the central atom, then decide what species type ($AX_2$, $AX_3$, ...) the molecule or ion is.

   A represents the central atom.

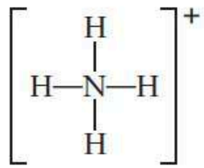
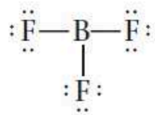
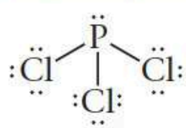
   X represents the terminal atoms.

   E represents the unshared electron pairs.
3. Recall Table 7.3, which matches the species type with the molecular geometry and ideal bond angles for the species.

*continued*

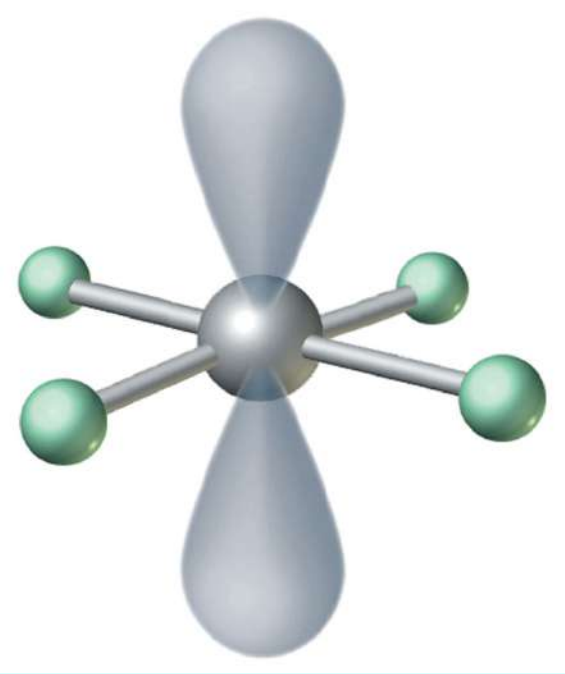
# Example 7.5, (Cont'd)

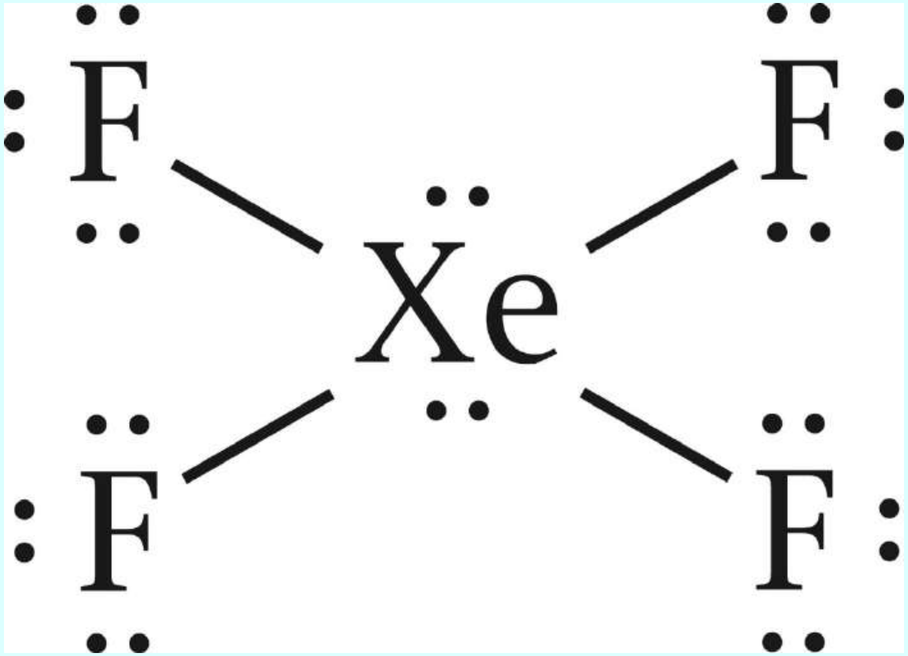
SOLUTION

| | |
|---|---|
| (a) Lewis structure |  |
| Species type | A = N, X = H (4), no E $\rightarrow AX_4$ |
| Geometry | tetrahedral, 109.5° bond angles |
| (b) Lewis structure |  |
| Species type | A = B, X = F (3), no E $\rightarrow AX_3$ |
| Geometry | trigonal planar, 120° bond angles |
| (c) Lewis structure |  |
| Species type | A = P, X = Cl (3), E = 1 $\rightarrow AX_3E$ |
| Geometry | trigonal pyramid (The ideal bond angles are 109.5° but actually are 104°.) |

# Lone Pairs and Expanded Octets

- Where expanded octets are possible, place the extra lone pairs on the central atom
- Example: $XeF_4$





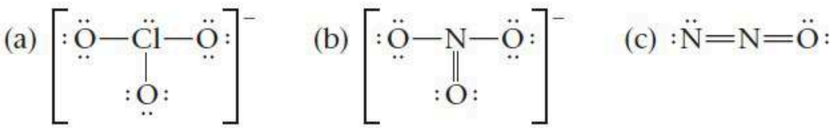
# Multiple Bonds

- For molecular geometry purposes, multiple bonds behave the same as single bonds
  - All of the electron pairs are located in the same place (between the nuclei)
  - The geometry of the molecule is determined by the number of terminal atoms, which is not affected by the presence of a double or triple bond

# Example 7.6

## EXAMPLE 7.6

Predict the geometries of the $ClO_3^-$ ion, the $NO_3^-$ ion, and the $N_2O$ molecule, which have the Lewis structures



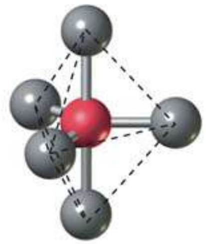
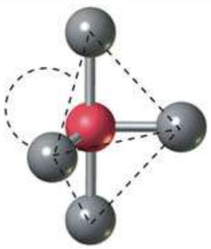
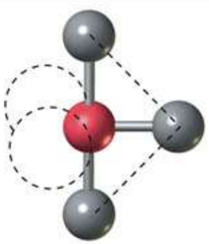
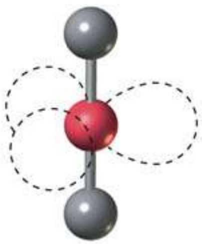
### STRATEGY

1. Classify each species as $AX_mE_n$ and use Table 7.3.
2. Multiple bonds count as single bonds. It is the number of terminal atoms (X) that are counted, not the number of bonds.

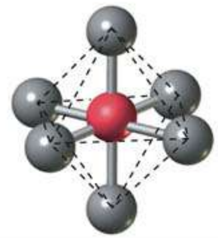
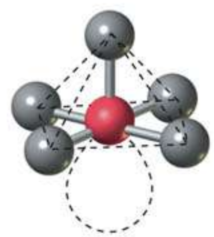
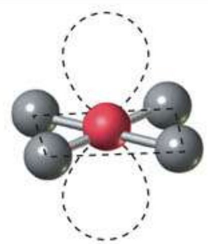
### SOLUTION

| | |
|---|---|
| (a) Species type | A = Cl, X = O = 3, E = 1 $\rightarrow$ $AX_3E$ |
| Geometry | trigonal pyramid, ideal bond angles are 109.5° |
| (b) Species type | A = N, X = O = 3, E = 0 $\rightarrow$ $AX_3$ |
| Geometry | trigonal planar, ideal bond angles are 120° |
| (c) Species type | A = N, X = N and O = 2, E = 0 $\rightarrow$ $AX_2$ |
| Geometry | linear, ideal bond angles are 180° |

# Figure 7.11 - Molecular Geometry Summary

| 5 ELECTRON PAIRS | | | | |
|---|---|---|---|---|
| Species type | Structure | Description | Example | Bond angles |
| $AX_5$ |  | Trigonal bipyramidal | $PF_5$ | 90°, 120°, 180° |
| $AX_4E$ |  | See-saw | $SF_4$ | 90°, 120°, 180° |
| $AX_3E_2$ |  | T-shaped | $ClF_3$ | 90°, 180° |
| $AX_2E_3$ |  | Linear | $XeF_2$ | 180° |

# Figure 7.11 - Molecular Geometry Summary, (Cont'd)

| Species type | Structure | Description | Example | Bond angles |
|---|---|---|---|---|
| **6 ELECTRON PAIRS** | | | | |
| $AX_6$ |  | Octahedral | $SF_6$ | 90°, 180° |
| $AX_5E$ |  | Square pyramidal | $ClF_5$ | 90°, 180° |
| $AX_4E_2$ |  | Square planar | $XeF_4$ | 90°, 180° |

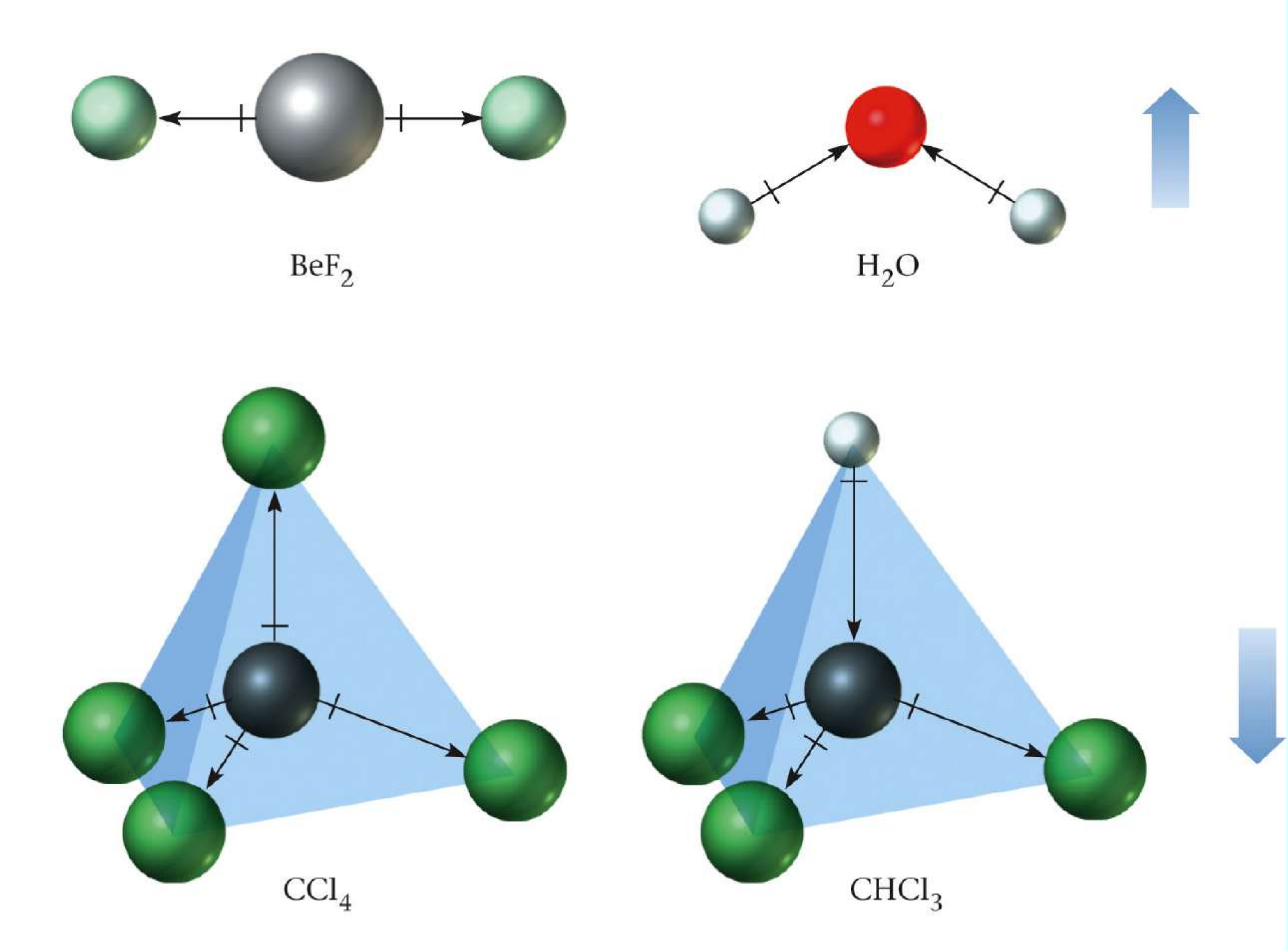
# Polarity - Bonds

- Recall that a polar bond has an asymmetric distribution of electrons
  - X-X is nonpolar
  - X-Y is polar
- Polarity of a bond increases with increasing difference in electronegativity between the two atoms
- Bond is a dipole
  - One end is ($\delta^+$), while the other is ($\delta^-$)

# Polarity - Molecules

- Molecules may also possess polarity
  - Positive and negative poles
  - Molecule is called a dipole
- Consider HF
  - H is $\delta^+$ while F is $\delta^-$
- Consider $BeF_2$
  - Be-F bond is polar
  - $BeF_2$ is nonpolar

# Figure 7.14 - Polarity of Molecules



# Example 7.7

## EXAMPLE 7.7

Determine whether each of the following is polar or nonpolar:

(a) $SO_2$ (b) $CO_2$ (c) $CHCl_3$

### STRATEGY

1. Write the Lewis structure.
2. Classify the molecule or ion as $AX_mE_n$.
3. Decide on the geometry (Table 7.3 or Figure 7.11).
4. Consider the A—X bonds and answer the following questions:

   (a) Are the terminal atoms identical?

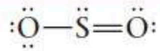
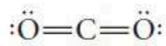
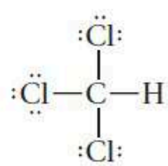
   Yes; possibly nonpolar (depends on symmetry). No; polar

   (b) Are the A—X bonds arranged symmetrically around the central atom?

   No; polar, Yes; nonpolar if the answer to (a) is also yes.

*continued*

# Example 7.7, (Cont'd)

| SOLUTION | |
|---|---|
| (a) Lewis structure |  |
| Species type | $AX_2E$ |
| Geometry | bent |
| Identical terminal atoms? | yes } polar |
| Symmetric A–X bonds? | no } polar |
| (b) Lewis structure |  |
| Species type | $AX_2$ |
| Geometry | linear |
| Identical terminal atoms? | yes } nonpolar |
| Symmetric A–X bonds? | yes } nonpolar |
| (c) Lewis structure |  |
| Species type | $AX_4$ |
| Geometry | tetrahedral |
| Identical terminal atoms? | no → polar |

# Example 7.8

## EXAMPLE 7.8 **CONCEPTUAL**

For each of the species in column A, choose the description in column B that best applies.

| A | B |
|---|---|
| (a) $CO_2$ | (e) polar, bent |
| (b) $CH_2Cl_2$ | (f) nonpolar, trigonal planar |
| (c) $XeF_2$ | (g) nonpolar, linear |
| (d) $BF_3$ | (h) nonpolar, trigonal pyramid |
| | (i) polar, tetrahedral |
| | (j) polar, trigonal pyramid |

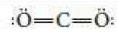
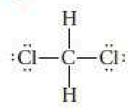
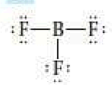
*continued*

# Example 7.8, (Cont'd)

STRATEGY

1. Note that the descriptions in column B are about geometry and polarity.
2. Draw the Lewis structures of the compounds in column A (Figure 7.3 or 7.6).
3. Determine series type and geometry (Table 7.3 or Figure 7.11).
4. Determine polarity.
5. Match your description with those given in column B.

SOLUTION

| | |
|---|---|
| (a) Lewis structure |  |
| species type → geometry | $AX_2$ → linear |
| polarity | nonpolar |
| match | g |
| (b) Lewis structure |  |
| species type → geometry | $AX_4$ → tetrahedral |
| polarity | polar |
| match | i |
| (c) Lewis structure |  |
| species type → geometry | $AX_2E_3$ → linear |
| polarity | nonpolar |
| match | g |
| (d) Lewis structure |  |
| species type → geometry | $AX_3$ → trigonal planar |
| polarity | nonpolar |
| match | f |

# Atomic Orbitals and Hybridization

- Valence Bond Model
  - Linus Pauling
    - Nobel Prize, 1954
  - Orbital diagrams
    - Isolated F atom (↑↓) (↑↓) (↑↓)(↑↓)(↑ )

      *1s* *2s* *2p*
    - F atom in HF (↑↓) (↑↓) (↑↓)(↑↓)(↑↓)

      *1s* *2s* *2p*

# Valence Bond Theory

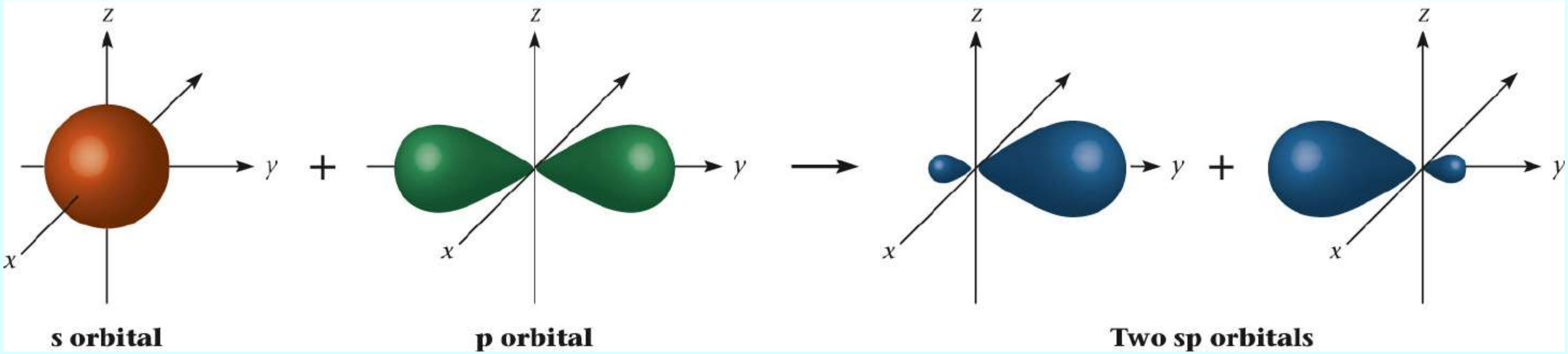
- Unpaired electrons from one atom pair with unpaired electrons from another atom and give rise to chemical bonds
- Simple extension of orbital diagrams

# Limitations of the Valence Bond Model

- Molecules that form from electron-deficient central atoms such as Be and B are not explained by the valence bond model
- Carbon forms four bonds – not the two that would be expected on the basis of the valence bond model

# Figure 7.15 - Atomic Orbital Mathematics

- The number of hybrid orbitals formed always equals the number of atomic orbitals that are combined
- Two atomic orbitals produce two hybrid orbitals
  - One s + one p → two sp



# Table 7.4 - Hybrid Orbitals and Geometry

**TABLE 7.4 Hybrid Orbitals and Their Geometries**

| Number of Electron Pairs | Atomic Orbitals | Hybrid Orbitals | Orientation | Examples |
|---|---|---|---|---|
| 2 | s, p | sp | Linear | $BeF_2$, $CO_2$ |
| 3 | s, two p | $sp^2$ | Trigonal planar | $BF_3$, $SO_3$ |
| 4 | s, three p | $sp^3$ | Tetrahedron | $CH_4$, $NH_3$, $H_2O$ |
| 5 | s, three p, d | $sp^3d$ | Trigonal bipyramid | $PCl_5$, $SF_4$, $ClF_3$ |
| 6 | s, three p, two d | $sp^3d^2$ | Octahedron | $SF_6$, $ClF_5$, $XeF_4$ |

# Hybrid Orbitals and Electron Occupancy

- Same rules we have seen before
  - In an atom, an orbital holds two electrons
  - In a molecule, an orbital also holds two electrons
- What electrons go into hybrid orbitals?
  - Lone pairs
  - One pair per bond
    - Even for a double bond, only one pair goes into the hybrid orbital

# Multiple bonds

- Sigma (σ) bonds
  - Electron density is located between the nuclei
  - One pair of each bond is called a sigma pair
- Pi bonds (π)
  - Electron density is located above and below or in front of and in back of the nuclei
    - One pair of a double bond is called pi (π)
    - Two pairs of a triple bond are called pi (π)

# Example 7.9

## EXAMPLE 7.9

Give the hybridization of

(a) carbon in $CH_3Cl$ (b) phosphorus in $PH_3$ (c) sulfur in $SF_4$

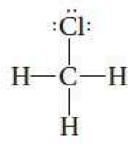
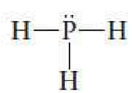
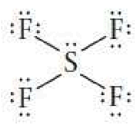
### STRATEGY

1. Draw the Lewis structure of the molecules.
2. Determine the species type: $AX_mE_n$.
3. Count bonds (m) and unshared pairs (n) around the atom in question.
4. Hybridization:

$m + n = 2 = sp$; $m + n = 3 = sp^2$; $m + n = 4 = sp^3$; $m + n = 5 = sp^3d$; $m + n = 6 = sp^3d^2$

*continued*

# Example 7.9 (Cont'd)

| SOLUTION | |
|---|---|
| (a) $CH_3Cl$ | |
| Lewis structure |  |
| species type | $AX_4$ |
| m + n | $4 + 0 = 4$ |
| hybridization | $m + n = 4 = sp^3$ |
| (b) $PH_3$ | |
| Lewis structure |  |
| species type | $AX_3E$ |
| m + n | $3 + 1 = 4$ |
| hybridization | $m + n = 4 = sp^3$ |
| (c) $SF_4$ | |
| Lewis structure |  |
| species type | $AX_4E$ |
| m + n | $4 + 1 = 5$ |
| hybridization | $m + n = 5 = sp^3d$ |

# Example 7.10

EXAMPLE 7.10

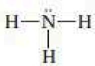
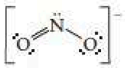
State the hybridization of nitrogen in

(a) $NH_3$ (b) $NO_2^-$ (c) $N_2$

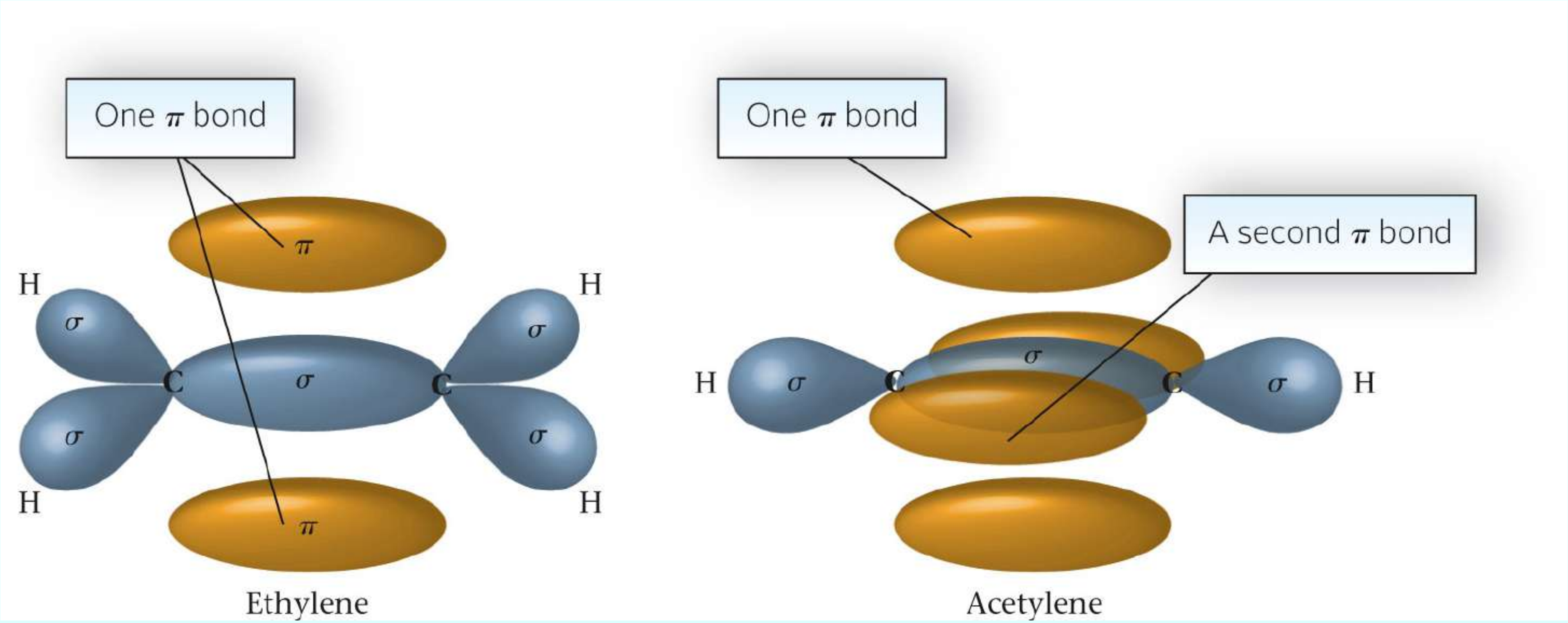
STRATEGY

1. Start by writing a Lewis structure for each species.
2. Determine the species type.
3. The extra electron pairs in a multiple bond are not located in a hybrid orbital. Thus the number of terminal atoms (m) equals the number of bonds in hybrid orbitals.
4. Add m + n.
5. See Example 7.9 for hybridization based on the (m + n) count.

SOLUTION

| | |
|---|---|
| (a) $NH_3$ | |
| Lewis structure |  |
| Species type | $AX_3E$ |
| m + n | 3 + 1 = 4 |
| hybridization | m + n = 4 = $sp^3$ |
| (b) $NO_2^-$ | |
| Lewis structure |  |
| Species type | $AX_2E$ |
| m + n | 2 + 1 = 3 |
| hybridization | m + n = 3 = $sp^2$ |
| (c) $N_2$ | |
| Lewis structure | :N≡N: |
| Species type | AXE |
| m + n | 1 + 1 = 2 |
| hybridization | m + n = 2 = sp |

# Figure 7.16 - Ethylene and Acetylene



# Example 7.11

## EXAMPLE 7.11

Give the number of pi and sigma bonds in

(a) $NH_3$ (b) $NO_2^-$ (c) $N_2$

### STRATEGY

1. The Lewis structures for these species are given in Example 7.10.
2. Determine the species type. The number of sigma bonds is m.
3. Count total bonds in the Lewis structure.

   pi bonds = total bonds − m

### SOLUTION

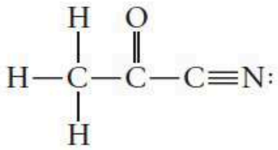
| | |
|---|---|
| (a) $NH_3$ | |
| species type | $AX_3$; m = 3 → 3 sigma (σ) bonds |
| number of bonds | 3 |
| number of pi (π) bonds | 3 − m = 3 − 3 = 0 → no pi (π) bonds |
| (b) $NO_2^-$ | |
| species type | $AX_2E$; m = 2 → 2 sigma (σ) bonds |
| number of bonds | 3 |
| number of pi (π) bonds | 3 − m = 3 − 2 = 1 → 1 pi (π) bond |
| (c) $N_2$ | |
| species type | AXE; m = 1 → 1 sigma (σ) bond |
| number of bonds | 3 |
| number of pi (π) bonds | 3 − m = 3 − 1 = 2 → 2 pi (π) bonds |

*continued*

# Example 7.11, (Cont'd)

END POINT

If the molecule does not have a defined central atom but instead has a long chain as in



Count all single bonds (in this case: 5), and all multiple bonds (here, 1 double bond and 1 triple bond).

The multiple bonds each contribute a sigma bond. The rest of the multiple bonds are pi bonds. Thus this molecule has

sigma bonds: 5 + 1 (from the double bond) + 1 (from the triple bond) = 7

pi bonds: 1 (from the double bond) + 2 (from the triple bond) = 3

# Key Concepts

1. Draw Lewis structures for molecules and polyatomic ions.
2. Write resonance forms.
3. Use VSEPR theory to predict molecular geometry.
4. From the geometry of a species, predict whether it will be polar or not.
5. State the hybridization of a species.
6. State the number of sigma and pi bonds in a species.