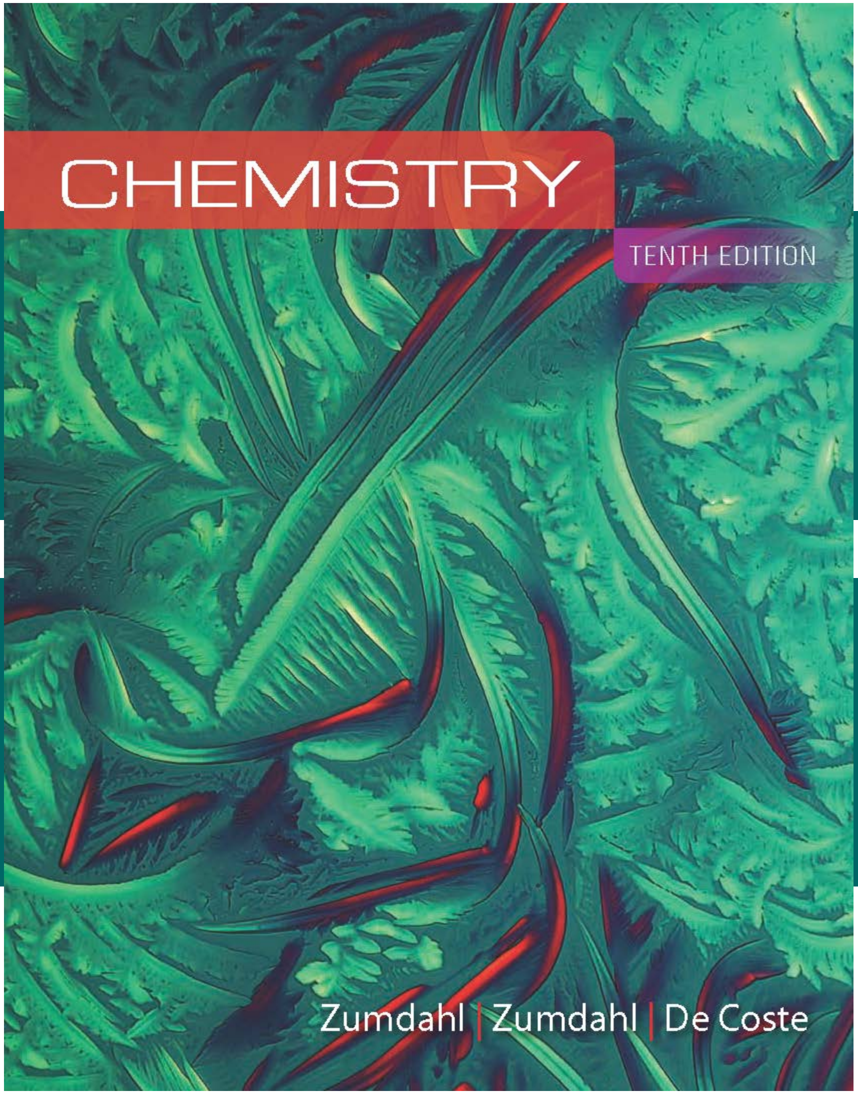

Chapter 8

Bonding: General Concepts

Chapter 8

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Chapter 8

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Localized Electron (LE) Model

- Assumes that a molecule is composed of atoms that are bound together by sharing pairs of electrons using the atomic orbitals of the bound atoms
  - **Lone pairs**: Pairs of electrons localized on an atom
  - **Bonding pairs**: Pairs of electrons found in the space between atoms

Parts of the LE Model

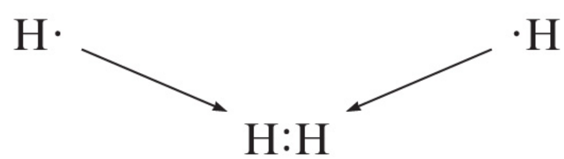
- Description of the valence electron arrangement in the molecule using Lewis structures
- Prediction of the geometry of the molecule using the valence shell electron-pair repulsion (VSEPR) model
- Description of the type of atomic orbitals used by the atoms to share electrons or hold lone pairs

Lewis Structure

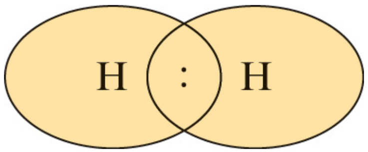
- Depicts the arrangement of valence electrons among atoms in a molecule
- Named after G.N. Lewis
- Only valence electrons are included
- Most important requirement for the formation of a stable compound
  - Atoms must attain noble gas electron configurations

Principle of Achieving a Noble Gas Electron Configuration - Hydrogen

- Follows a **duet rule**
  - Forms stable molecules where it shares two electrons
- Example - Two hydrogen atoms, each with one electron, combine to form the H_2 molecule



  - By sharing electrons, each hydrogen has a filled valence shell



Principle of Achieving a Noble Gas Electron Configuration - Helium

- Does not form bonds because it is a noble gas
  - Valence orbital is already filled
- Electron configuration - $1s^2$
- Represented by the following Lewis structure:

He:

Principle of Achieving a Noble Gas Electron Configuration - Second-Row Nonmetals (Carbon through Fluorine)

- Form stable molecules when surrounded by enough electrons to fill valence orbitals
- Obey the octet rule
  - **Octet rule**: Elements form stable molecules when surrounded by eight electrons

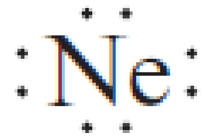
F atom with seven valence electrons | F_2 molecule | F atom with seven valence electrons

Principle of Achieving a Noble Gas Electron Configuration - Second-Row Nonmetals (Carbon Through Fluorine) (continued)

- Each fluorine atom in F_2 is surrounded by eight electrons
  - Two electrons that are shared with the other atom constitute a bonding pair
- Each fluorine atom also has three pairs of electrons not involved in bonding
  - These are the lone pairs

Principle of Achieving a Noble Gas Electron Configuration - Neon

- Does not form bonds because it already has an octet of valence electrons
- Represented by the following Lewis structure:



  - Only the valence electrons ($2s^22p^6$) are represented in the Lewis structure

Problem Solving Strategy - Steps for Writing Lewis Structures

1. Sum the valence electrons from all the atoms
2. Use a pair of electrons to form a bond between each pair of bound atoms
3. Arrange the remaining electrons to satisfy the duet rule for hydrogen and the octet rule for the second-row elements

Drawing the Lewis Structure of Water

- Sum the valence electrons for H_2O

$$\underset{\text{H}}{1} + \underset{\text{H}}{1} + \underset{\text{O}}{6} = 8 \text{ valence electrons}$$

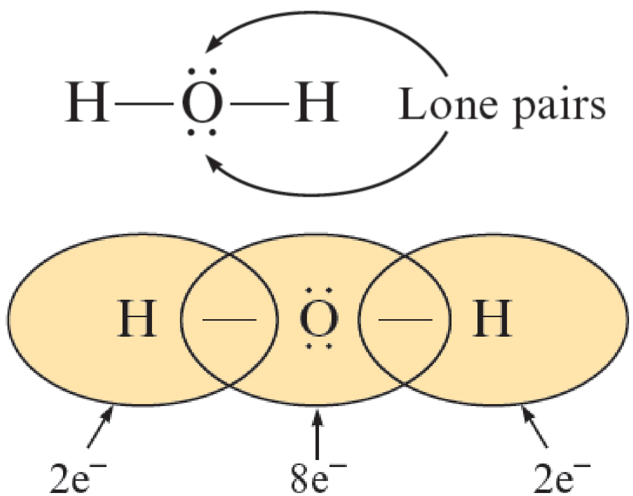
- Using a pair of electrons per bond, draw the O—H single bonds

H—O—H

  - A line is used to indicate each pair of bonding electrons

Drawing the Lewis Structure of Water (continued)

- Distribute the remaining electrons to achieve a noble gas electron configuration for each atom
  - Dots represent lone electron pairs



Interactive Example 8.6 - Writing Lewis Structures

- Give the Lewis structure for each of the following:
  a. HF
  b. N_2
  c. NH_3
  d. CH_4
  e. CF_4
  f. NO^+

Interactive Example 8.6 - Solution

- In each case, apply the three steps for writing Lewis structures
  - Recall that lines are used to indicate shared electron pairs and that dots are used to indicate nonbonding pairs (lone pairs)

Interactive Example 8.6 - Solution (continued)

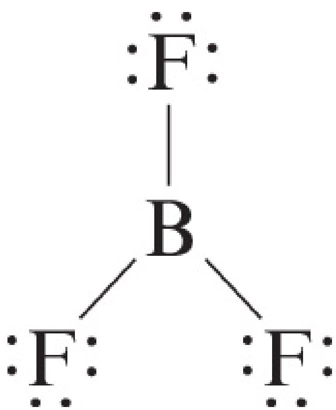
	Total Valence Electrons	Draw Single Bonds	Calculate Number of Electrons Remaining	Use Remaining Electrons to Achieve Noble Gas Configurations	Check Number of Electrons
a. HF	$1 + 7 = 8$	H—F	6	$H-\underset{\cdot\cdot}{\ddot{F}}:$	H, 2 F, 8
b. N_2	$5 + 5 = 10$	N—N	8	$:N\equiv N:$	N, 8
c. NH_3	$5 + 3(1) = 8$	H—N—H, with H bonded below N	2	$H-\ddot{N}-H$, with H bonded below N	H, 2 N, 8
d. CH_4	$4 + 4(1) = 8$	H—C—H, with H bonded above and below C	0	H—C—H, with H bonded above and below C	H, 2 C, 8
e. CF_4	$4 + 4(7) = 32$	F—C—F, with F bonded above and below C	24	$:\underset{\cdot\cdot}{\ddot{F}}-C-\underset{\cdot\cdot}{\ddot{F}}:$, with $:\underset{\cdot\cdot}{\ddot{F}}:$ bonded above and below C	F, 8 C, 8
f. NO^+	$5 + 6 - 1 = 10$	N—O	8	$[:N\equiv O:]^+$	N, 8 O, 8

Join In (11)

- Which of the following does not contain at least one double bond in the Lewis structure?
  a. H_2CO
  b. C_2H_4
  c. CO_2
  d. C_3H_8

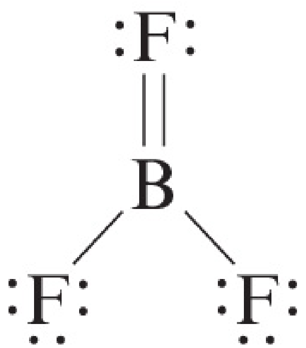
Boron

- Tends to form compounds in which the boron atom has fewer than eight electrons around it
- Boron trifluoride (BF_3)
  - Reacts energetically with molecules that have available lone pairs
    - Boron atom is electron-deficient
  - Has 24 valence electrons



Boron (continued)

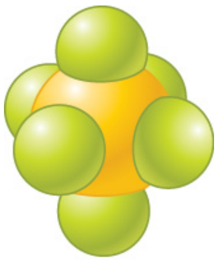
- Octet rule is satisfied by drawing the structure with a double bond



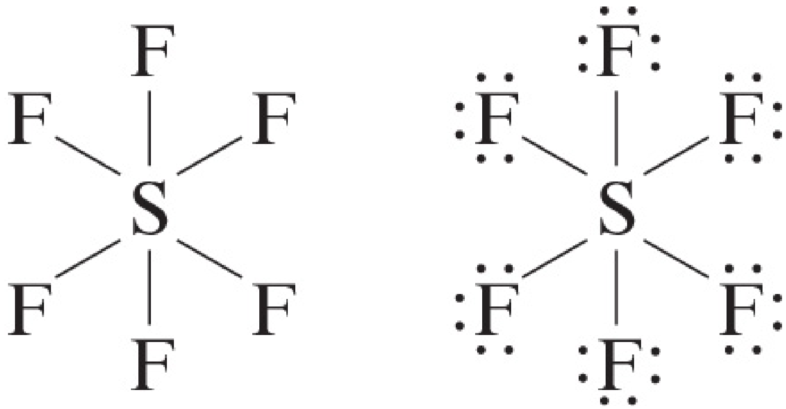
- Characteristic of boron to form molecules in which the boron atom is electron-deficient

Sulfur Hexafluoride (SF_6)

- Very stable molecule
- Sum of valence electrons
  - 6 + 6(7) = 48 electrons



SF_6



Sulfur Hexafluoride (SF_6) (continued)

- Sulfur exceeds the octet rule
  - Localized electron model assumes that the empty 3*d* orbitals can be used to accommodate extra electrons
    - Sulfur atom in SF_6 can have 12 electrons around it by using the 3*s* and 3*p* orbitals to hold 8 electrons, with the extra 4 electrons placed in the formerly empty 3*d* orbitals

Interactive Example 8.7 - Lewis Structures for Molecules That Violate the Octet Rule I

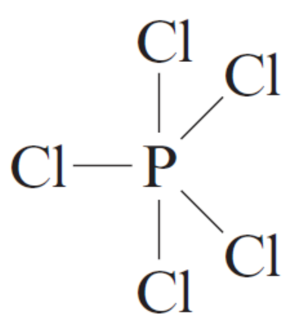
- Write the Lewis structure for PCl_5

Interactive Example 8.7 - Solution

1. Sum the valence electrons

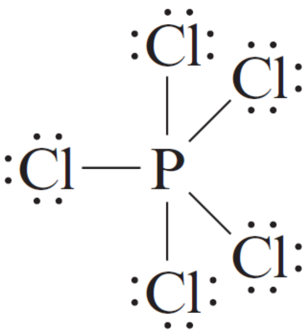
$$\underset{\text{P}}{\underset{\uparrow}{5}} + 5\underset{\text{Cl}}{\underset{\uparrow}{(7)}} = 40 \text{ electrons}$$

2. Indicate single bonds between bound atoms



Interactive Example 8.7 - Solution (continued)

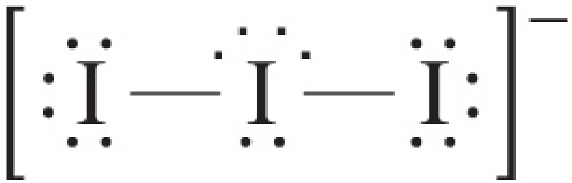
3. Distribute the remaining electrons
   - In this case, 30 electrons (40 – 10) remain
     - These are used to satisfy the octet rule for each chlorine atom
   - Final Lewis structure is



   - Phosphorus, a third-row element, has exceeded the octet rule by two electrons

Lewis Structure of Molecules with More Than One Atom That Exceed the Octet Rule

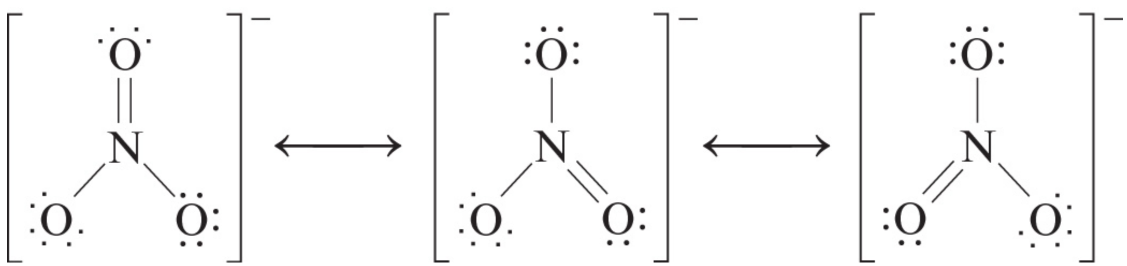
- Assume that the extra electrons should be placed on the central atom
- Example - Lewis structure of I_3^- (22 valence electrons)



  - Central iodine exceeds the octet rule

Resonance: An Introduction

- Invoked when more than one valid Lewis structure can be written for a particular molecule
  - Resulting electron structure of the molecule is given by the average of these **resonance structures**
- Represented by double-headed arrows



Resonance: An Introduction (continued)

  - Arrangement of nuclei is the same across all structures
  - Placement of electrons differs
  - Arrows show that the actual structure is an average of the three resonance structures
- Concept is necessary to compensate for the defective assumption of the LE model
  - LE model postulates that electrons are localized between a given pair of atoms

Example 8.9 - Resonance Structures

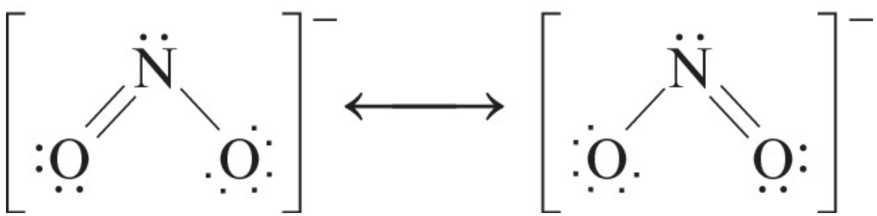
- Describe the electron arrangement in the nitrite anion (NO_2^-) using the localized electron model

Example 8.9 - Solution

- NO_2^- possesses 18 valence electrons (5 + 2(6) + 1 = 18)
- Indicating the single bonds gives the structure

O—N—O

  - Remaining 14 electrons (18 – 4) can be used to produce these structures:



Example 8.9 - Solution (continued)

- This is a resonance situation, and two equivalent Lewis structures can be drawn
- The electronic structure of the molecule is correctly represented not by either resonance structure but by the average of the two
    - There are two equivalent N—O bonds, each one intermediate between a single and a double bond

Odd-Electron Molecules

- Few molecules formed from nonmetals contain odd numbers of electrons
- Example - Nitric oxide (NO)
  - Emitted into the air where it reacts with oxygen to form NO_2 (*g*), which is another odd-electron molecule

Formal Charge

- Difference between the number of valence electrons on the free atom and the number of valence electrons assigned to the atom in the molecule
- Used to evaluate nonequivalent Lewis structures
  - Nonequivalent Lewis structures contain different numbers of single and multiple bonds

Determining Formal Charge of an Atom in a Molecule

- Information required
  - Number of valence electrons on the free neutral atom
    - Free neutral atom has zero net charge because the number of electrons equals the number of protons
  - Number of valence electrons belonging to the atom in a molecule

Determining Formal Charge of an Atom in a Molecule
(continued 1)

- Assign valence electrons in the molecule to the various atoms, making the following assumptions:
  - Lone pair electrons belong entirely to the atom in question
  - Shared electrons are divided equally between the two sharing atoms

Determining Formal Charge of an Atom in a Molecule

(continued 2)

- Number of valence electrons assigned to a given atom is calculated as follows:

$$(\text{Valence electrons})_{\text{assigned}} = (\text{number of lone pair electrons}) + \frac{1}{2}(\text{number of shared electrons})$$

Fundamental Assumptions about Formal Charges to Evaluate Lewis Structures

- Atoms in molecules try to achieve formal charges as close to zero as possible
- Any negative formal charges are expected to reside on the most electronegative atoms

Rules Governing Formal Charge

- To calculate the formal charge on an atom:
  1. Take the sum of the lone pair electrons and one-half the shared electrons
     - This is the number of valence electrons assigned to the atom in the molecule
  2. Subtract the number of assigned electrons from the number of valence electrons on the free, neutral atom to obtain the formal charge

Rules Governing Formal Charge (continued)

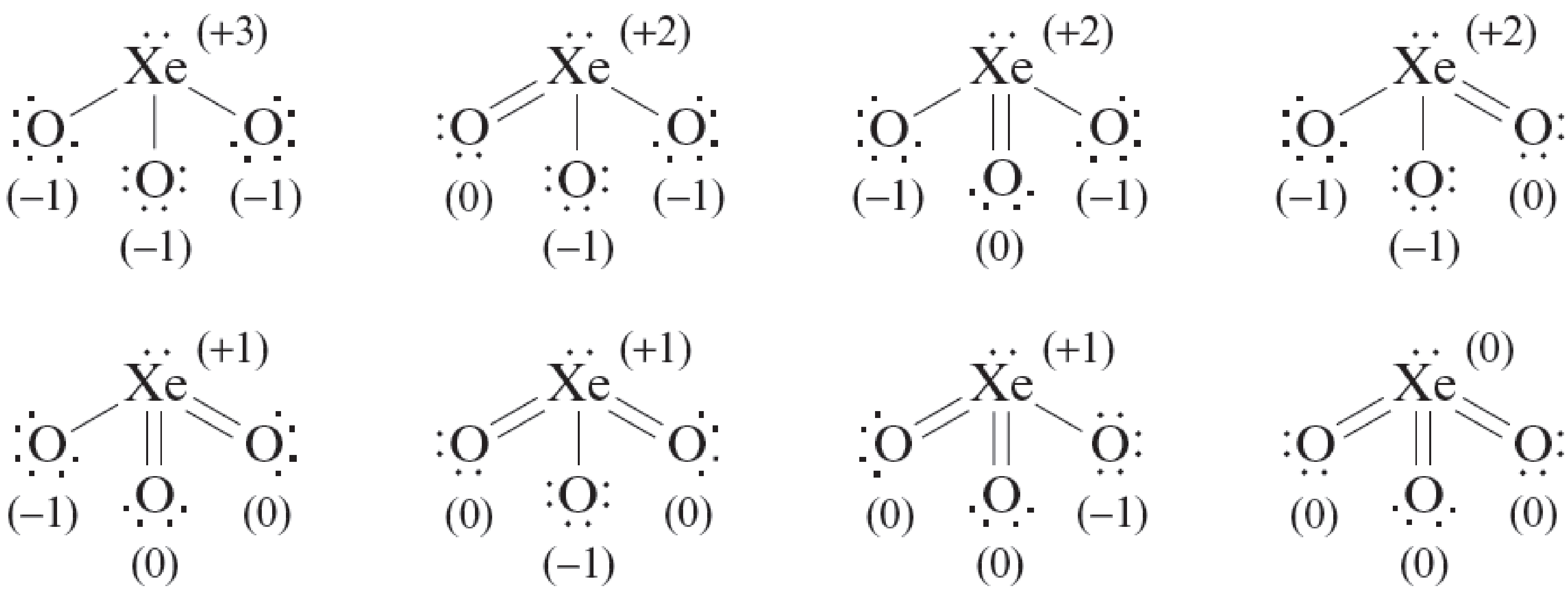
- Sum of the formal charges of all atoms in a given molecule or ion must be equal to the overall charge on that species
- Nonequivalent Lewis structures
  - Species with formal charges closest to zero and with any negative formal charges on the most electronegative atoms are considered to best describe the bonding in the molecule or ion

Example 8.10 - Formal Charges

- Give possible Lewis structures for XeO_3, an explosive compound of xenon
  - Which Lewis structure or structures are most appropriate according to the formal charges?

Example 8.10 - Solution

- For XeO_3 (26 valence electrons) we can draw the following possible Lewis structures:

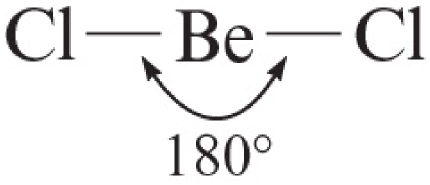


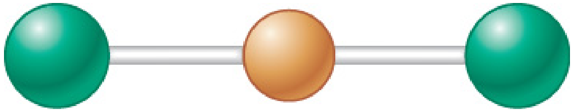
Valence Shell Electron-Pair Repulsion (VSEPR) Model

- Used to predict the molecular structure of molecules formed from nonmetals
  - **Molecular structure**: Three-dimensional arrangement of molecules in an atom
- Main postulate
  - Structure around a given atom is determined principally by minimizing electron-pair repulsions
    - Bonding and nonbonding pairs around a given atom will be placed as far apart as possible

Molecular Structure: Types

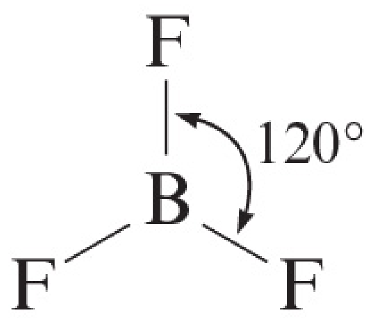
- **Linear structure**
  - Molecule has a 180-degree bond angle
  - Example - $BeCl_2$

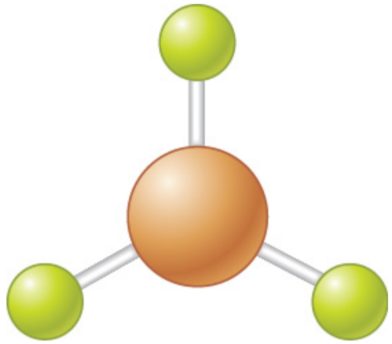




Molecular Structure: Types (continued 1)

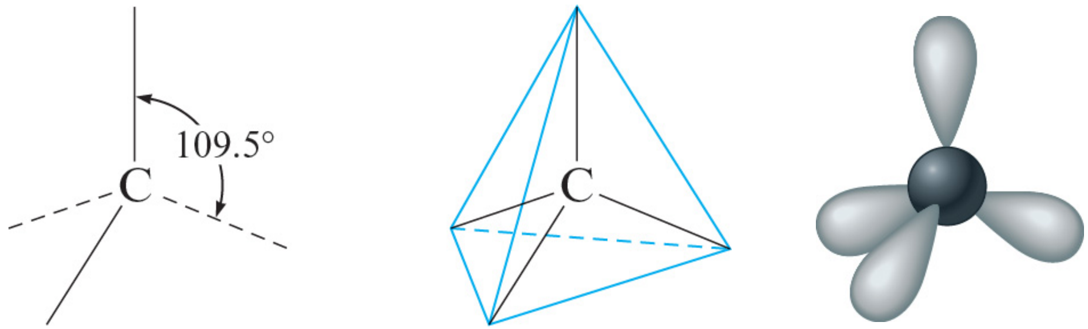
- **Trigonal planar structure**
  - Molecule has a planar (flat) and triangular structure with 120° bond angles
  - Example - BF_3





Molecular Structure: Types (continued 2)

- **Tetrahedral structure**
  - Molecule has bond angles of 109.5 degrees
  - Example - CH_4



  - Whenever four pairs of electrons are present around an atom, they should always be arranged tetrahedrally

Problem-Solving Strategy - Steps to Apply the VSEPR Model

1. Draw the Lewis structure for the molecule
2. Count the electron pairs and arrange them in the way that minimizes repulsion
3. Determine the positions of the atoms from the way the electron pairs are shared
4. Determine the name of the molecular structure from the positions of the atoms

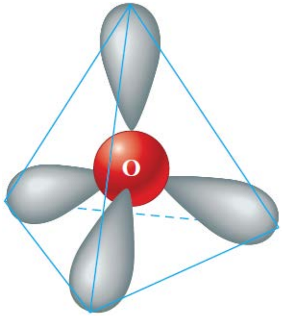
Example 8.11 - Prediction of Molecular Structure I

- Describe the molecular structure of the water molecule

Example 8.11 - Solution

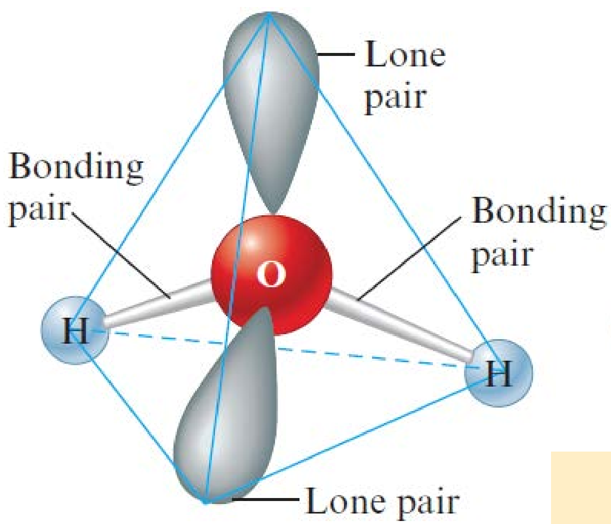
- The Lewis structure for water is

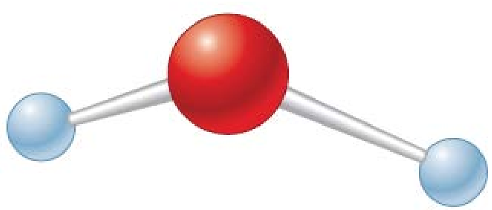
- There are four pairs of electrons: two bonding pairs and two nonbonding pairs
    - To minimize repulsions, these pairs are best arranged in a tetrahedral array



Example 8.11 - Solution (continued)

- Although H_2O has a tetrahedral arrangement of electron pairs, it is not a tetrahedral molecule
  - The atoms in the H_2O molecule form a V shape



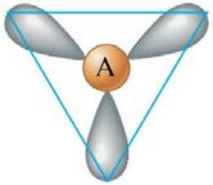
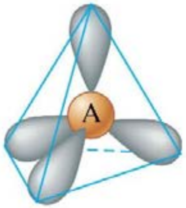


	CH_4	NH_3	H_2O
Number of Lone Pairs	0	1	2
Bond Angle	109.5°	107°	104.5°

Addition to the Original Postulate of the VSEPR Model

- Lone pairs require more room than bonding pairs and tend to compress the angles between the bonding pairs

Table 8.7 - Arrangements of Electron Pairs around an Atom Yielding Minimum Repulsion

Number of Electron Pairs	Arrangement of Electron Pairs		Example
2	Linear		
3	Trigonal planar		
4	Tetrahedral		

Section 8.13
Molecular Structure: The VSEPR Model

Table 8.7 - Arrangements of Electron Pairs around an Atom Yielding Minimum Repulsion (continued)

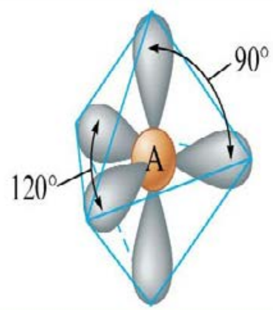
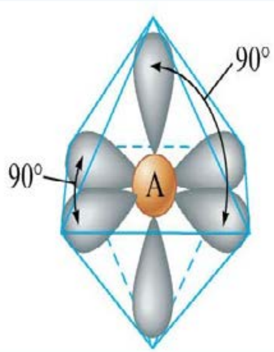
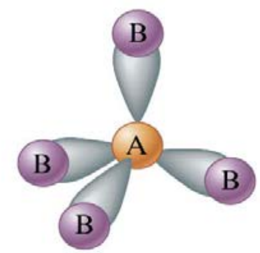
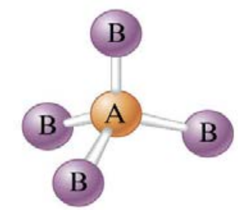
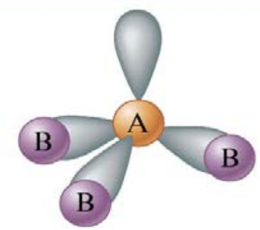
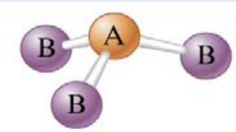
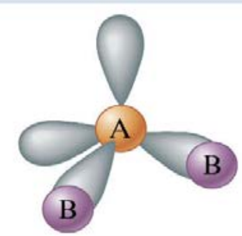
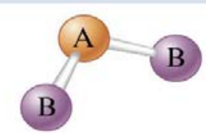
Number of Electron Pairs	Arrangement of Electron Pairs		Example
5	Trigonal bipyramidal		
6	Octahedral		

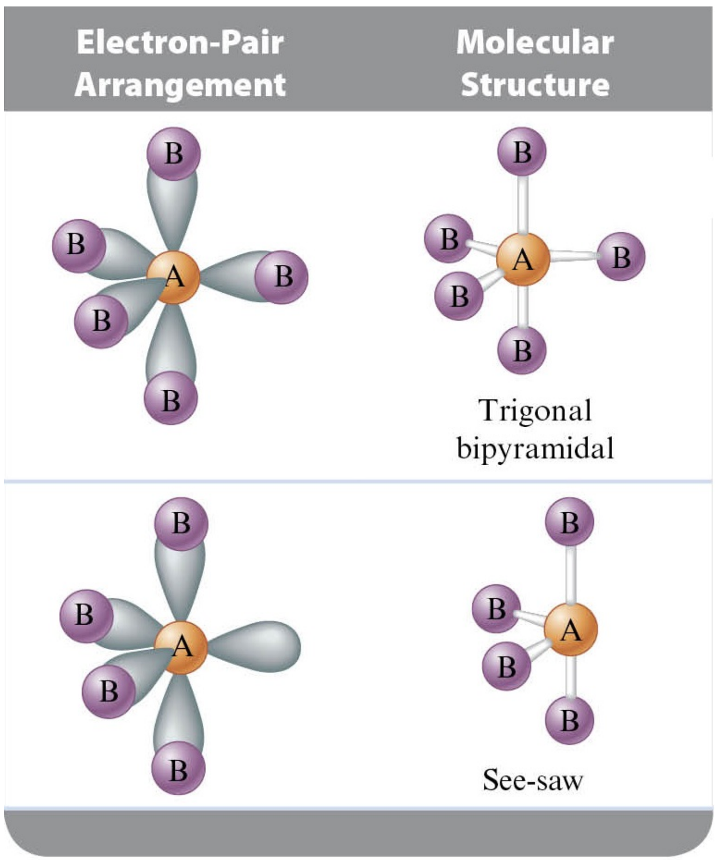
Table 8.8 - Structures of Molecules with Four Electron Pairs around the Central Atom

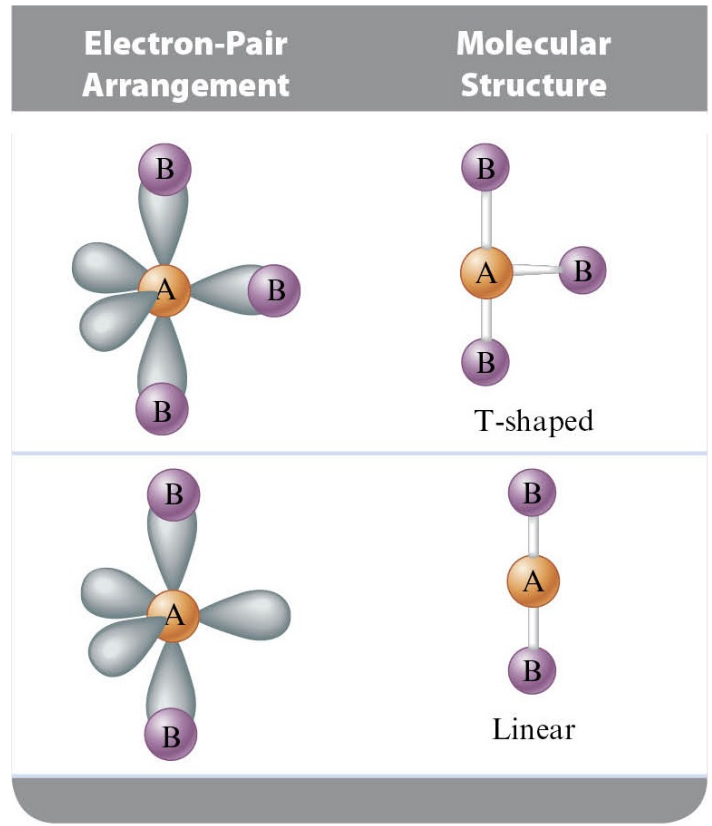
Electron-Pair Arrangement	Molecular Structure
	 Tetrahedral
	 Trigonal pyramid
	 V-shaped (bent)

Molecular Structure: Types (continued 3)

- Trigonal bipyramidal structure
  - Produces minimum repulsion for molecules that contain five pairs of electrons around the central atom
  - Bond angles - 90° and 120°
- **Octahedral structure**
  - Produces minimum repulsion for molecules that contain six pairs of electrons around the central atom
  - Bond angle - 90°

Table 8.9 - Structures of Molecules with Five Electron Pairs around the Central Atom





Critical Thinking

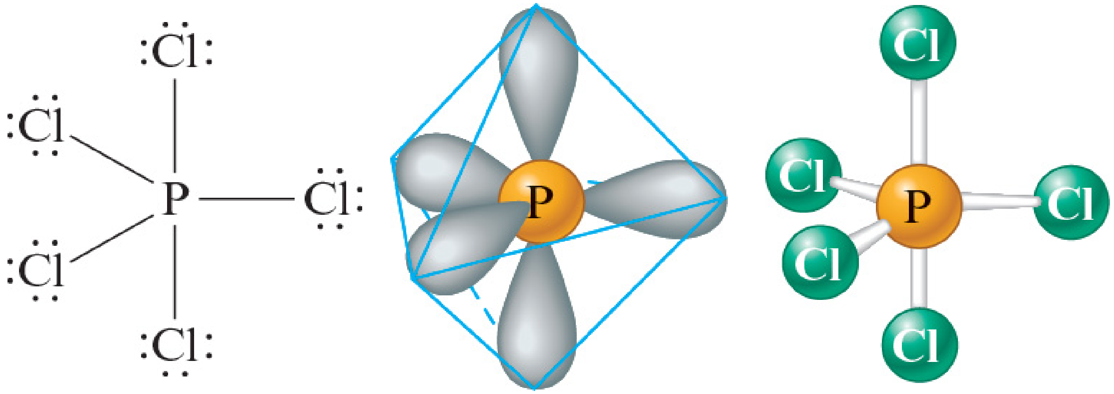
- You and a friend are studying for a chemistry exam
  - What if your friend tells you that all molecules with polar bonds are polar molecules?
    - How would you explain to your friend that this is not correct?
    - Provide two examples to support your answer

Interactive Example 8.12 - Prediction of Molecular Structure II

- When phosphorus reacts with excess chlorine gas, the compound phosphorus pentachloride (PCl_5) is formed
    - In the gaseous and liquid states, this substance consists of PCl_5 molecules, but in the solid state it consists of a 1:1 mixture of PCl_4^+ and PCl_6^- ions
    - Predict the geometric structures of PCl_5, PCl_4^+, and PCl_6^-

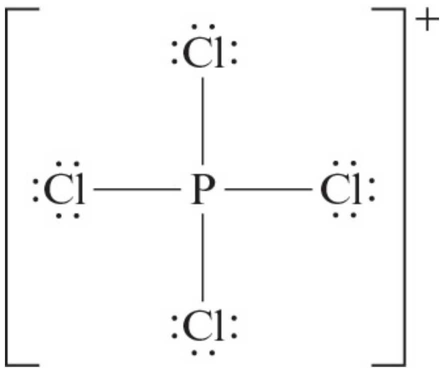
Interactive Example 8.12 - Solution

- The Lewis structure for PCl_5 is shown
  - Five pairs of electrons around the phosphorus atom require a trigonal bipyramidal arrangement
    - When chlorine atoms are included, a trigonal bipyramidal molecule results:



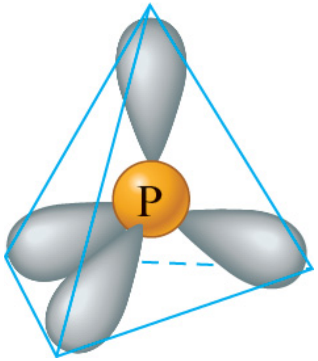
Interactive Example 8.12 - Solution (continued 1)

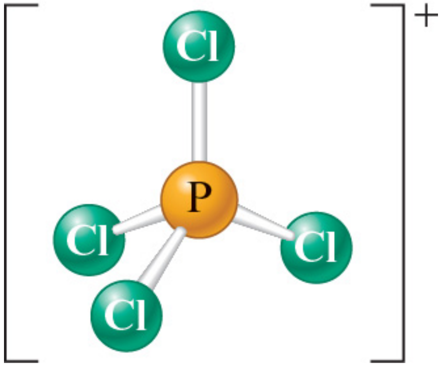
- The Lewis structure for the PCl_4^+ ion [5 + 4(7) – 1 = 32 valence electrons] is shown below



Interactive Example 8.12 - Solution (continued 2)

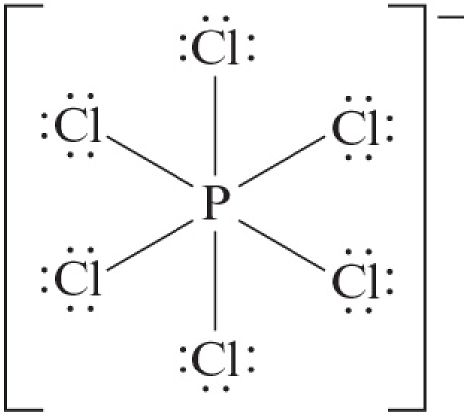
- There are four pairs of electrons surrounding the phosphorus atom in the PCl_4^+ ion, which requires a tetrahedral arrangement of the pairs
- Since each pair is shared with a chlorine atom, a tetrahedral PCl_4^+ cation results





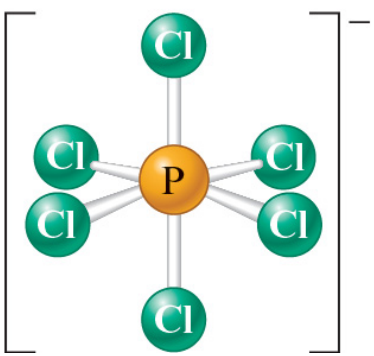
Interactive Example 8.12 - Solution (continued 3)

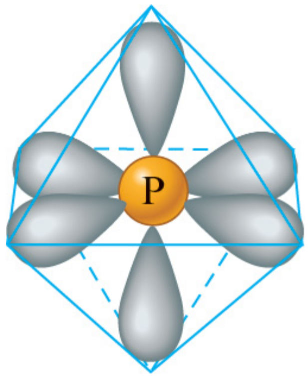
- The Lewis structure for PCl_6^- [5 + 6(7) + 1 = 48 valence electrons] is shown below



Interactive Example 8.12 - Solution (continued 4)

- Since phosphorus is surrounded by six pairs of electrons, an octahedral arrangement is required to minimize repulsions, as shown below





- Since each electron pair is shared with a chlorine atom, an octahedral PCl_6^- anion is predicted

Interactive Example 8.13 - Prediction of Molecular Structure III

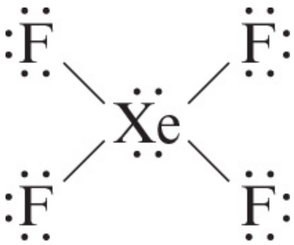
- Because the noble gases have filled *s* and *p* valence orbitals, they were not expected to be chemically reactive
  - In fact, for many years these elements were called inert gases because of this supposed inability to form any compounds
  - However, in the early 1960s several compounds of krypton, xenon, and radon were synthesized

Interactive Example 8.13 - Prediction of Molecular Structure III (continued)

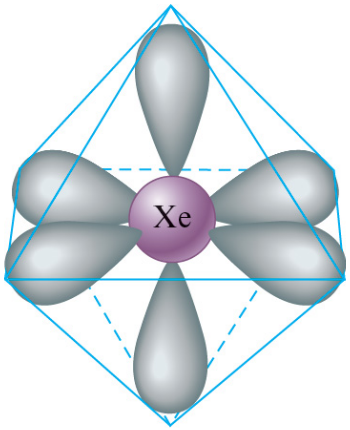
- For example, a team at the Argonne National Laboratory produced the stable colorless compound xenon tetrafluoride (XeF_4)
  - Predict its structure and whether it has a dipole moment

Interactive Example 8.13 - Solution

- The Lewis structure for XeF_4 is

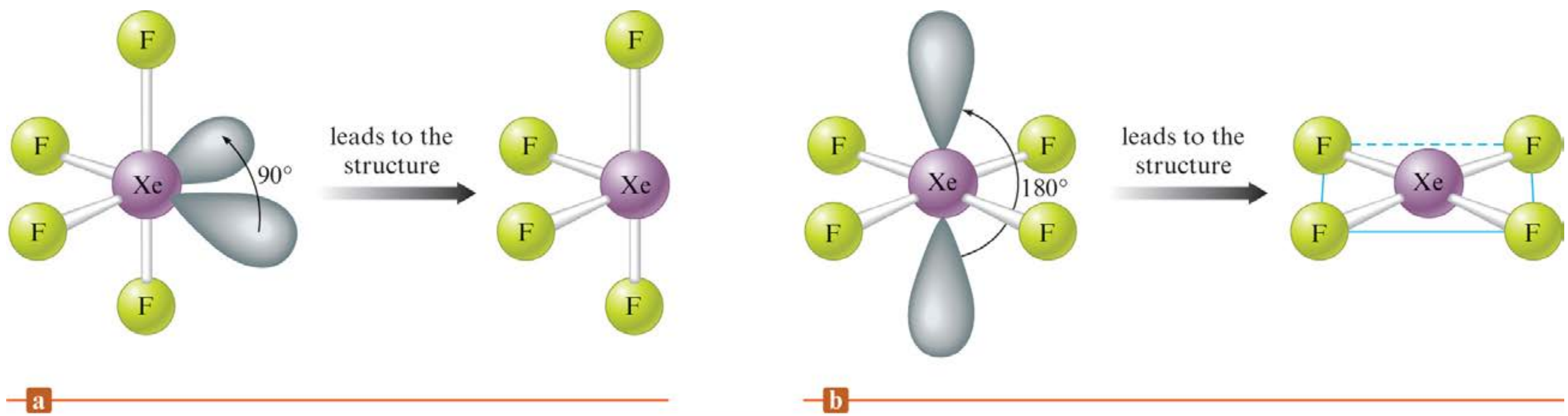


  - The xenon atom in this molecule is surrounded by six pairs of electrons, which means an octahedral arrangement



Interactive Example 8.13 - Solution (continued 1)

- The structure predicted will depend on the arrangement of lone pairs and bonding pairs
  - Consider the following possibilities:



Interactive Example 8.13 - Solution (continued 2)

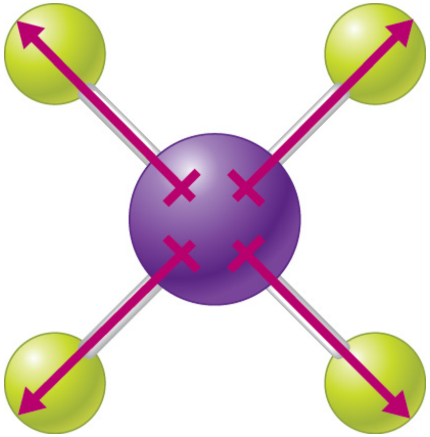
- The bonding pairs are indicated by the presence of the fluorine atoms
- Since the structure predicted differs in the two cases, we must decide which of these arrangements is preferable, and the key is to look at the lone pairs
  - In the structure in part (a), the lone pair–lone pair angle is 90 degrees
  - In the structure in part (b), the lone pairs are separated by 180 degrees

Interactive Example 8.13 - Solution (continued 3)

- Since lone pairs require more room than bonding pairs, a structure with two lone pairs at 90 degrees is unfavorable
- Thus the arrangement (b) is preferred, and the molecular structure is predicted to be square planar
  - Note that this molecule is not described as being octahedral
  - There is an octahedral arrangement of electron pairs, but the atoms form a **square planar structure**

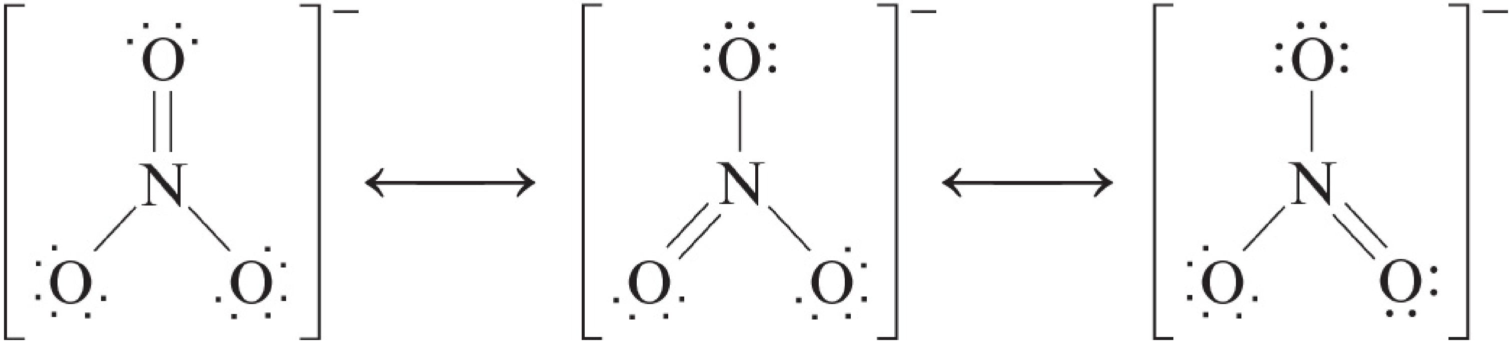
Interactive Example 8.13 - Solution (continued 4)

- Although each Xe—F bond is polar (fluorine has a greater electronegativity than xenon), the square planar arrangement of these bonds causes the polarities to cancel
  - Thus XeF_4 has no dipole moment



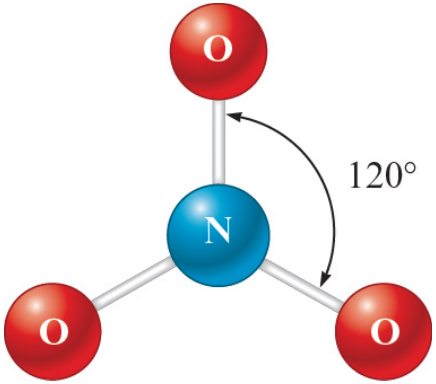
The VSEPR Model and Multiple Bonds

- Consider the NO_3^- ion
  - Requires three resonance structures to describe its electronic structure:



The VSEPR Model and Multiple Bonds (continued 1)

- Known to be planar with 120-degree bond angles



  - Structure is expected for three pairs of electrons around a central atom, which means that a double bond should be counted as one effective pair in using the VSEPR model

The VSEPR Model and Multiple Bonds (continued 2)

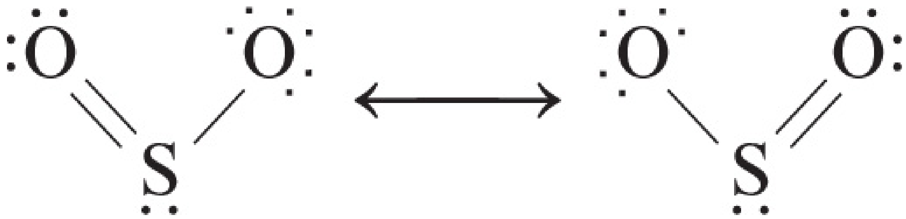
- Rules
  - Multiple bonds count as one effective electron pair
  - When a molecule exhibits resonance, any one of the resonance structures can be used to predict the molecular structure using the VSEPR model

Interactive Example 8.14 - Structures of Molecules with Multiple Bonds

- Predict the molecular structure of the sulfur dioxide molecule
  - Is this molecule expected to have a dipole moment?

Interactive Example 8.14 - Solution

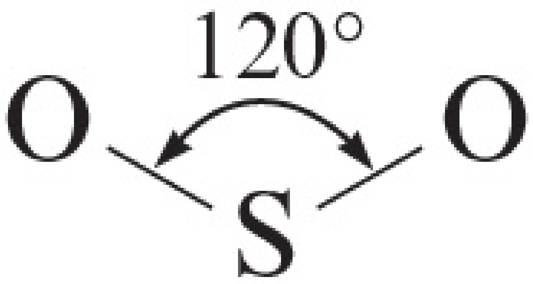
- First, we must determine the Lewis structure for the SO_2 molecule, which has 18 valence electrons
  - Expected resonance structures are



- To determine the molecular structure, we must count the electron pairs around the sulfur atom

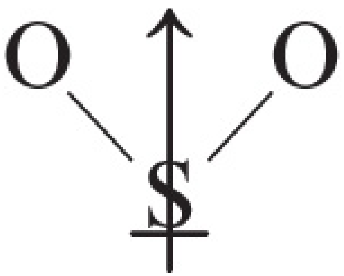
Interactive Example 8.14 - Solution (continued 1)

- In each resonance structure the sulfur has one lone pair, one pair in a single bond, and one double bond
  - Counting the double bond as one pair yields three effective pairs around the sulfur
  - A trigonal planar arrangement is required, which yields a V-shaped molecule



Interactive Example 8.14 - Solution (continued 2)

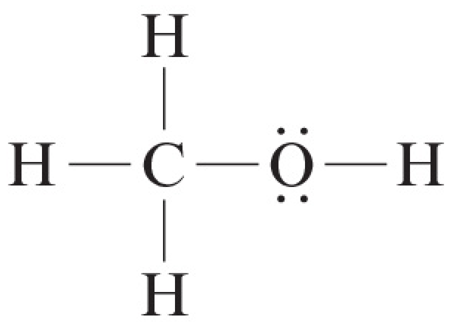
- Thus the structure of the SO_2 molecule is expected to be V-shaped, with a 120-degree bond angle
  - The molecule has a dipole moment directed as shown



  - Since the molecule is V-shaped, the polar bonds do not cancel

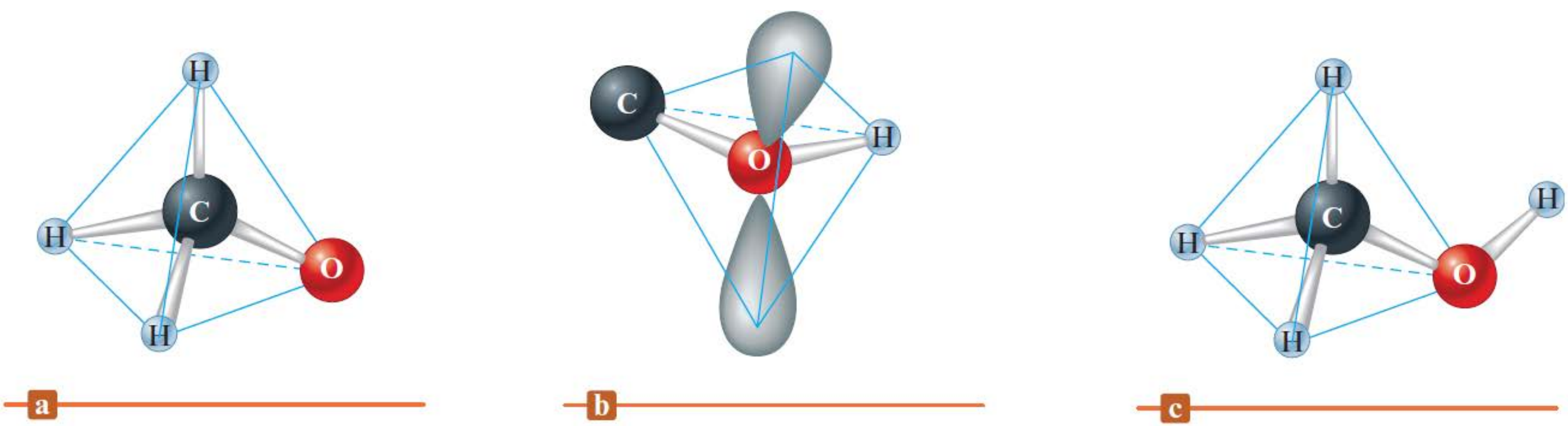
Molecules Containing No Single Central Atom

- Consider methanol (CH_3OH)



  - Molecular structure can be predicted from the arrangement of pairs around the carbon and oxygen atoms

Figure 8.22 - The Molecular Structure of Methanol



The arrangement of electron pairs and atoms around the carbon atom

The arrangement of bonding and lone pairs around the oxygen atom

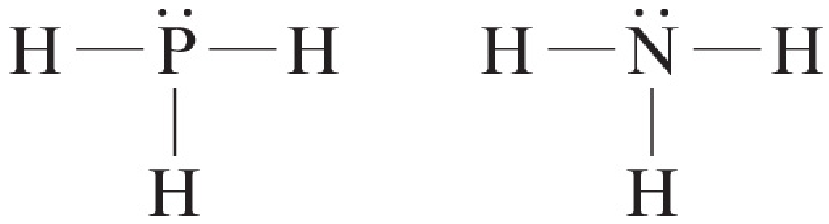
The molecular structure

VSEPR Model: Advantages

- Correctly predicts the molecular structures of most molecules formed from nonmetallic elements
- Used to predict the structures of molecules with hundreds of atoms

Limitation of the VSEPR Model

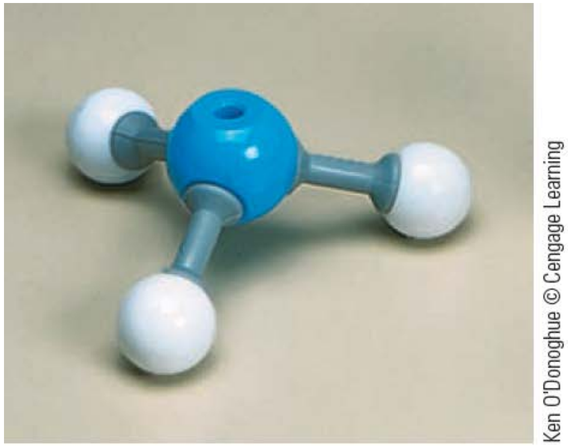
- Does not always provide an accurate prediction
  - Example - Phosphine (PH_3)
    - Lewis structure of PH_3 is analogous to that of ammonia (NH_3)

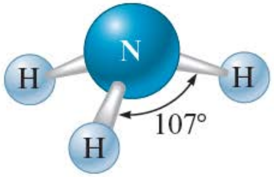


    - Predicted molecular structure of PH_3 is similar to that of NH_3, with bond angles of approximately 107°

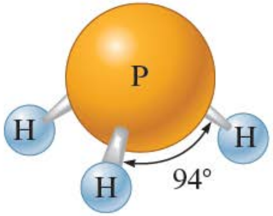
Limitation of the VSEPR Model (continued)

- Bond angles of phosphine are 94˚





NH_3



PH_3

Join In (16)

- Which of the following molecules is polar?
  a. XeF_4
  b. XeF_2
  c. BF_3
  d. NF_3

Join In (22)

Homework

- What type of structure does the $XeOF_2$ molecule have?
  a. Pyramidal
  b. Tetrahedral
  c. T-shaped
  d. Trigonal planar
  e. Octahedral

Join In (23) Homework

- Which of the following statements best describes BF_3 and NF_3? (Note: Geometry refers to the electron pair arrangement, and shape refers to the atom arrangement)
  a. They have variable geometries and shapes due to their potential resonance structures
  b. They have the same geometry and different shapes

Join In (23) (continued)

c. They have the same geometry and the same shape
d. They have different geometries and the same shape
e. They have different geometries and different shapes