# Chapter 3
# Lewis Structure – VSEPR Model

**Chapter 13 Bonding: General Concepts**
*13.2 Electronegativity*
*13.3 Bond Polarity and Dipole Moments*
*13.9 The Localized Electron Bonding Model*
*13.10 Lewis Structure*
*13.11 Resonance*
*13.12 Exceptions to the Octet Rule*
*13.13 Molecular Structure: The VSEPR Model*

**Chapter 14 Covalent bonding: Orbitals**
*14.1 Hybridization and the Localized Electron Model*

# Electronegativity

**Electronegativity**: *the ability of an atom in a molecule to attract shared electrons to itself*.

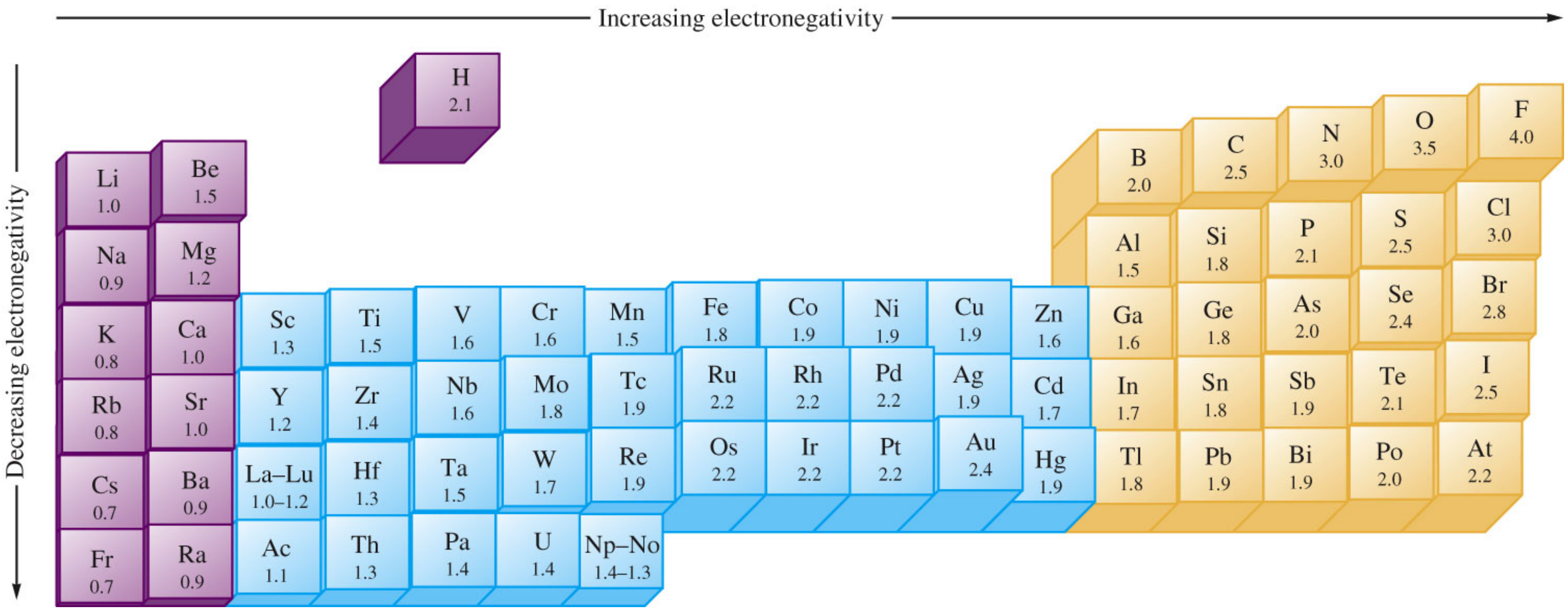



**Figure 13.3 - The Pauling electronegativity values. Electronegativity generally increases across a period and decreases down a group.**

# Bond Polarity and Dipole Moments

When a molecule has a center of positive charge and a center of negative charge is said to be **dipolar,** or to have **a dipole moment.**

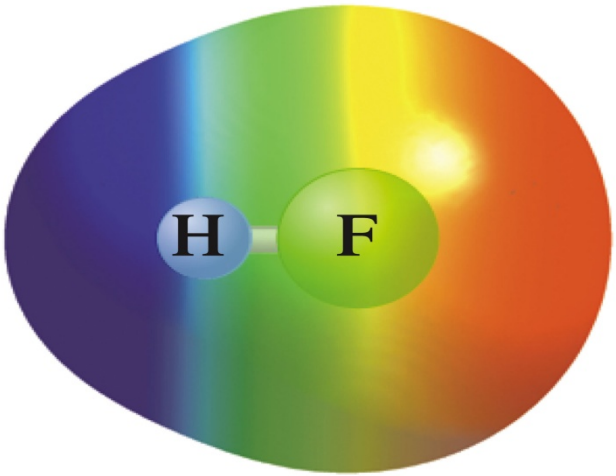
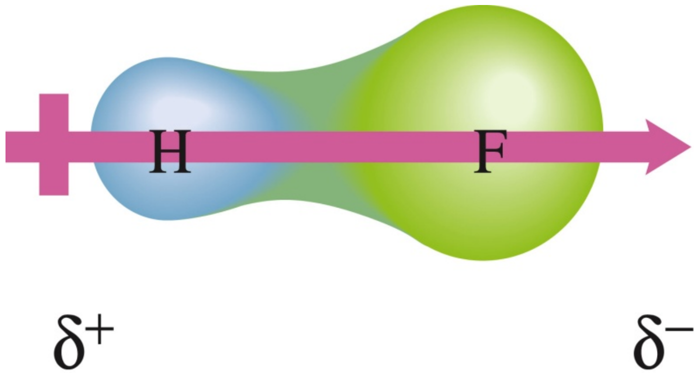



**Figure 13.4 - An electrostatic potential diagram of HF. Red indicates the most electronrich area (the fluorine atom) and blue indicates the most electron-poor region (the hydrogen atom).**



# Bond Polarity and Dipole Moments

**Table 13.1**

The Relationship Between Electronegativity and Bond Type

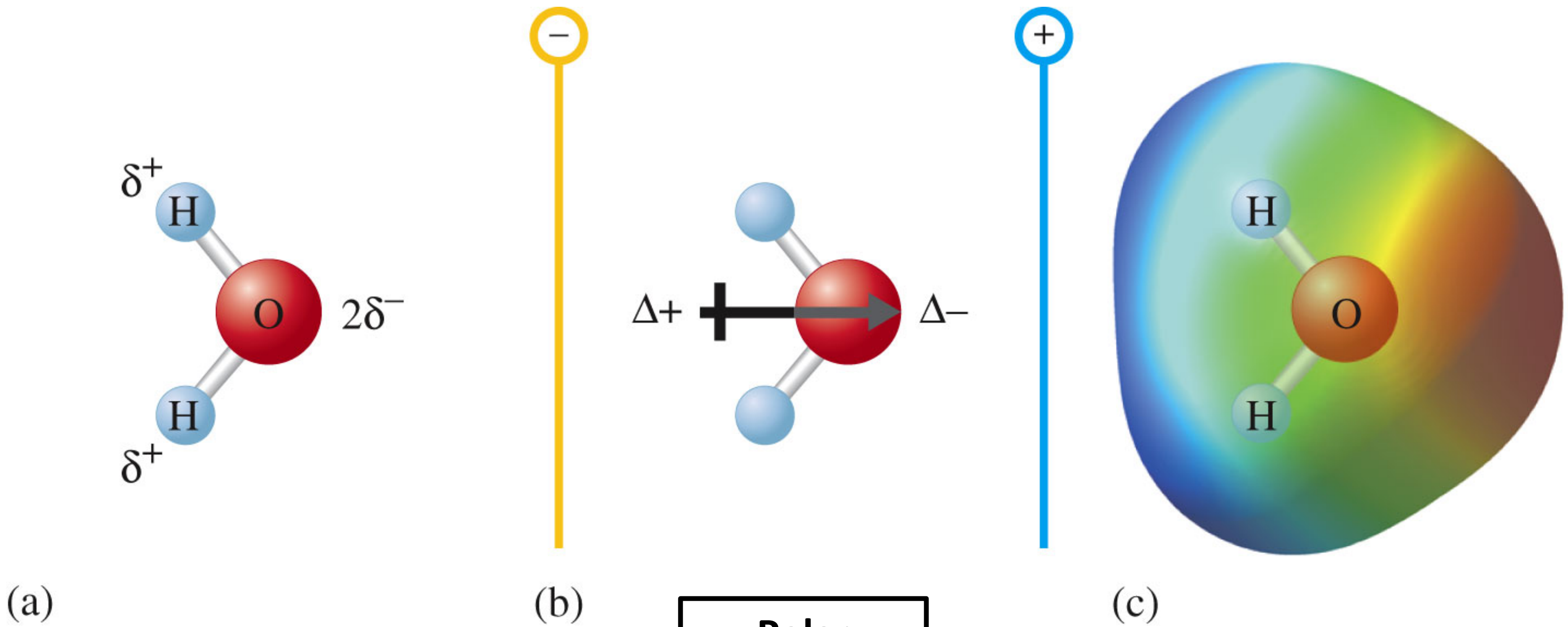
| Electronegativity Difference in the Bonding Atoms | Bond Type |
|---|---|
| Zero | Covalent |
| ↓ | ↓ |
| Intermediate | Polar covalent |
| ↓ | ↓ |
| Large | Ionic |

**Table 13.3**

The Dipole Moments of Some Diatomic Molecules (gas phase)

| Molecule | Dipole Moment (D) |
|---|---|
| CO | 0.112 |
| HF | 1.83 |
| HCl | 1.11 |
| HBr | 0.78 |
| HI | 0.38 |
| NaCl | 9.00 |
| LiF | 6.33 |
| KF | 8.60 |
| KBr | 10.41 |

# Bond Polarity and Dipole Moments




Polar molecule

**Figure 13.5 - (a) The charge distribution in the water molecule. (b) The water molecule in an electric field. (c) The electrostatic potential diagram of the water molecule.**

# Bond Polarity and Dipole Moments

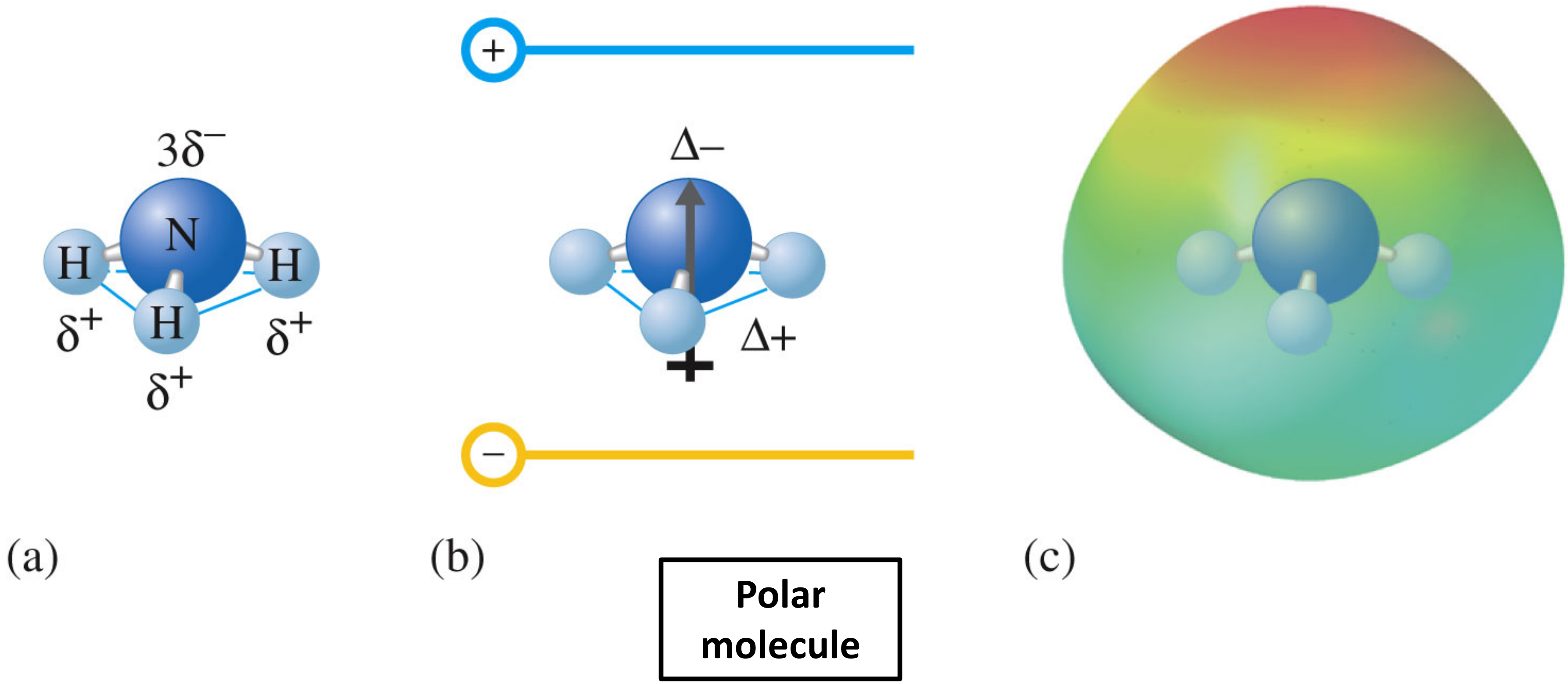
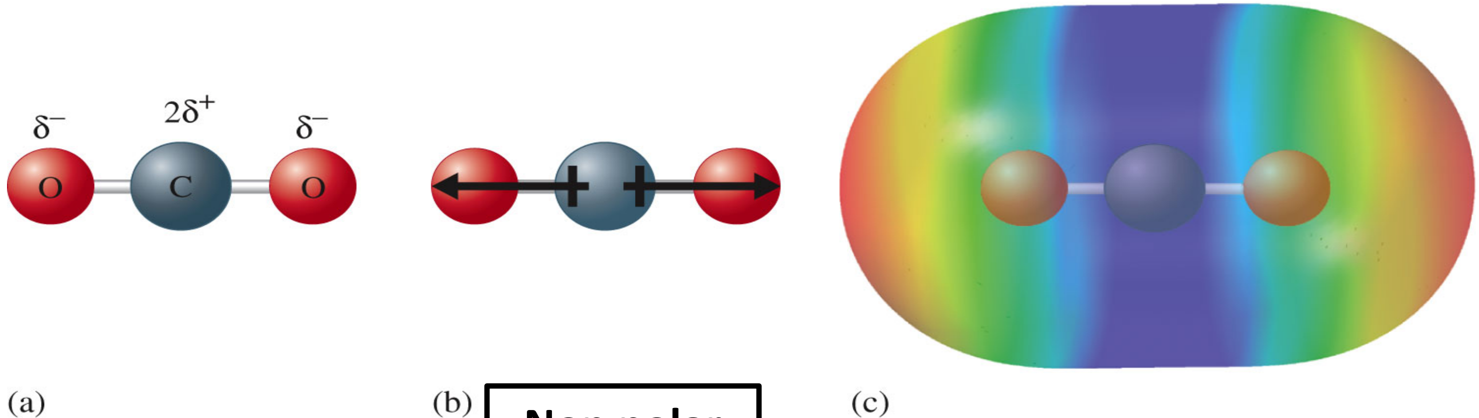



**Figure 13.6 - (a) The structure and charge distribution of the ammonia molecule. The polarity of the NOH bonds occurs because nitrogen has a greater electronegativity than hydrogen. (b) The dipole moment of the ammonia molecule oriented in an electric field. (c) The electrostatic potential diagram for ammonia.**

# Bond Polarity and Dipole Moments

Some molecules have polar bonds but do not have a dipole moment. This occurs when the individual bond polarities are arranged in such a way that they cancel each other out.



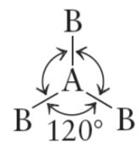
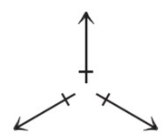
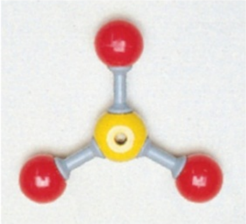
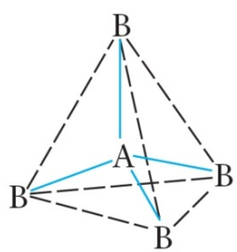
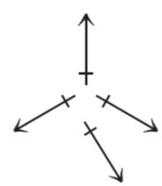

Non polar molecule

**Figure 13.7 - (a) The carbon dioxide molecule. (b) The opposed bond polarities cancel out, and the carbon dioxide molecule has no dipole moment. (c) The electrostatic potential diagram for carbon dioxide.**

# Bond Polarity and Dipole Moments

**Table 13.4**

Types of Molecules with Polar Bonds but No Resulting Dipole Moment

| Type | | Cancellation of Polar Bonds | Example | Ball-and-Stick Model |
|---|---|---|---|---|
| Linear molecules with two identical bonds | B—A—B |  | $CO_2$ |  |
| Planar molecules with three identical bonds 120 degrees apart |  |  | $SO_3$ |  |
| Tetrahedral molecules with four identical bonds 109.5 degrees apart |  |  | $CCl_4$ |  |

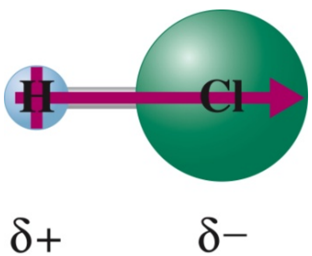
# Bond Polarity and Dipole Moments

**Example 13.2**

For each of the following molecules, show the direction of the bond polarities. Also indicate which ones have dipole moments: HCl, $Cl_2$, $SO_3$ (planar), $CH_4$ (tetrahedral), and $H_2S$ (V-shaped)

# Bond Polarity and Dipole Moments

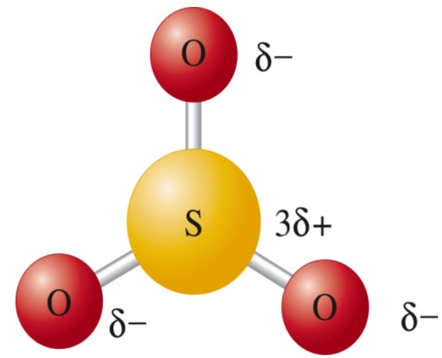
**SOLUTION**



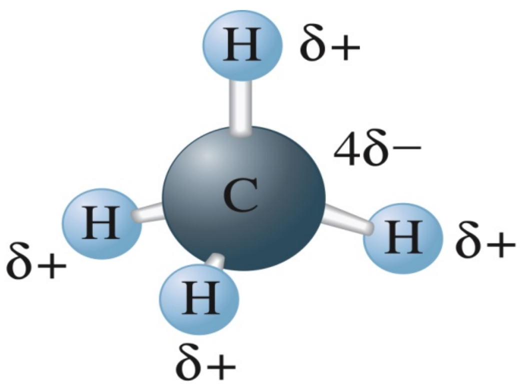

**Polar molecule**

**$Cl_2$**

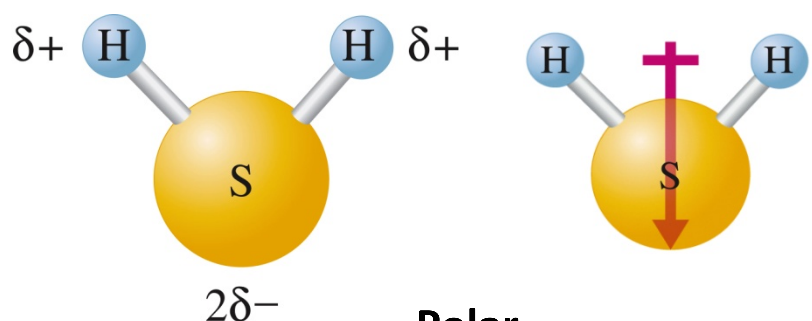
**non polar molecule**




**Non polar molecule**




**Non polar molecule**




**Polar molecule**

# The Localized Electron Bonding Model

- Assumes that a molecule is composed of atoms that are bound together by using atomic orbitals to share electron pairs.

- Electron pairs in the molecule are assumed to be localized on a particular atom or in the space between two atoms. Those pairs of electrons localized on an atom are called **lone pairs**, and those found in the space between the atoms are called **bonding pairs**.

The LE model has three parts:

- Decsription of the valence electron arrangement in the molecule using Lewis structures.
- Prediction of the geometry of the molecule (VSEPR)
- Description the types of atomic orbitals used by the atoms to share electrons or hold lone pairs.

# Lewis Structures

- The Lewis structure of a molecule shows how the valence electrons are arranged among the atoms in the molecule.

- The most important requirement for the formation of a stable compound is that the atoms achieve noble gas electron configuration.

# Noble Gas Electron Configuration – Octet Rule

Noble gas have 8 electrons on the valence shell except He (2 electrons). They have a stable configuration at the ground state.

$_{2}$He (Helium) : $1s^2$ $\Rightarrow$ 2 valence electrons

$_{10}$Ne (Neon) : $1s^2$ / $\underline{2s^2\ 2p^6}$ $\Rightarrow$ 8 valence electrons

$_{18}$Ar (Argon) : $1s^2\ 2s^2\ 2p^6$ / $\underline{3s^2\ 3p^6}$ $\Rightarrow$ 8 valence electrons

$_{54}$Xe (Xenon) : $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^6\ 4d^{10}$ / $\underline{5s^2\ 5p^6}$ $\Rightarrow$ 8 valence electrons

The Octet is reached by gaining, loosing or sharing one or many valence electrons

# Noble Gas Electron Configuration – Octet Rule

a) Elements of groups I and II : **loosing** 1 or 2 electrons to satisfy the octet rule

$${}_{11}Na : 1s^2\ 2s^2\ 2p^6 / \underline{3s^1} \xrightarrow{-e^-} Na^+ : 1s^2\ \underline{2s^2\ 2p^6}\ (\text{ or [Ne] })$$

b) Elements of groups VI and VII : **gaining** 1 or 2 electrons to satisfy the octet rule

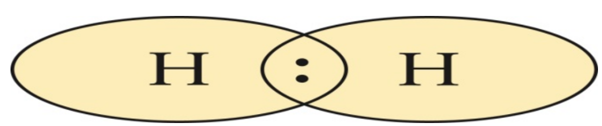
$${}_{17}Cl : 1s^2\ 2s^2\ 2p^6 / \underline{3s^2\ 3p^5} \xrightarrow{+e^-} Cl^- : 1s^2\ 2s^2\ 2p^6/\underline{3s^2\ 3p^6}\ (\text{or [Ar]})$$

# Lewis Structures

- Hydrogen follows the duet rule when it forms a stable molecule.


Two hydrogen atoms each with one electron combine to form the $H_2$ molecule.

By sharing electrons, each hydrogen in $H_2$, in effect, has two electrons; that is each hydrogen has filled valence shell.



# Lewis Structures

- Helium does not form bonds because its valence orbital is already filled; it is a noble gas.

He:

- The second-row nonmetals carbon through fluorine form stable molecules when they are surrounded by 8 electrons to fill the valence *2s* and *2p* orbitals (octet rule).

# Lewis Structures

F atom with seven valence electrons

$F_2$ molecule

F atom with seven valence electrons

Each fluorine atom in $F_2$ is surrounded by eight electrons, two of which are shared with the other atom. This is a **bonding pair** of electrons.

Each fluorine atom also has three pairs of electrons not involved in bonding. These are the **lone pairs**.

# Lewis Structures

- Sum the valence electrons from all the atoms. Do not worry about keeping track of which electrons come from which atoms. It is the *total* number of electrons that is important.
- Use a pair of electrons to form a bond between each pair of bound atoms.
- Arrange the remaining electrons to satisfy the duet rule for hydrogen and the octet rule for the second-row elements.

# Lewis Structures

**Consider the water molecule:**

1) We sum the valence electrons for $H_2O$:

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

2) Using a pair of electrons per bond, we draw in the two O–H single bonds.

H–O–H

note that a line instead of a pair of dots is used to indicate each pair of bonding electrons.

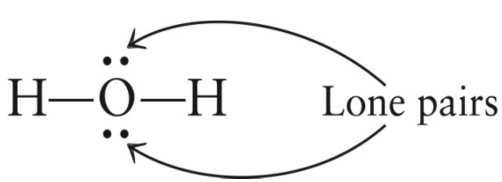
# Lewis Structures

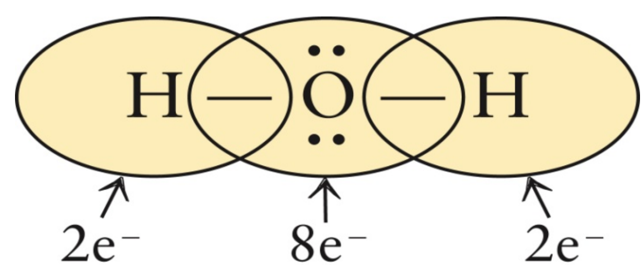
3) We distribute the remaining electrons to achieve a noble gas electron configuration for each atom.

since four electrons have been used in forming the two bonds, four electrons (8-4) remain to be distributed.

hydrogen is satisfied with two electrons but oxygen needs eight electrons to have a noble gas configuration.

→ Thus the remaining four electrons are added to oxygen as two lone pairs.



# Lewis Structures

**Consider $CO_2$:**

1) Valence electrons:

$$\underset{\mathrm{C}}{4} + \underset{\mathrm{O}}{6} + \underset{\mathrm{O}}{6} = 16$$

2) After forming a bond between the carbon and each oxygen

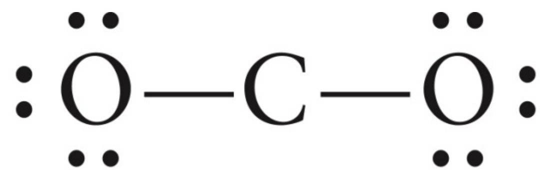
O–C–O

the remaining electrons (16 – 4) = 12 electrons

$\rightarrow$ 6 pairs of electrons to distribute

# Lewis Structures

Suppose we try 3 pairs on each oxygen to give:




**Is this correct?**

Check the octet rule for each atom.

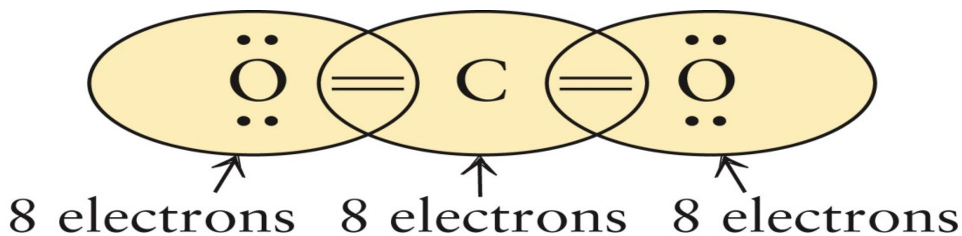
Each oxygen atom has 8 electrons,

but the carbon has only 4

=> This cannot be the correct Lewis structure.

# Lewis Structures

Suppose there are 2 shared pairs between the carbon and each oxygen:




Electrons left (16 – 8) = 8 → four lone pairs placed on the oxygens.

Now each atom is surrounded by 8 electrons.

# Lewis Structures

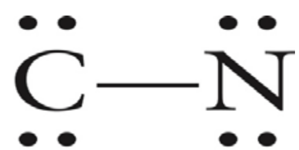
**Consider $CN^-$:**

Summing the valence electrons:

$$CN^-$$
$$4 + 5 + 1 = 10$$

***Note that the negative charge means an extra electron is present.* (*A positive charge means one less electron is present*).**

Incorrect structure:



Correct structure:

# Lewis Structures

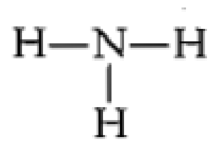
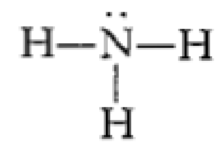
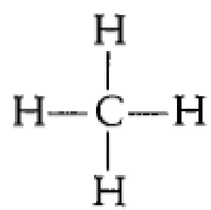
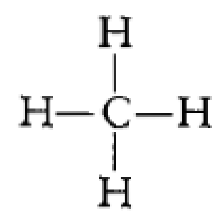
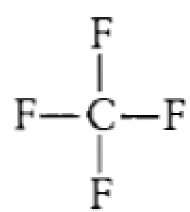
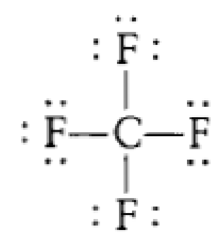
## Example 13.6

Give the Lewis structure for each of the following

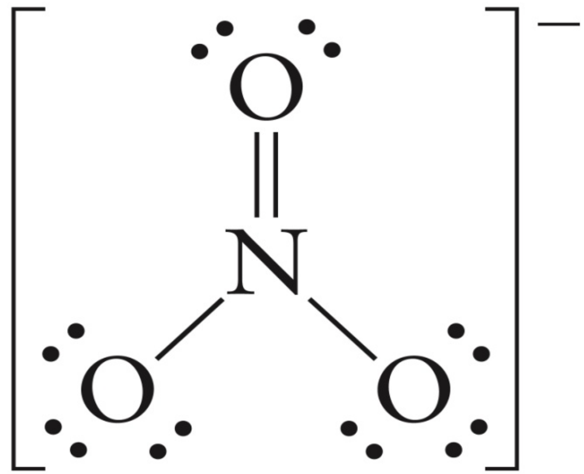
a. HF
b. $N_2$
c. $NH_3$
d. $CH_4$
e. $CF_4$
f. $NO^+$

# Lewis Structures

**SOLUTION**

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

# Resonance

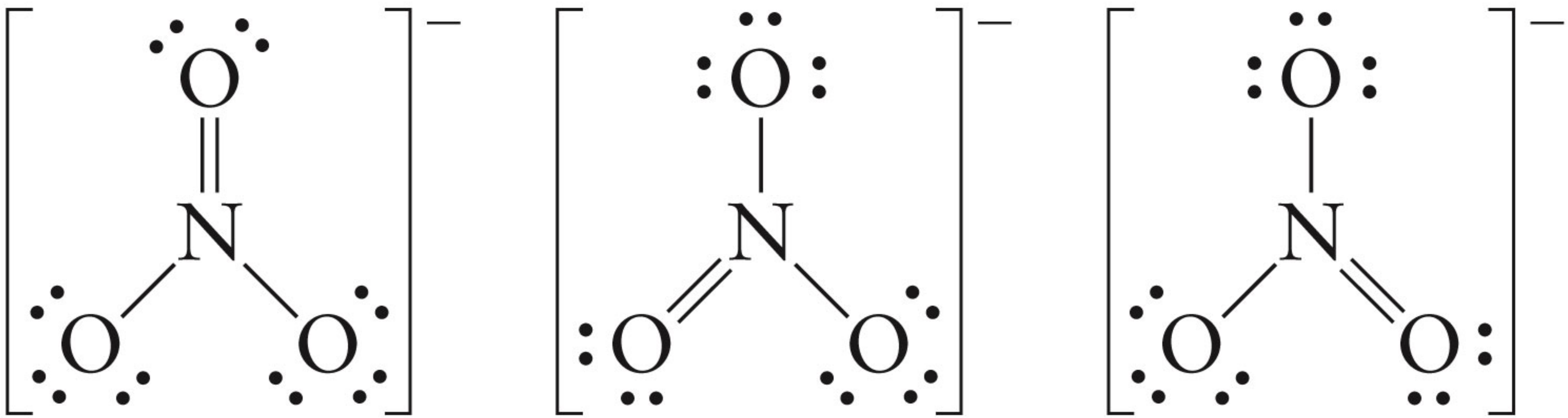



- If this structure accurately represents the bonding in $NO_3^-$, there should be two types of N–O bonds observed in the molecule: one shorter bond (the double bond) and two identical longer ones (the two single bonds).

- However, experiments show that $NO_3^-$ exhibits only one type of N–O bond with a length and strength between those expected for a single bond and a double bond.

# Resonance

- There are really three valid Lewis structures:

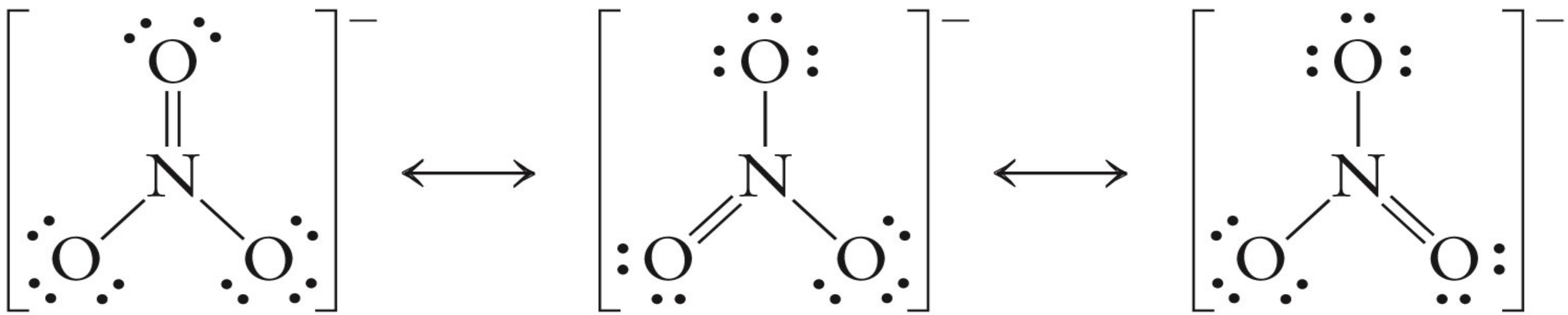



- The correct description of $NO_3^-$ is given by the superposition of all three.

- $NO_3^-$ exists as an average of al three structures.

# Resonance

- Resonance occurs when more than one valid Lewis structure can be written for a particular molecule.
- The structure of the molecule (or polyatomic ion) is given by the average of these resonance structures.



- Different resonance structures of a compound are linked by double-headed arrows **(↔)** that indicate that the actual electronic structure is an average of those shown and not that the molecule oscillates between the two structures.

***Remember: the arrangement of the nuclei is the same, only the placement of the electrons differ.***

# Resonance

## Example 13.7

Describe the electron arrangement in the nitrite anion ($NO_2^-$), using the LE model.

# Resonance

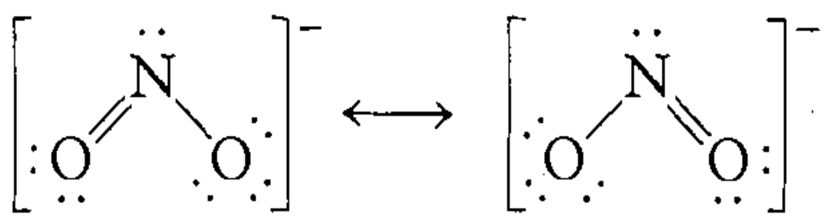
**Solution**

We will follow the usual procedure for obtaining the Lewis structure for the $NO_2^-$ ion.

In $NO_2^-$ there are $5 + 2(6) + 1 = 18$ valence electrons.
Indicating the single bonds gives the structure

$$\mathrm{O{-}N{-}O}$$

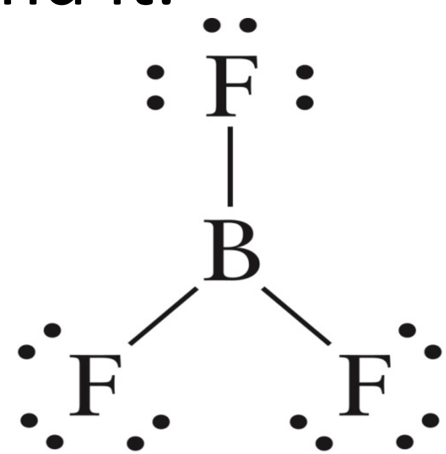
The remaining 14 electrons $(18 - 4)$ can be distributed to produce these structures:



This is a resonance situation. Two equivalent Lewis structures can be drawn. *The electronic structure of the molecule is not correctly represented 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 double bond.

# Exceptions to the Octet Rule

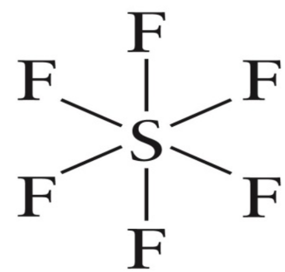
- The rules we have used for Lewis structures apply to most molecules.
- However, some exceptions are inevitable.
- Boron, for example, tends to form compounds in which the boron atom has fewer than eight electrons around it.

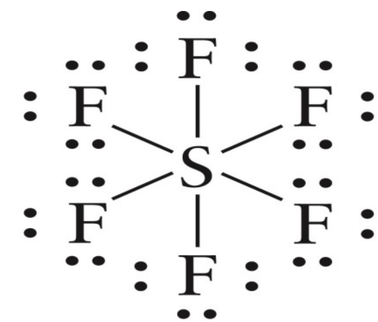


# Exceptions to the Octet Rule

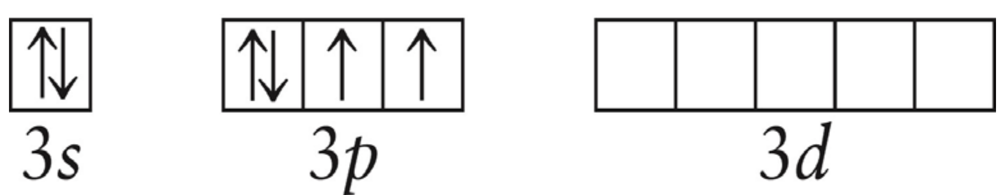
- Some atoms exceed the octet rule. This behavior is observed only for those elements in Period 3 of the periodic table and beyond.

- Example is $SF_6$:
  $6 + 6(7) = 48$ electrons
  sulfur exceeds the octet rule





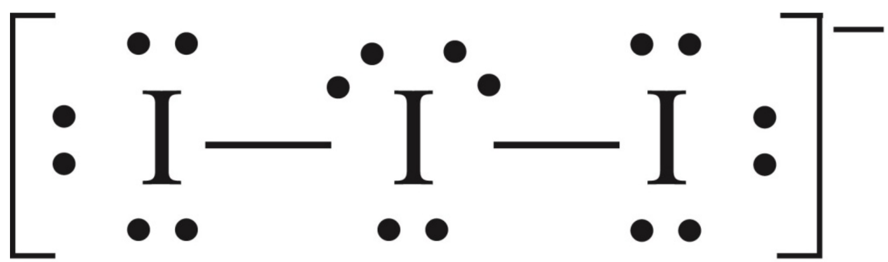
The empty *3d* orbitals on S can accommodate extra electrons.



# Exceptions to the Octet Rule

- Another example is the triiodide ion $I_3^-$:

$$\underset{\mathrm{I}}{\underset{\uparrow}{3(7)}} + \underset{-1\text{ charge}}{\underset{\uparrow}{1}} = 22 \text{ valence electrons}$$



***When it is necessary to exceed the octet rule for one of several third-row (or higher) elements, assume that the extra electrons should be placed on the central atom.***

# Exceptions to the Octet Rule

**Example 13.8**

Write the Lewis structure for $PCl_5$

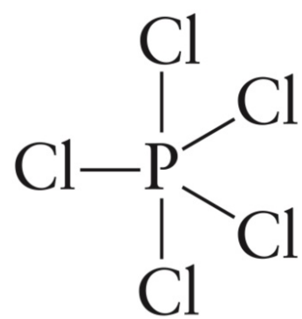
# Exceptions to the Octet Rule

**SOLUTION**

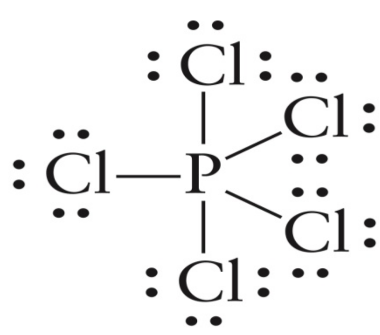
1- Sum the valence electrons.

$$5 + 5(7) = 40 \text{ electrons}$$

2- Indicate single bonds between bound atoms.



3- Distribute the remaining electrons to satisfy the octet rule.



# Exceptions to the Octet Rule

## Example 13.9

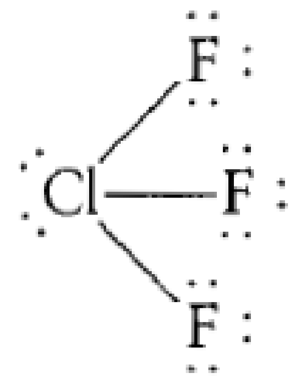
Write the Lewis structure for each molecule or ion.

a. $ClF_3$ b. $XeO_3$ c. $RnCl_2$ d. $BeCl_2$ e. $ICl_4^-$

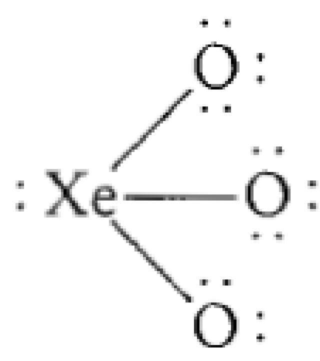
# Exceptions to the Octet Rule

**Solution**

a. The chlorine atom (third row) accepts the extra electrons.

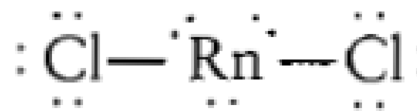



b. All atoms obey the octet rule.

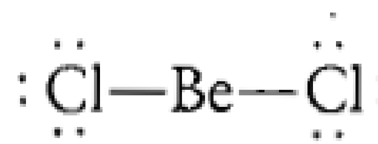


# Exceptions to the Octet Rule

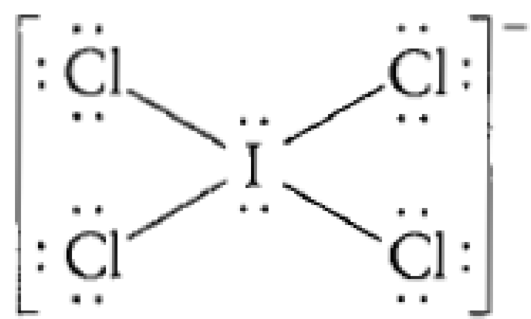
c. Radon, a noble gas in Period 6, accepts the extra electrons.



d. Beryllium is electron-deficient.



e. Iodine exceeds the octet rule.



# Formal Charge

Molecules of polyatomic ions containing atoms that can exceed the octet rule often have many nonequivalent Lewis structures.

The formal charge can be used to evaluate Lewis structures.

An arithmetic formula for calculating formal charge.

Formal charge =

number of valence electrons on the free atom − number of valence electrons assigned to the atom in the molecule

# Formal Charge

To compute the number of valence electrons assigned to the atom in the molecule:

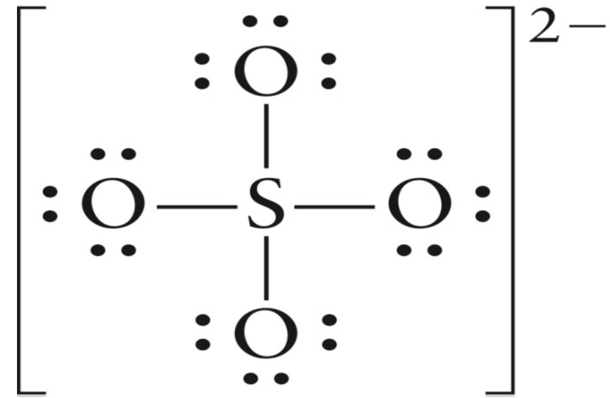
1) Lone pair electrons belong entirely to the atom in question

2) Shared electrons are divided equally between the two sharing atoms

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

# Formal Charge

**One possible structure of $SO_4^{2-}$:**



Valence electrons assigned to each oxygen = 6 plus $\frac{1}{2}(2)$ = 7

$\uparrow$ Lone pair electrons

$\uparrow$ Shared electrons

Formal charge on oxygen = 6 − 7 = −1

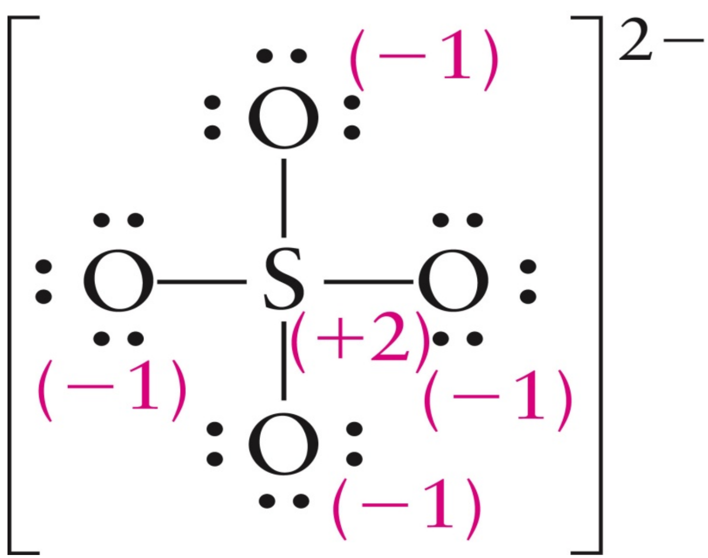
$\uparrow$ Valence electrons on a free O atom

$\uparrow$ Valence electrons assigned to each O in $SO_4^{2-}$

# Formal Charge

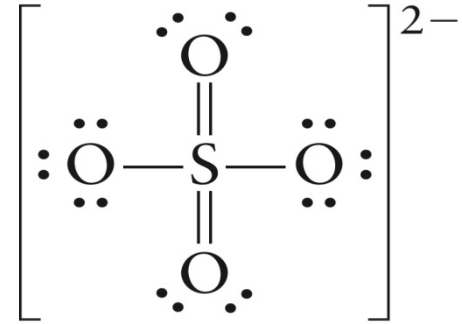
$$\text{Valence electrons assigned to sulfur} = \underset{\substack{\uparrow \\ \text{Lone pair electrons}}}{0} + \frac{1}{2}(\underset{\substack{\uparrow \\ \text{Shared electrons}}}{8}) = 4$$

$$\text{Formal charge on sulfur} = \underset{\substack{\uparrow \\ \text{Valence electrons on free S atom}}}{6} - \underset{\substack{\uparrow \\ \text{Valence electrons assigned to S in } SO_4^{2-}}}{4} = 2$$



# Formal Charge

A second possible Lewis structure of $SO_4^{2-}$ is:



*For oxygen atoms with single bonds:*

$$\text{Valence electrons assigned} = 6 + \tfrac{1}{2}(2) = 7$$

$$\text{Formal charge} = 6 - 7 = -1$$

*For oxygen atoms with double bonds:*

$$\text{Valence electrons assigned} = 4 + \underbrace{\tfrac{1}{2}(4)}_{\substack{\text{Each double bond}\\ \text{has 4 electrons}}} = 6$$

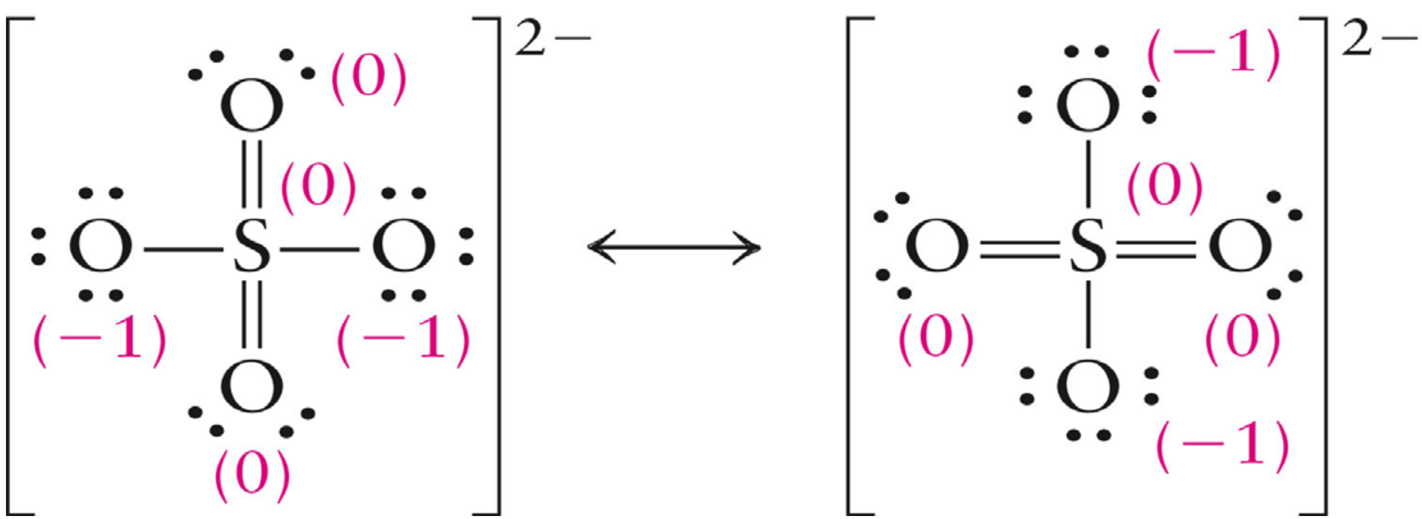
$$\text{Formal charge} = 6 - 6 = 0$$

# Formal Charge

*For the sulfur atom:*

$$\text{Valence electrons assigned} = 0 + \tfrac{1}{2}(12) = 6$$

$$\text{Formal charge} = 6 - 6 = 0$$



# Formal Charge

To evaluate Lewis structures:

1. Atoms in molecules try to achieve formal charges as close to zero as possible.

2. Structures that have the more negative formal charge on the more electronegative atom are more stable

For $SO_4^{2-}$, the structure with two double bonds is preferred, it has lower formal charges and the -1 formal charges are on the electronegative oxygen atoms.

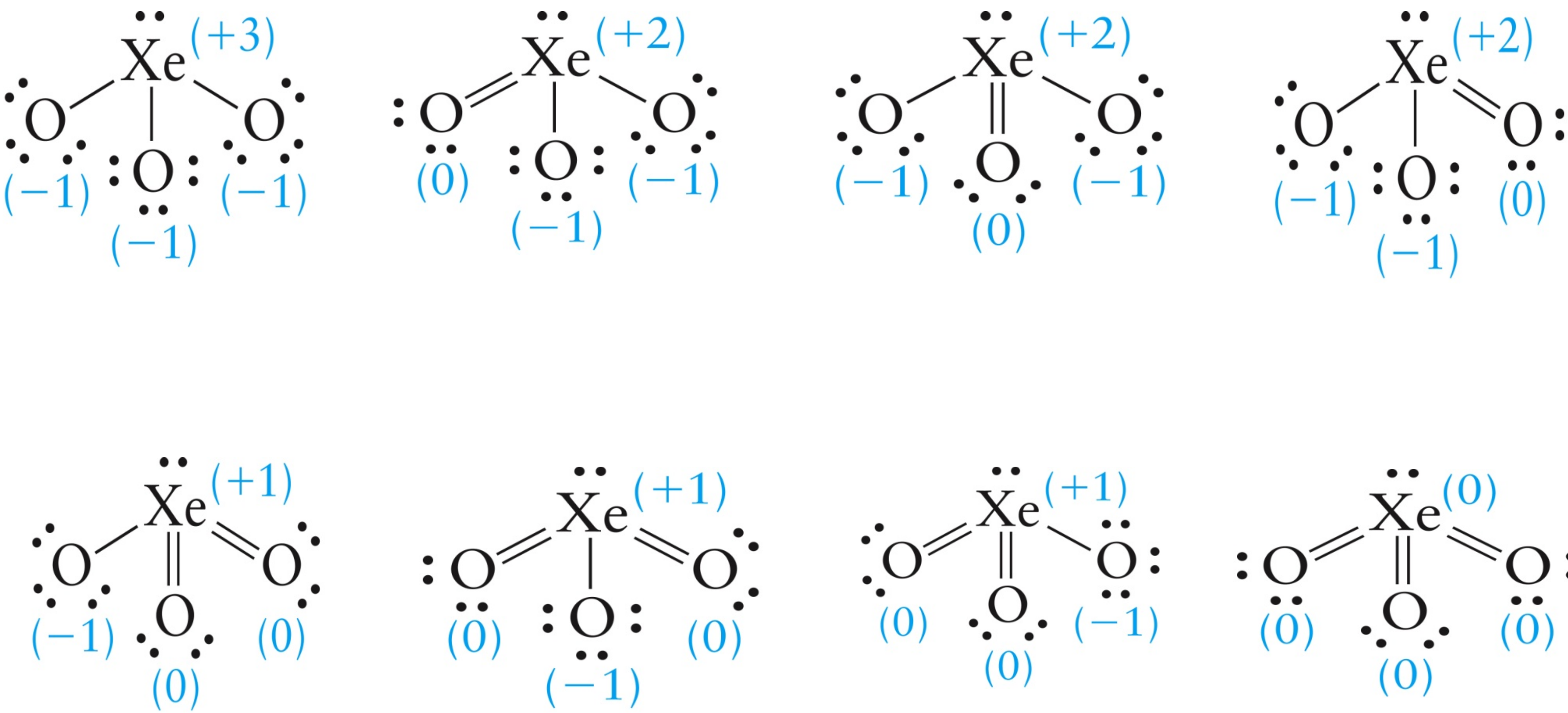
# Formal Charge

**Example 13.10**

Give possible Lewis structures for $XeO_3$, an explosive compound of xenon. Determine the formal charges of each atom in the various Lewis structures.

# Formal Charge

## SOLUTION



# Molecular Structure: The VSEPR Model

**Valence Shell Electron Pair Repulsion (VSEPR model)** is important to predict the geometries of molecules formed from nonmetals.

- The structure around a given atom is determined principally by minimizing electron-pair repulsions.

- Thus, bonding and nonbonding pairs around a given atom should be positioned as far apart as possible.

$$\boxed{AB_mE_n}$$

**A : central atom**

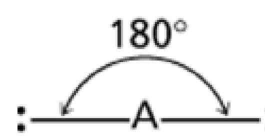
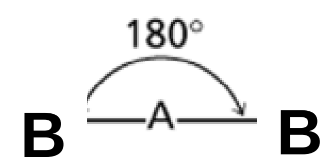
**B : atom bonded to A**

**m : number of B bonded to A**

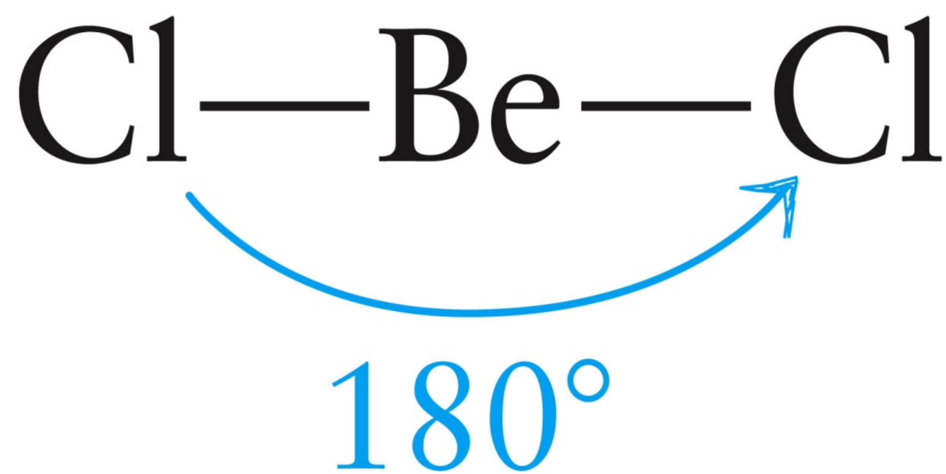
**E : free lone pair around A**

**n : number of free lone pairs around A**

# Molecular Structure: The VSEPR Model

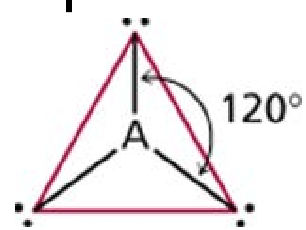
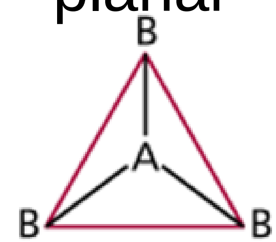
| Class | # of atoms bonded to central atom | # lone pairs on central atom | Arrangement of electron pairs | Molecular Geometry |
|---|---|---|---|---|
| $AB_2$ | 2 | 0 | linear   | linear   |

# Molecular Structure: The VSEPR Model

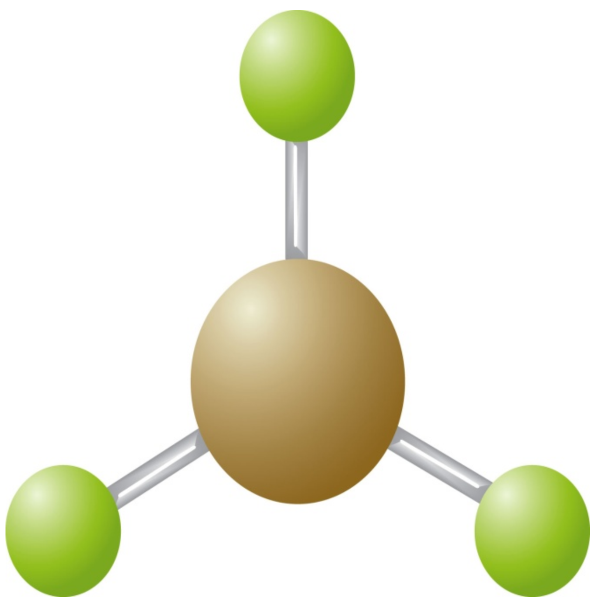



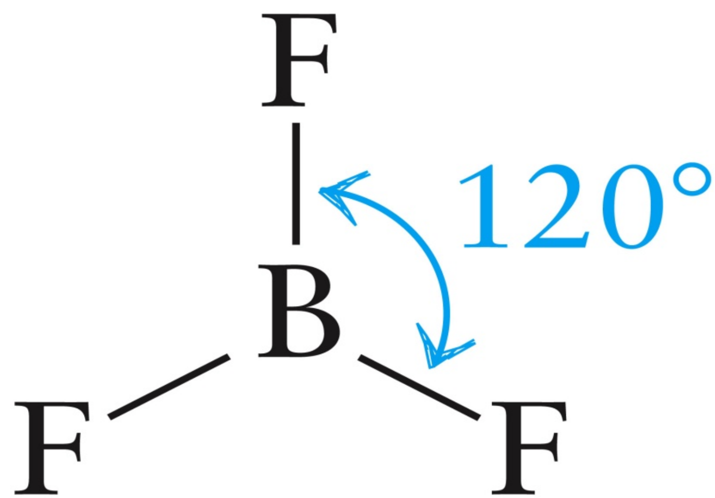

The best arrangement (min repulsion) places the pairs on opposite sides of the beryllium atom at 180 degrees from each other.

# Molecular Structure: The VSEPR Model

| Class | # of atoms bonded to central atom | # lone pairs on central atom | Arrangement of electron pairs | Molecular Geometry |
|---|---|---|---|---|
| $AB_2$ | 2 | 0 | linear | linear |
| $AB_3$ | 3 | 0 | trigonal planar   | trigonal planar   |

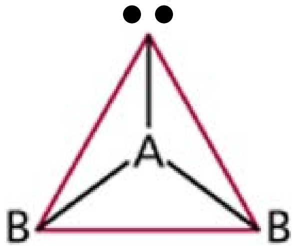
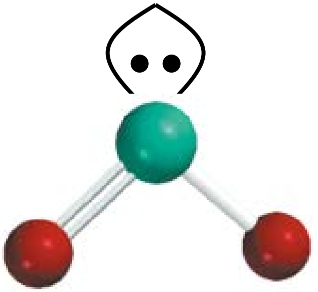
# Molecular Structure: The VSEPR Model





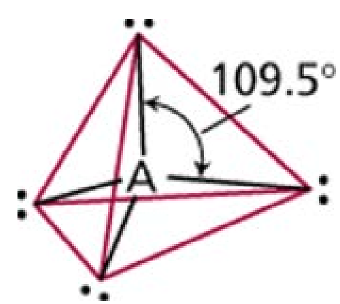

The minimum repulsion is when the electron pairs are farthest apart at angles of 120 degrees.

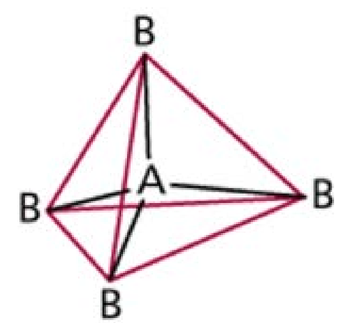
# Molecular Structure: The VSEPR Model

| Class | # of atoms bonded to central atom | # lone pairs on central atom | Arrangement of electron pairs | Molecular Geometry |
|---|---|---|---|---|
| $AB_3$ | 3 | 0 | trigonal planar | trigonal planar |
| $AB_2E$ | 2 | 1 | trigonal planar  | bent  |

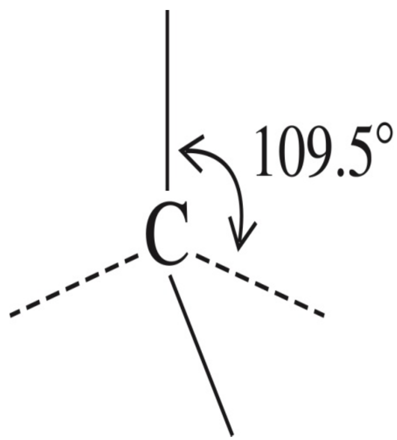
# Molecular Structure: The VSEPR Model

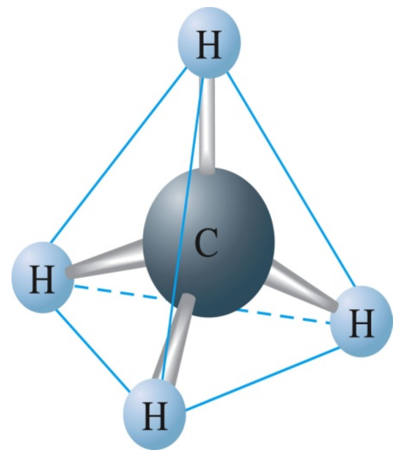
| Class | # of atoms bonded to central atom | # lone pairs on central atom | Arrangement of electron pairs | Molecular Geometry |
|---|---|---|---|---|
| $AB_2$ | 2 | 0 | linear | linear |
| $AB_3$ | 3 | 0 | trigonal planar | trigonal planar |
| $AB_4$ | 4 | 0 | tetrahedral | tetrahedral |

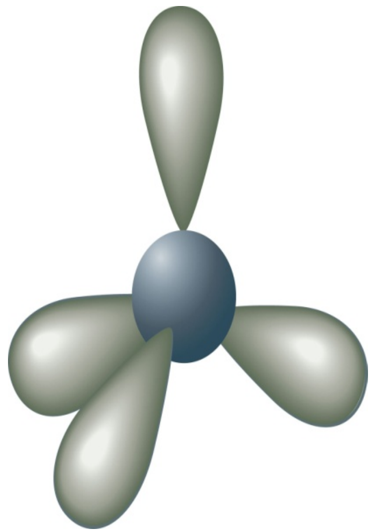


# Molecular Structure: The VSEPR Model



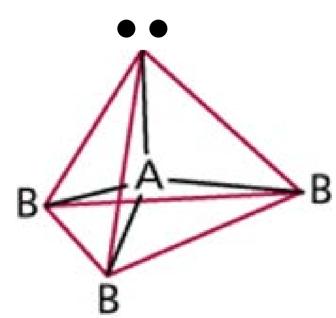



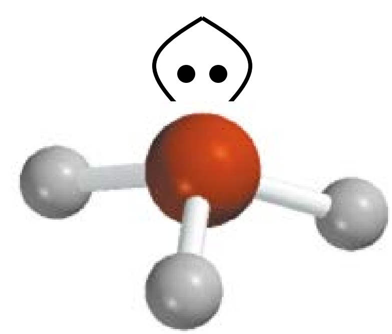



The maximum possible separation of the four pairs around the central atom, is when they are arranged tetrahedrally.

# Molecular Structure: The VSEPR Model

| Class | # of atoms bonded to central atom | # lone pairs on central atom | Arrangement of electron pairs | Molecular Geometry |
|---|---|---|---|---|
| $AB_4$ | 4 | 0 | tetrahedral | tetrahedral |
| $AB_3E$ | 3 | 1 | tetrahedral | trigonal pyramidal |



# Molecular Structure: The VSEPR Model

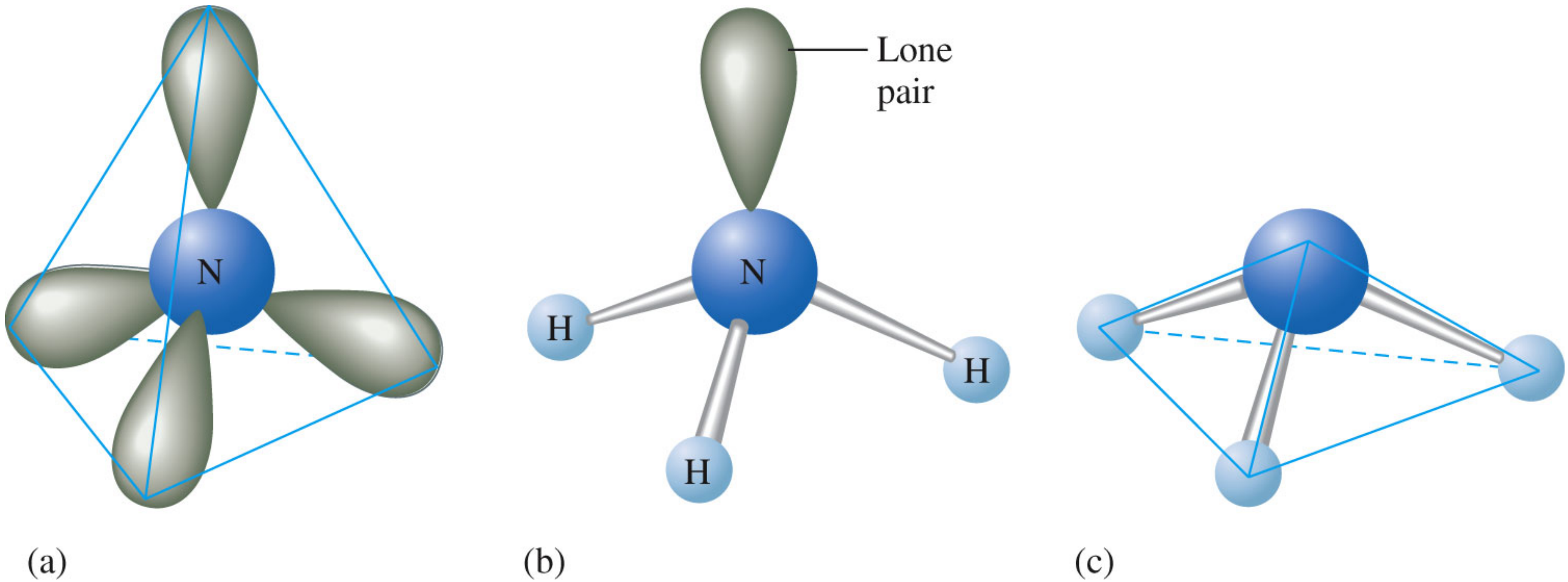
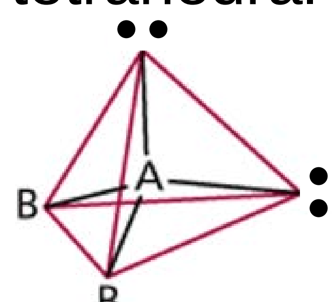
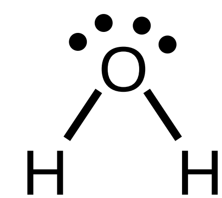



**Figure 13.16 - (a) The tetrahedral arrangement of electron pairs around the nitrogen atom in the ammonia molecule. (b) Three of the electron pairs around nitrogen are shared with hydrogen atoms, as shown, and the fourth is a lone pair. Although the arrangement of *electron pairs* is tetrahedral, as in the methane molecule, the hydrogen atoms in the ammonia molecule occupy only three corners of the tetrahedron. A lone pair occupies the fourth corner. (c) Note that molecular geometry is trigonal pyramidal, not tetrahedral.**

# Molecular Structure: The VSEPR Model

| Class | # of atoms bonded to central atom | # lone pairs on central atom | Arrangement of electron pairs | Molecular Geometry |
|---|---|---|---|---|
| $AB_4$ | 4 | 0 | tetrahedral | tetrahedral |
| $AB_3E$ | 3 | 1 | tetrahedral | trigonal pyramidal |
| $AB_2E_2$ | 2 | 2 | tetrahedral | bent |



# Molecular Structure: The VSEPR Model

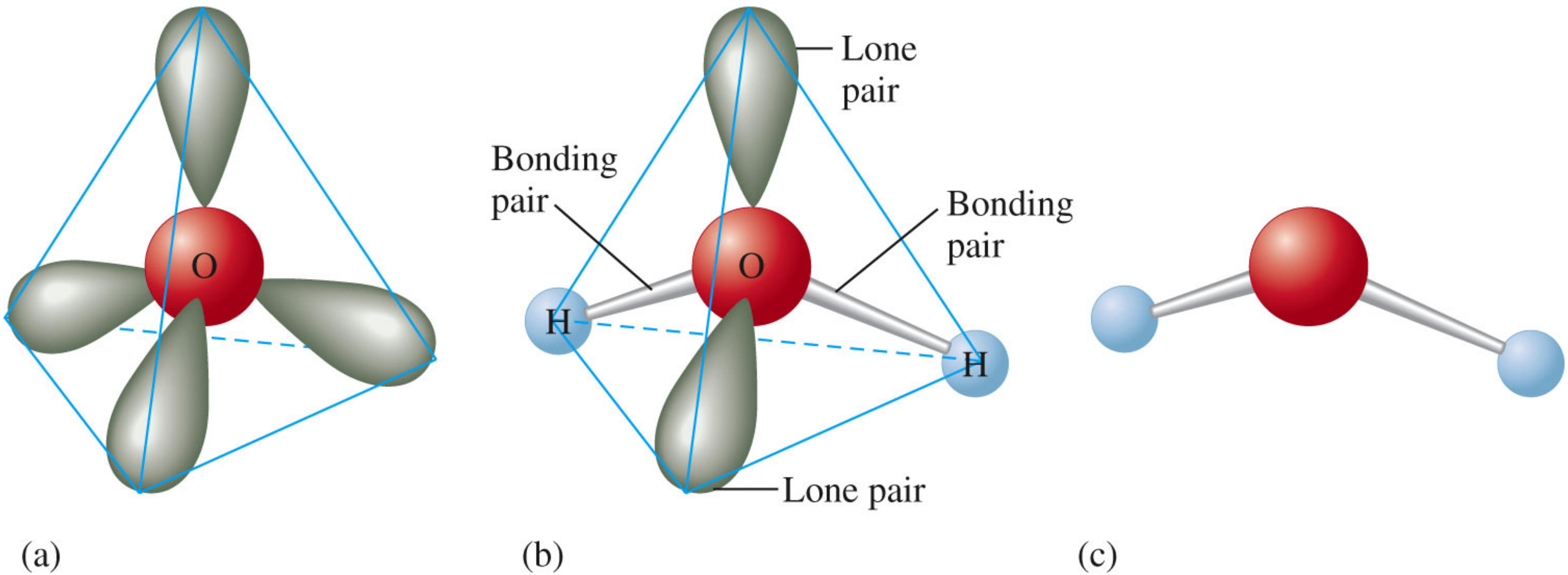
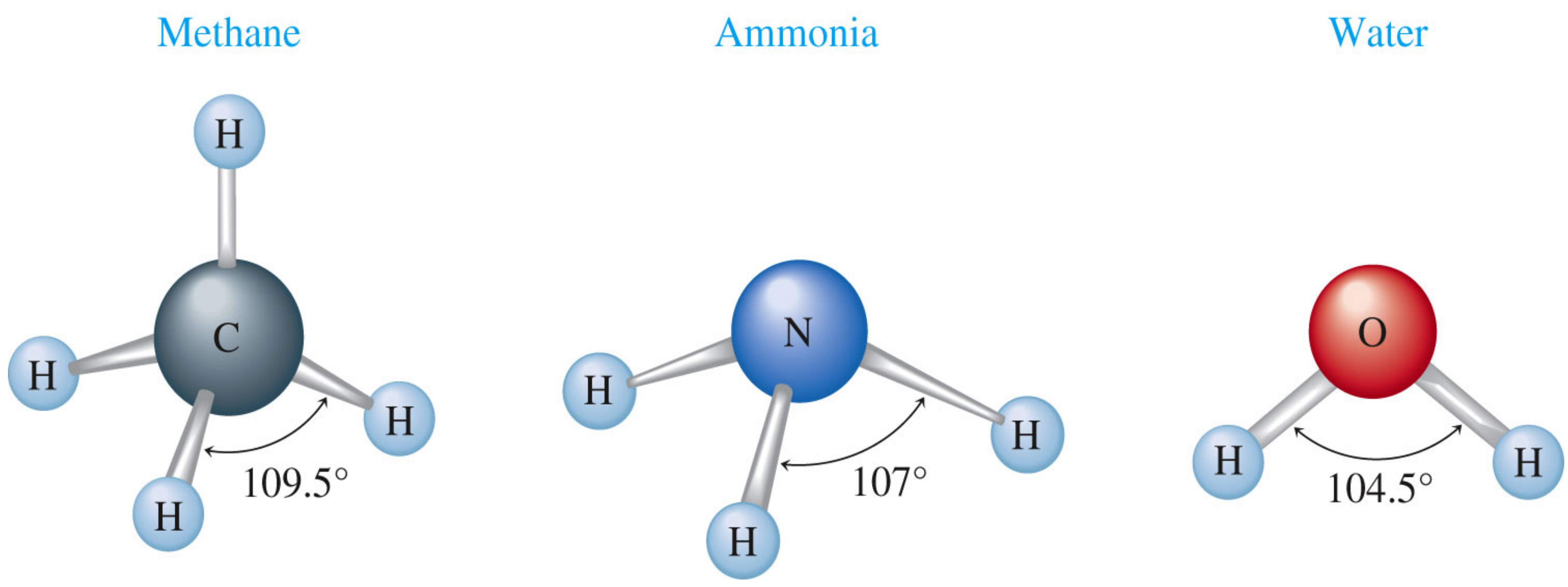



**Figure 13.17 - (a) The tetrahedral arrangement of the four electron pairs around oxygen in the water molecule. (b) Two of the electron pairs are shared between oxygen and the hydrogen atoms, and two are lone pairs. (c) The V-shaped molecular structure of the water molecule.**

# Molecular Structure: The VSEPR Model

A bonding pair is shared between two nuclei, and the electrons are relatively confined between the two nuclei, however a lone pair is localized on only one nucleus.

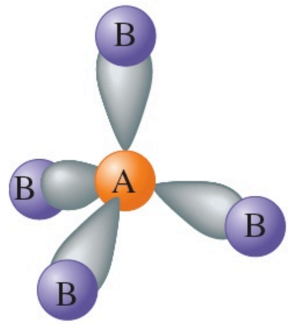
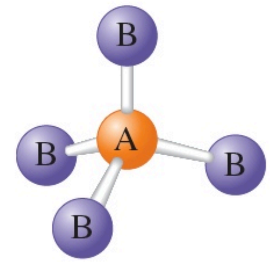
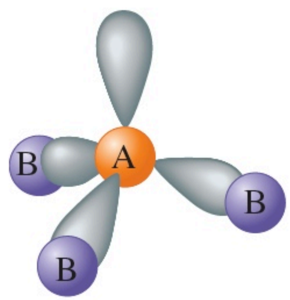
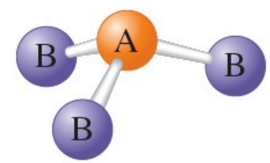
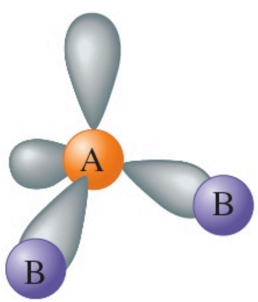
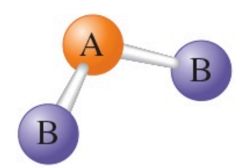
Lone pairs require more space than bonding pairs, as the number of lone pairs increases, the bonding pairs are increasingly squeezed together resulting in smaller bond angles.



# Molecular Structure: The VSEPR Model

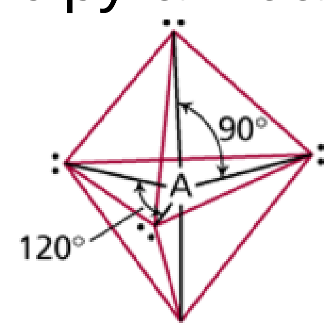
**Table 13.9**

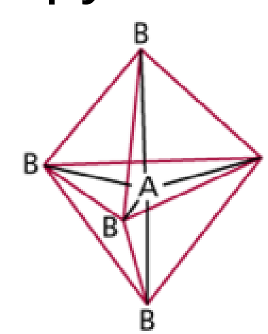
Structures of Molecules That Have Four Electron Pairs Around the Central Atom

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

# Molecular Structure: The VSEPR Model

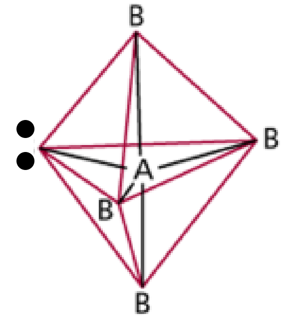
| Class | # of atoms bonded to central atom | # lone pairs on central atom | Arrangement of electron pairs | Molecular Geometry |
|---|---|---|---|---|
| $AB_2$ | 2 | 0 | linear | linear |
| $AB_3$ | 3 | 0 | trigonal planar | trigonal planar |
| $AB_4$ | 4 | 0 | tetrahedral | tetrahedral |
| $AB_5$ | 5 | 0 | trigonal bipyramidal | trigonal bipyramidal |

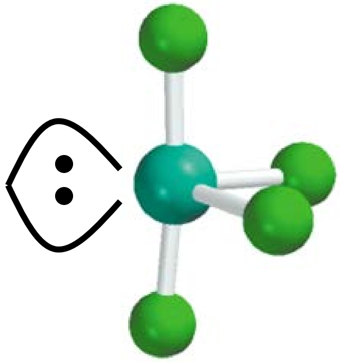


# Molecular Structure: The VSEPR Model

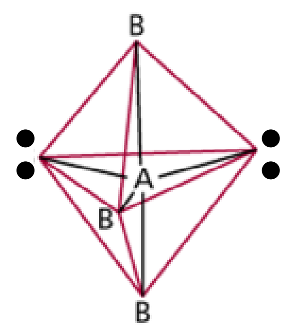
| Class | # of atoms bonded to central atom | # lone pairs on central atom | Arrangement of electron pairs | Molecular Geometry |
|---|---|---|---|---|
| $AB_5$ | 5 | 0 | trigonal bipyramidal | trigonal bipyramidal |
| $AB_4E$ | 4 | 1 | trigonal bipyramidal | See-Saw (distorted tetrahedron) |

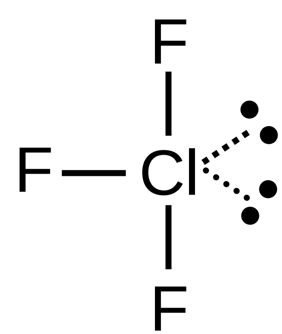


# Molecular Structure: The VSEPR Model

| Class | # of atoms bonded to central atom | # lone pairs on central atom | Arrangement of electron pairs | Molecular Geometry |
|---|---|---|---|---|
| $AB_5$ | 5 | 0 | trigonal bipyramidal | trigonal bipyramidal |
| $AB_4E$ | 4 | 1 | trigonal bipyramidal | See-Saw |
| $AB_3E_2$ | 3 | 2 | trigonal bipyramidal | T-shaped |

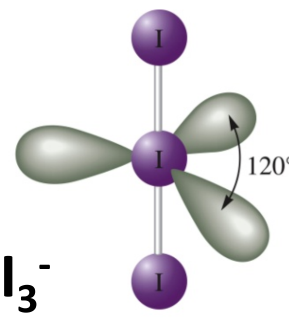


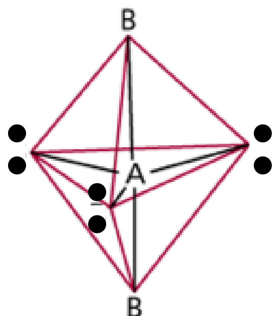



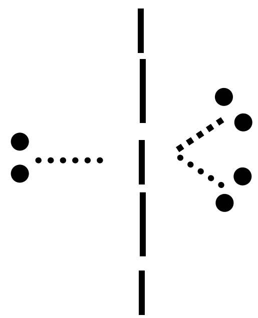
# Molecular Structure: The VSEPR Model

| Class | # of atoms bonded to central atom | # lone pairs on central atom | Arrangement of electron pairs | Molecular Geometry |
|---|---|---|---|---|
| $AB_5$ | 5 | 0 | trigonal bipyramidal | trigonal bipyramidal |
| $AB_4E$ | 4 | 1 | trigonal bipyramidal | See-Saw |
| $AB_3E_2$ | 3 | 2 | trigonal bipyramidal | T-shaped |
| $AB_2E_3$ | 2 | 3 | trigonal bipyramidal | linear |

$I_3^-$



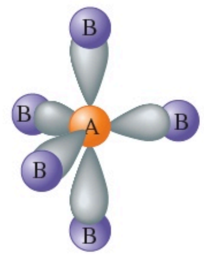
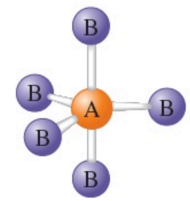
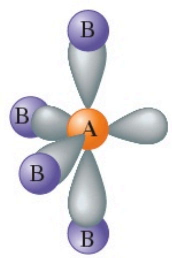
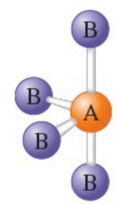
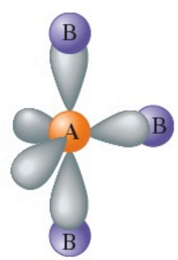
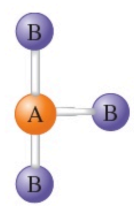
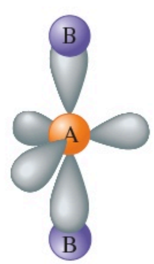
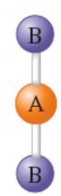



# Molecular Structure: The VSEPR Model

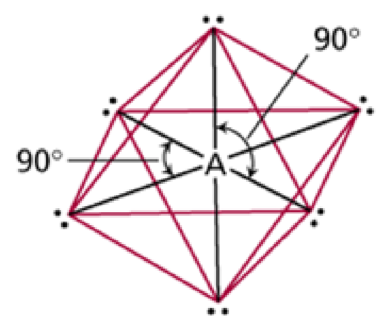
**Table 13.10**

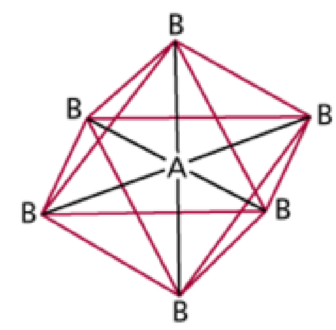
Structures of Molecules with Five Electron Pairs Around the Central Atom

| Electron-Pair Arrangement | Molecular Structure |
|---|---|
|  | <br>Trigonal bipyramidal |
|  | <br>See-saw |
|  | <br>T-shaped |
|  | <br>Linear |

# Molecular Structure: The VSEPR Model

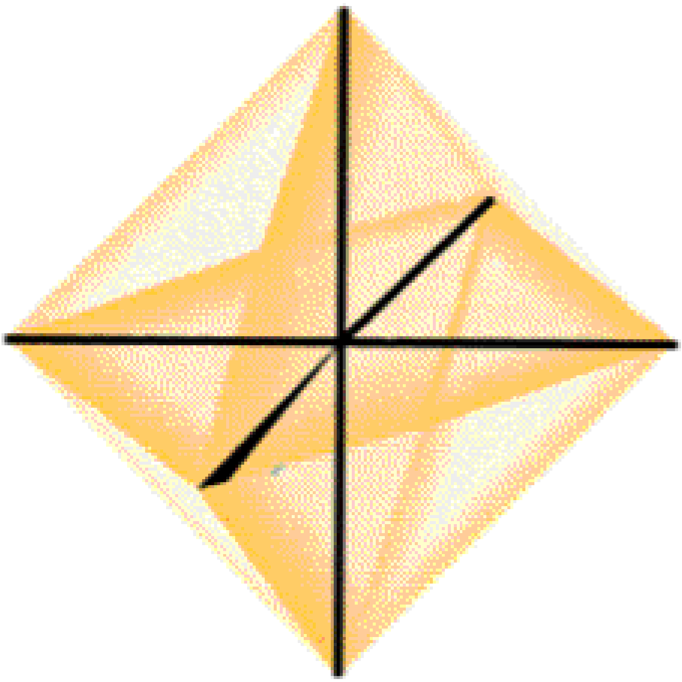
| Class | # of atoms bonded to central atom | # lone pairs on central atom | Arrangement of electron pairs | Molecular Geometry |
|---|---|---|---|---|
| $AB_2$ | 2 | 0 | linear | linear |
| $AB_3$ | 3 | 0 | trigonal planar | trigonal planar |
| $AB_4$ | 4 | 0 | tetrahedral | tetrahedral |
| $AB_5$ | 5 | 0 | trigonal bipyramidal | trigonal bipyramidal |
| $AB_6$ | 6 | 0 | octahedral | octahedral |



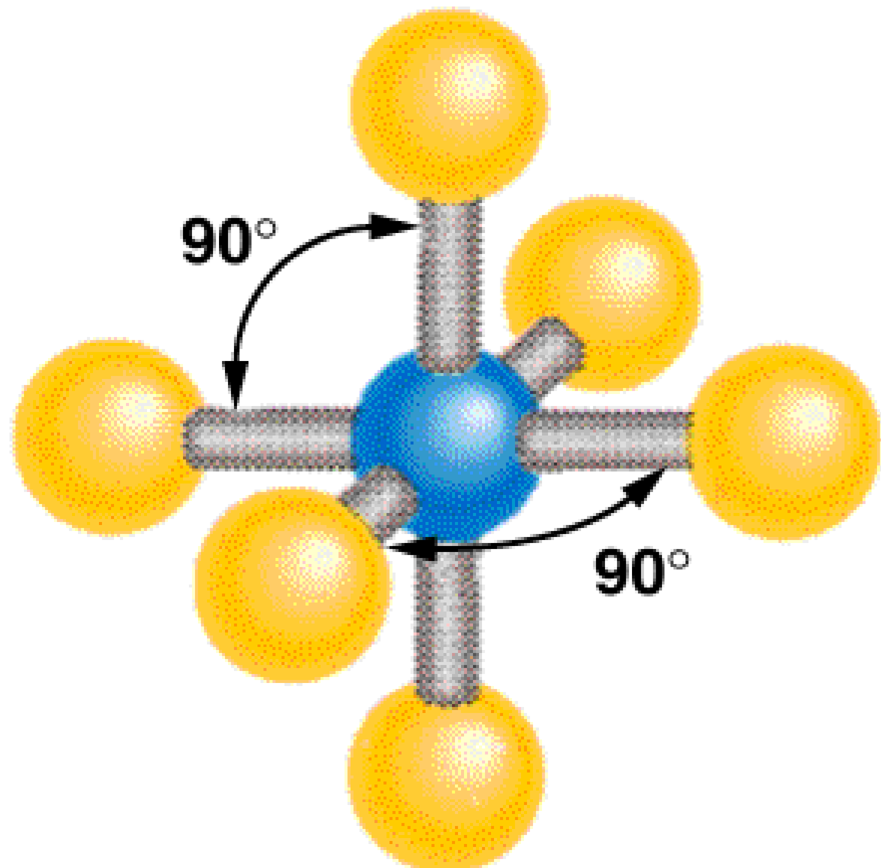



# Molecular Structure: The VSEPR Model

## Sulfur Hexafluoride

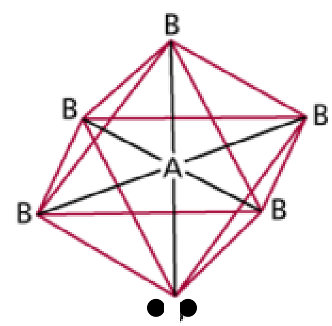


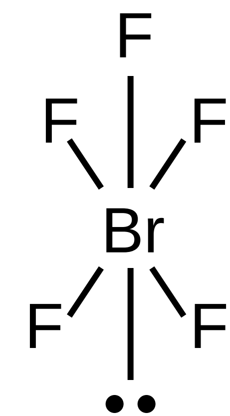
Octahedral



# Molecular Structure: The VSEPR Model

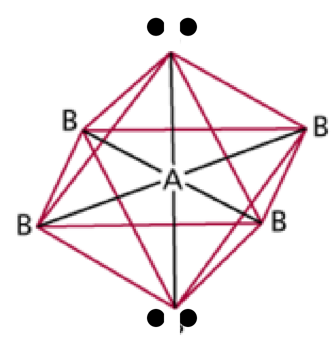
| Class | # of atoms bonded to central atom | # lone pairs on central atom | Arrangement of electron pairs | Molecular Geometry |
|---|---|---|---|---|
| $AB_6$ | 6 | 0 | octahedral | octahedral |
| $AB_5E$ | 5 | 1 | octahedral | square pyramidal |

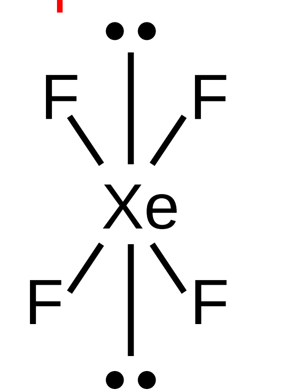


# Molecular Structure: The VSEPR Model

| Class | # of atoms bonded to central atom | # lone pairs on central atom | Arrangement of electron pairs | Molecular Geometry |
|---|---|---|---|---|
| $AB_6$ | 6 | 0 | octahedral | octahedral |
| $AB_5E$ | 5 | 1 | octahedral | square pyramidal |
| $AB_4E_2$ | 4 | 2 | octahedral | square planar |

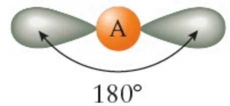
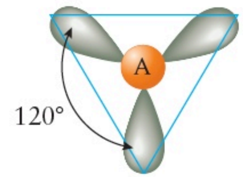
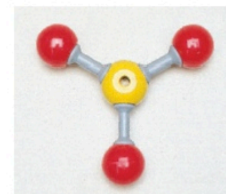
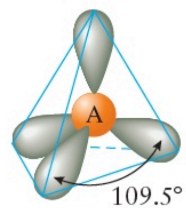
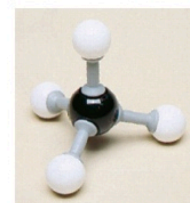
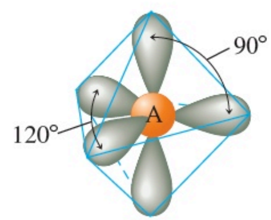
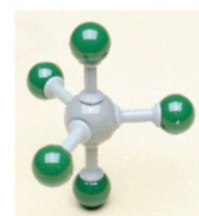
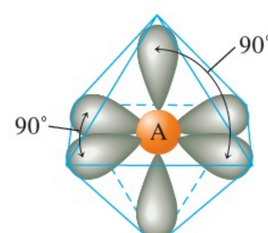
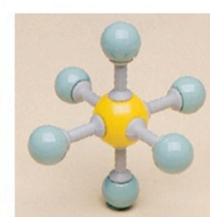


# Molecular Structure: The VSEPR Model

**Table 13.8**

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 |  |  |
| 5 | Trigonal bipyramidal |  |  |
| 6 | Octahedral |  |  |

# Molecular Structure: The VSEPR Model

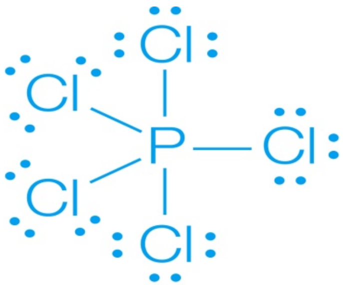
**Example 13.12**

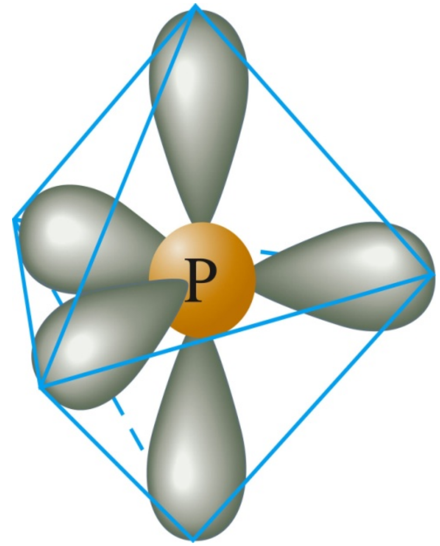
When phosphorus reacts with excess chlorine gas, the compound phosphorus pentachloride ($PCl_5$) is formed. In the gaseous and liquid states, this substance consists of $PCl_5$ molecules, but in the solid state, it consists of a 1:1 mixture of $PCl_4^+$ and $PCl_6^-$ ions. Predict the geometric structures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

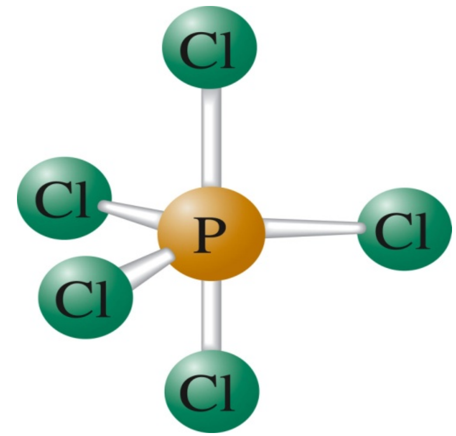
# Molecular Structure: The VSEPR Model

**SOLUTION**

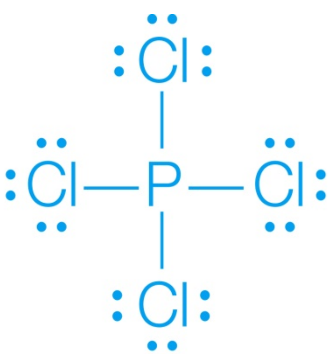
$PCl_5$

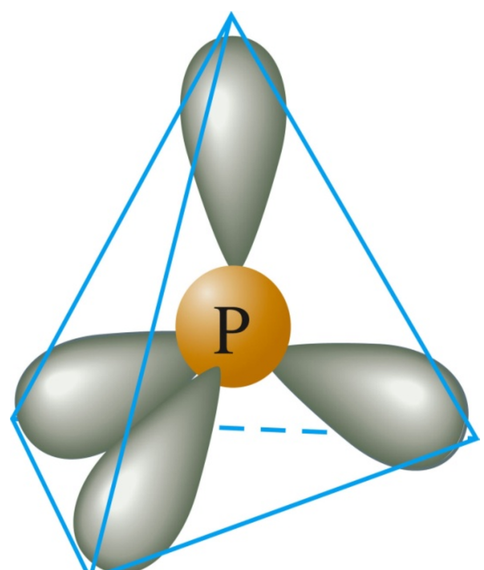


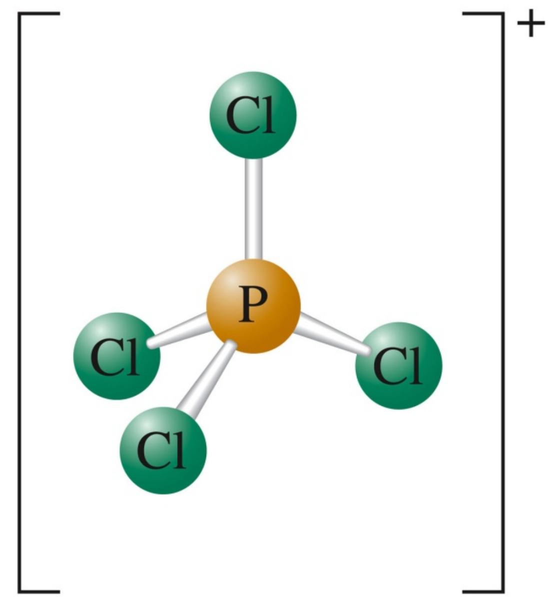



$PCl_4^+$





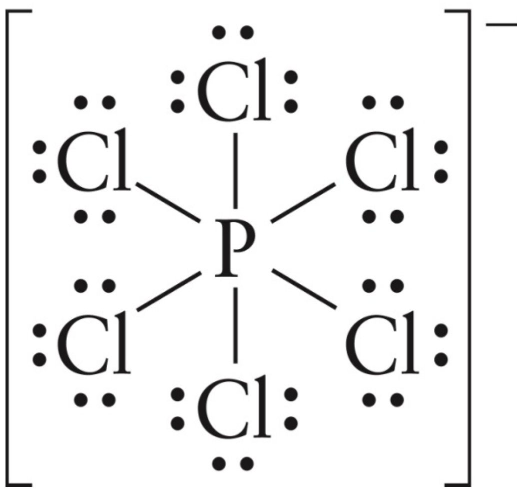



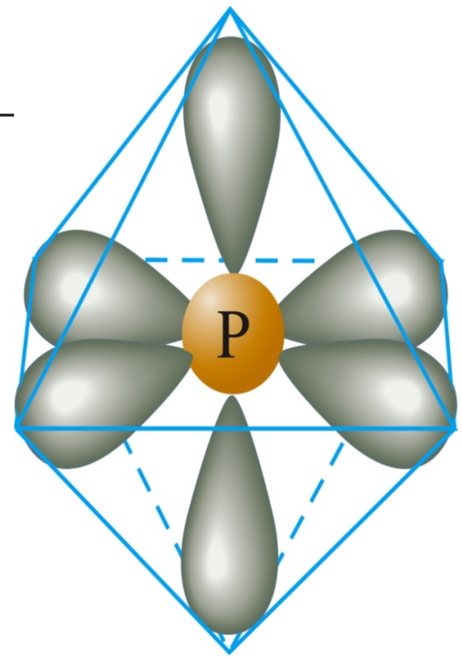

Tetrahedral $PCl_4^+$ cation

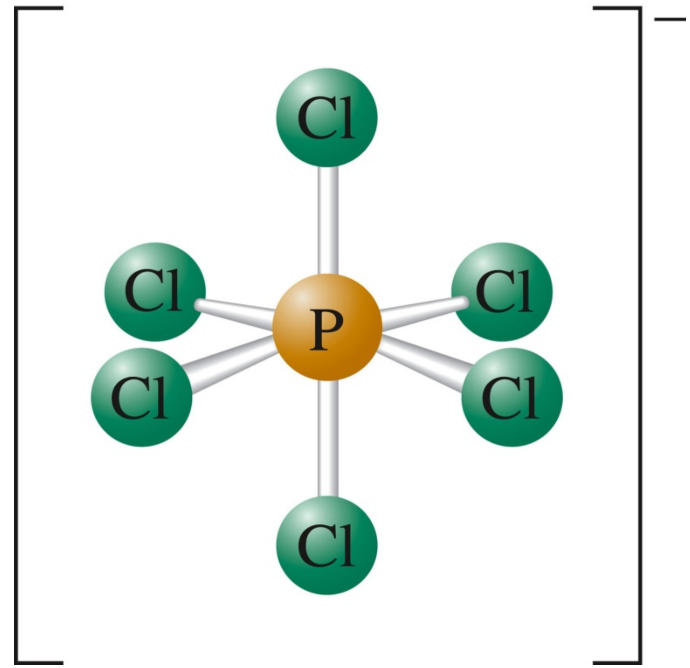
# Molecular Structure: The VSEPR Model

**SOLUTION**

$PCl_6^-$



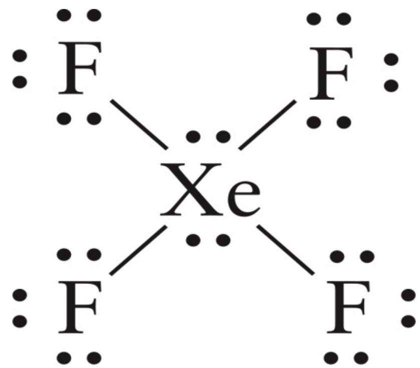
# Molecular Structure: The VSEPR Model

**Example 13.13**

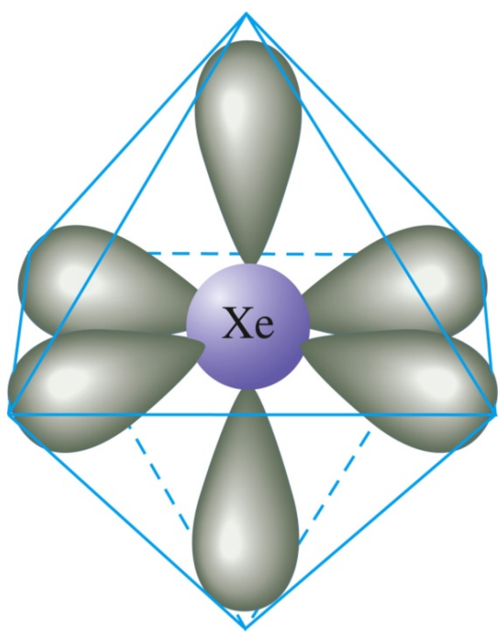
Because the noble gases have filled s and p valence orbitals, they are not expected to be chemically reactive. In fact, for many years these elements were called inert gases because of this supposed inability to form any compounds. However, in the early 1960s, several compounds of krypton, xenon, and radon were synthesized. For example, a team at the Argonne National Laboratory produced the stable colorless compound xenon tetrafluoride ($XeF_4$). Predict its structure and determine whether it has a dipole moment.

# Molecular Structure: The VSEPR Model

**SOLUTION**



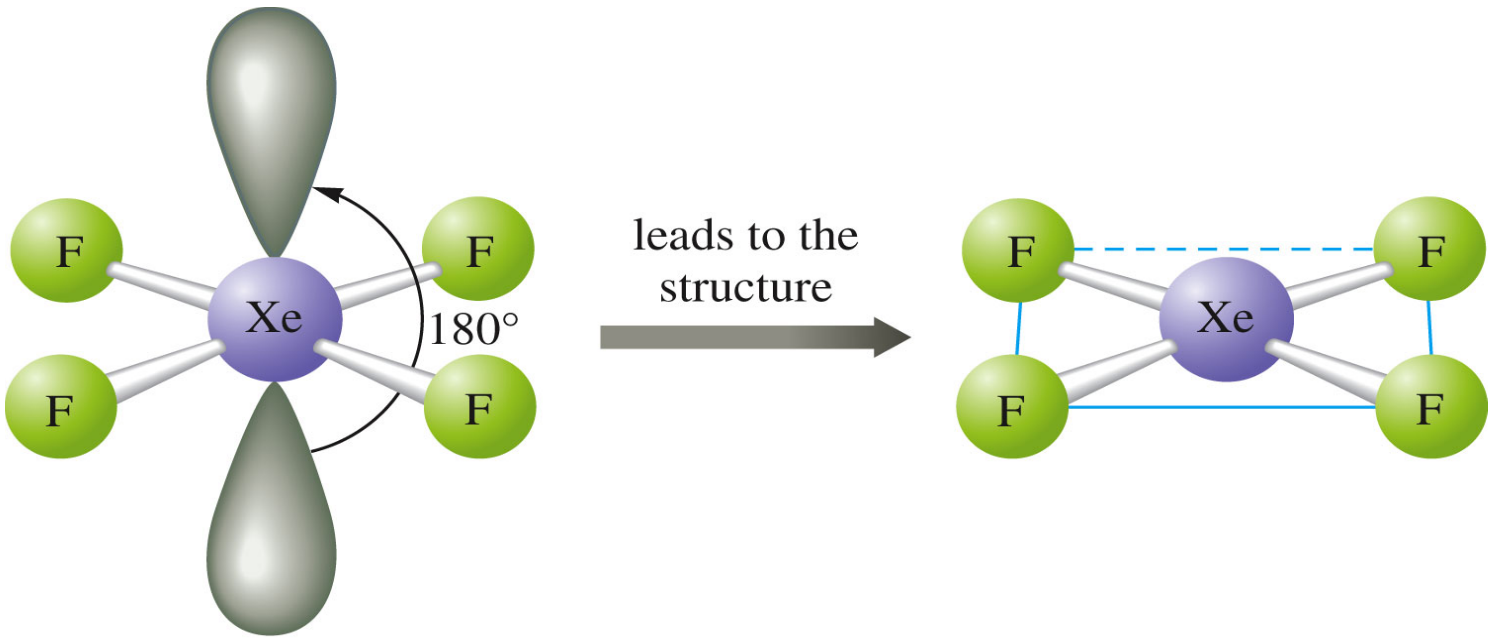

**6 pairs of electrons $\longrightarrow$ octahedral arrangement**



# Molecular Structure: The VSEPR Model

**SOLUTION**

**Octahedral arrangement of electron pairs but square planar structure**

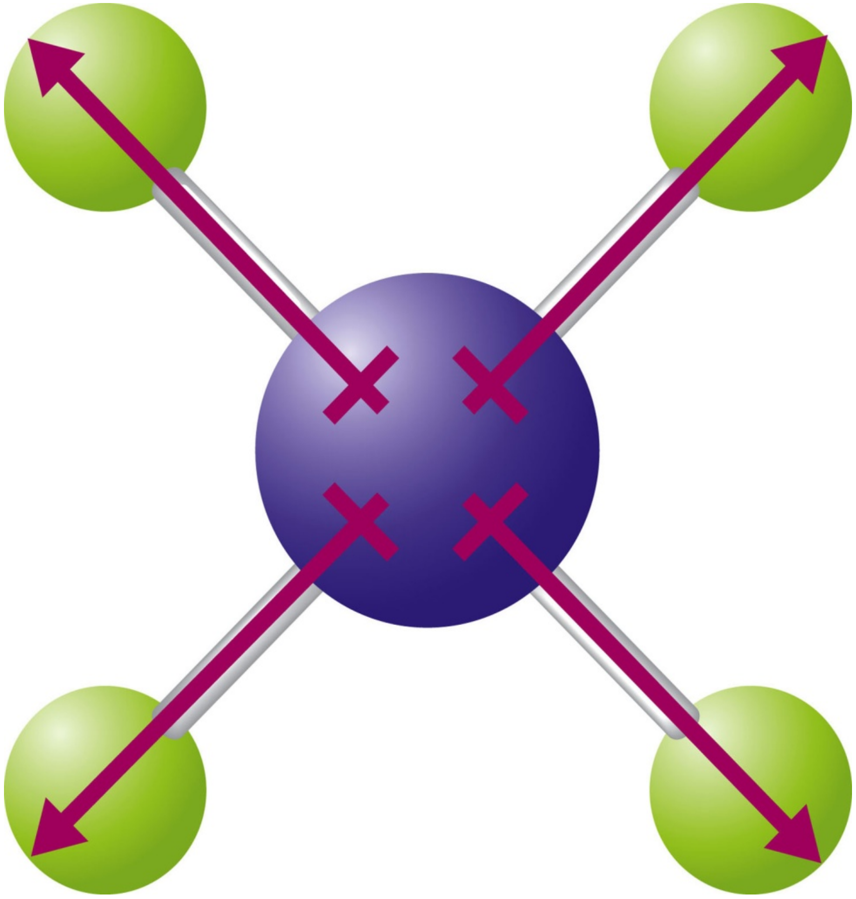



(b)

# Molecular Structure: The VSEPR Model

**SOLUTION**

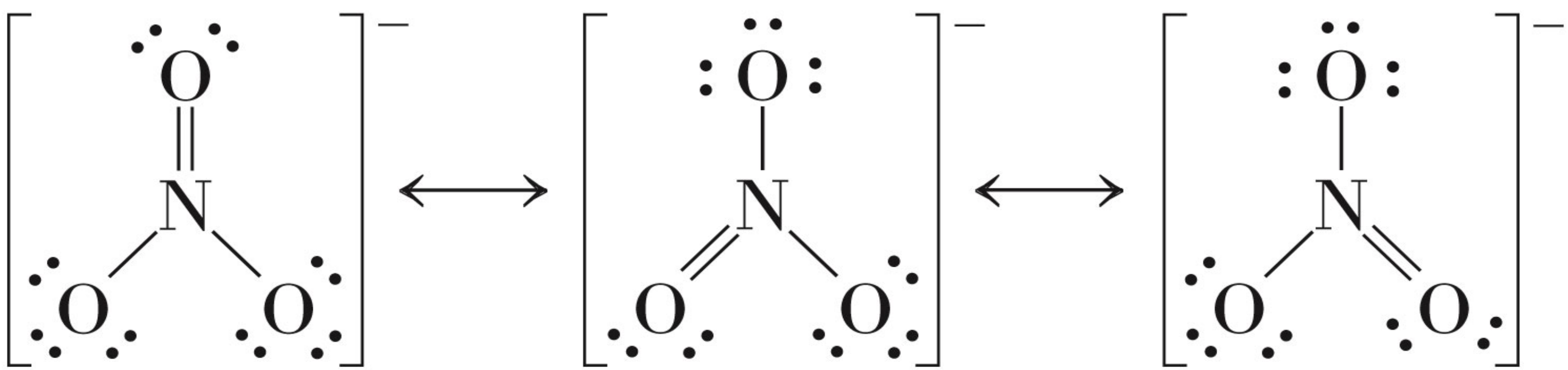
**Although Xe-F are polar bonds, $XeF_4$ has no dipole moment.**

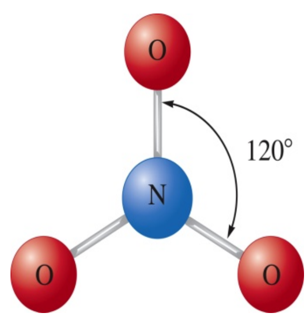


# The VSEPR Model and Multiple Bonds

Multiple bonds should be counted as one effective pair.

When a molecule exhibits resonance, any one of the resonance structures can be used to predict the molecular structure using the VSEPR model.




**Trigonal Planar**

# The VSEPR Model and Multiple Bonds

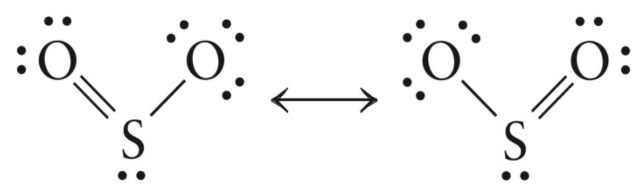
**Example 13.14**

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

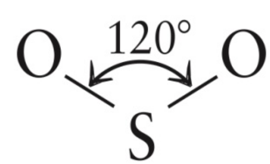
# The VSEPR Model and Multiple Bonds

## SOLUTION

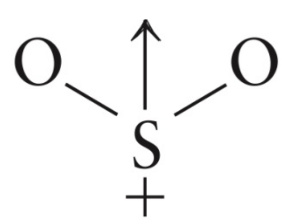
The Lewis structure of $SO_2$ molecule has 18 valence electrons.



Three effective pairs around the sulfur yield a trigonal planar arrangement and a V-shaped geometry




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



# The VSEPR Model

The following rules are helpful in using the VSEPR model to predict molecular structure.

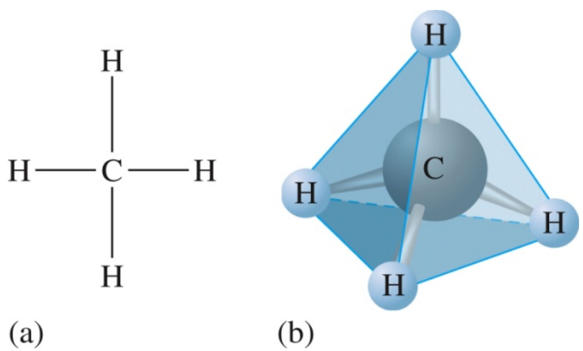
1. Determine the Lewis structure(s) for the molecule.
2. For molecules with resonance structures, use any of the structures to predict molecular structure.
3. Sum the electron pairs around the central atom.
4. When counting pairs, count each multiple bond as single effective pair.
5. Determine the arrangement of the pairs that minimizes electron-pair repulsions. These arrangements are shown in Table 13.8.
6. Lone pairs required more space than bonding pairs. Choose an arrangement that gives the lone pairs as much room as possible, although it appears that an angle of at least 120 degrees may produce distortions from the idealized structure.

# Hybridization and the Localized Electron Model

**Hybridization** describes the types of atomic orbitals used to share the electrons and hence to form the bonds.

1. Mix at least 2 nonequivalent atomic orbitals (*e.g.* s and p). Hybrid orbitals have very different shape from original atomic orbitals.
2. Number of hybrid orbitals is equal to number of pure atomic orbitals used in the hybridization process.
3. Covalent bonds are formed by:
    a. Overlap of hybrid orbitals with atomic orbitals
    b. Overlap of hybrid orbitals with other hybrid orbitals

# $sp^3$ *Hybridization*




$_6C : 1s^2\ /\underline{2s^2\ 2p^2} \Rightarrow \boxed{\uparrow\downarrow}\quad \boxed{\uparrow}\boxed{\uparrow}\boxed{\phantom{\uparrow}}$

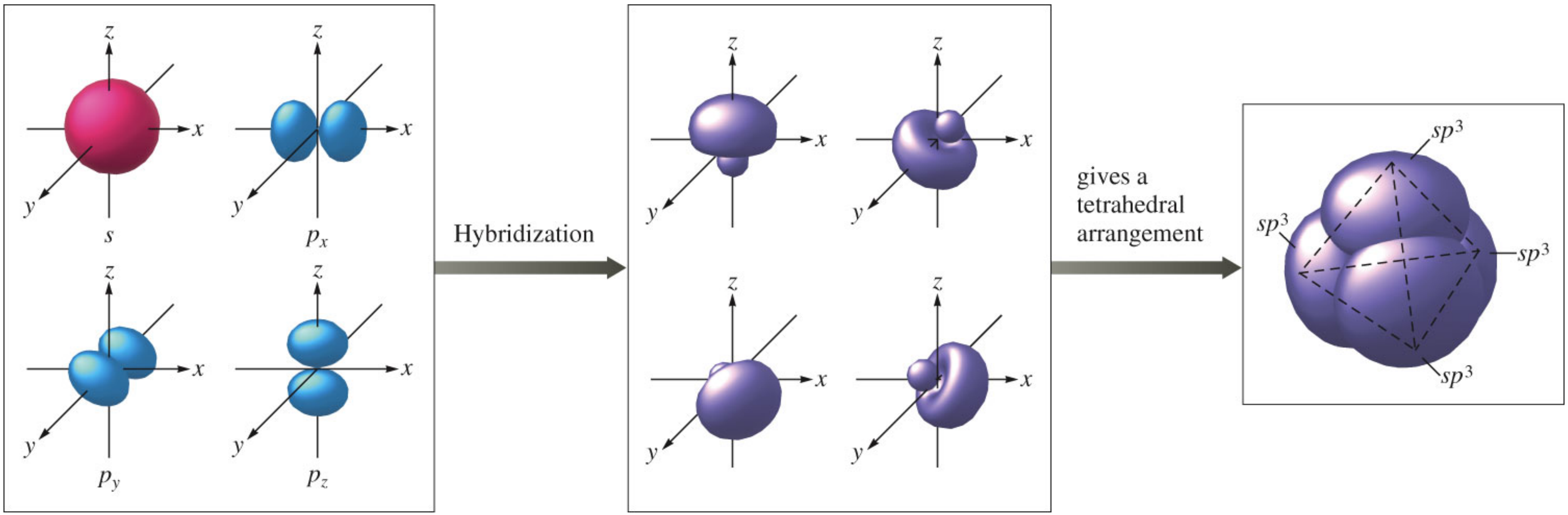
$H : 1s^1 \Rightarrow \boxed{\uparrow}$

The hydrogen atoms in methane use 1s orbitals and the carbon atom uses the 2s and 2p orbitals for bonding.

Carbon adopts a set of four equivalent atomic orbitals to bond to the hydrogen atoms.

The mixing of the native atomic orbitals to form special orbitals for bonding is called **hybridization**.

# $sp^3$ Hybridization

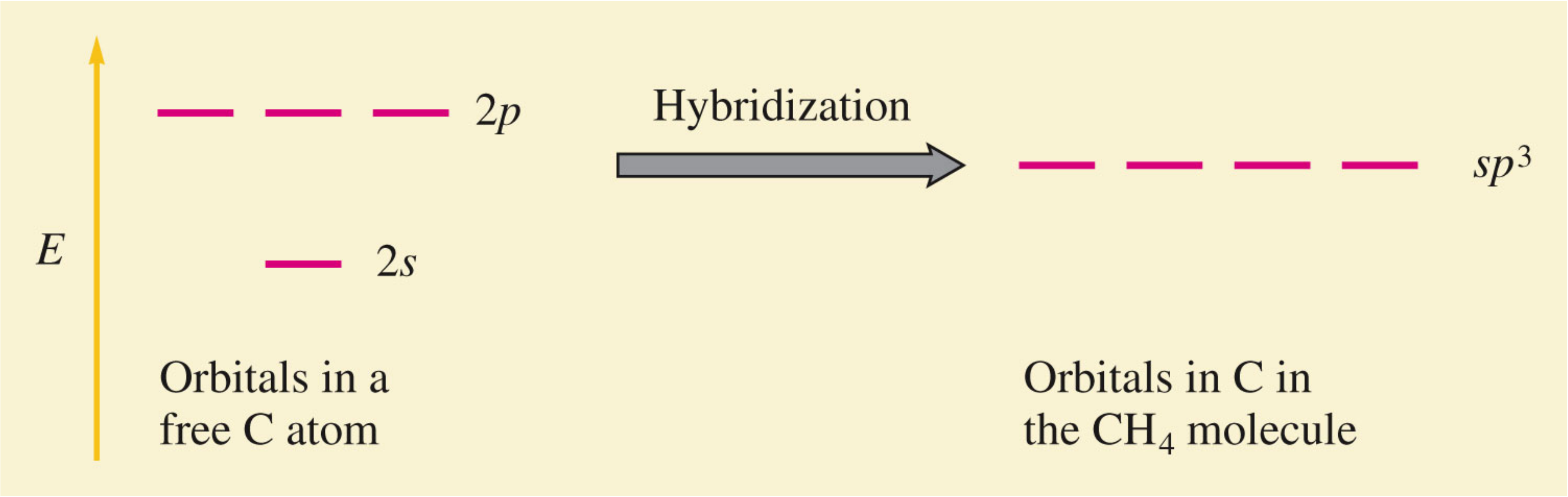



The four new orbitals are called $sp^3$ orbitals because they are formed from one 2s and three 2p orbitals.

# *$sp^3$ Hybridization*

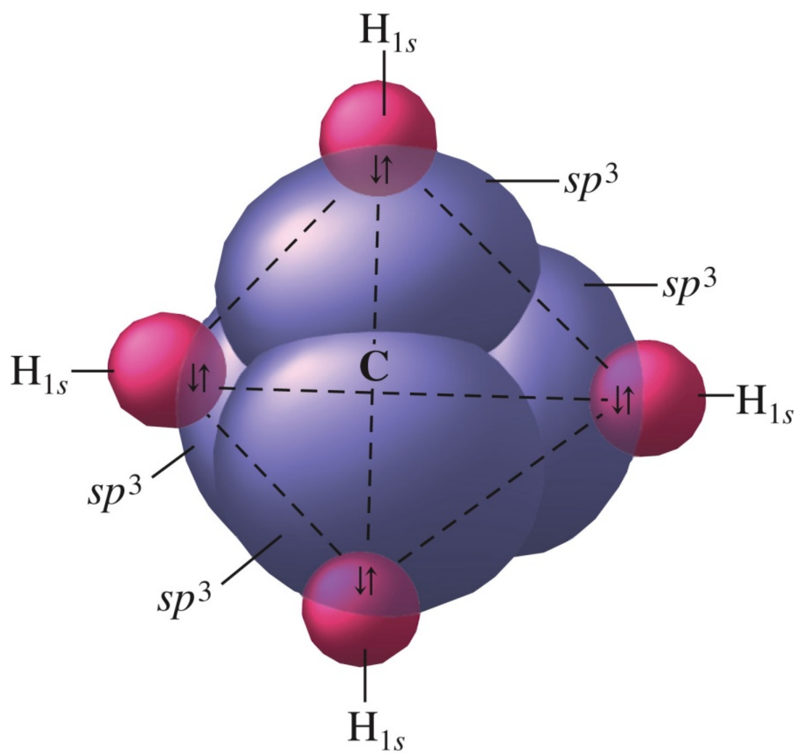
The four $sp^3$ orbitals are identical in shape and are oriented in space so that a tetrahedral arrangement is formed.

The hybridization of the carbon 2s and 2p orbitals can be represented by an orbital energy-level diagram:



# $sp^3$ Hybridization

The new $sp^3$ atomic orbitals on carbon are used to share electron pairs with the 1s orbitals from the four hydrogen atoms.



# *$sp^3$ Hybridization*

**Example 14.1**

Describe the bonding in the ammonia molcecule using the LE model.

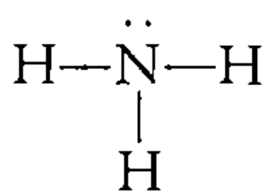
# $sp^3$ Hybridization

**Solution**

A complete description of the bonding involves three steps:

1. Write the Lewis structure.
2. Determine the arrangement of electron pairs using the VSEPR model.
3. Determine the hybrid atomic orbitals used for bonding in the molecule.

The Lewis structure for $NH_3$ is



The four electron pairs around the nitrogen atom require a tetrahedral arrangement. We have seen that a tetrahedral set of $sp^3$ hybrid orbitals is obtained by combining the 2*s* and three 2*p* orbitals. In the $NH_3$ molecule three of the $sp^3$ orbitals are used to form bonds to the three hydrogen atoms, and the fourth $sp^3$ orbital is used to hold the lone pair, as shown in Fig. 14.7.

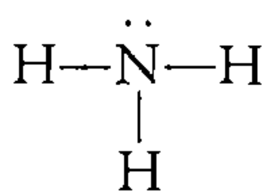
# $sp^3$ Hybridization

**Solution**

A complete description of the bonding involves three steps:

1. Write the Lewis structure.
2. Determine the arrangement of electron pairs using the VSEPR model.
3. Determine the hybrid atomic orbitals used for bonding in the molecule.

The Lewis structure for $NH_3$ is



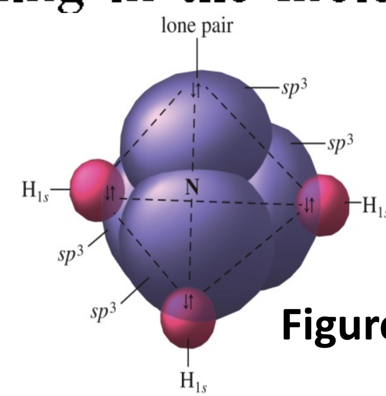
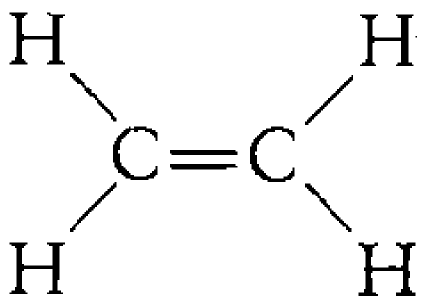


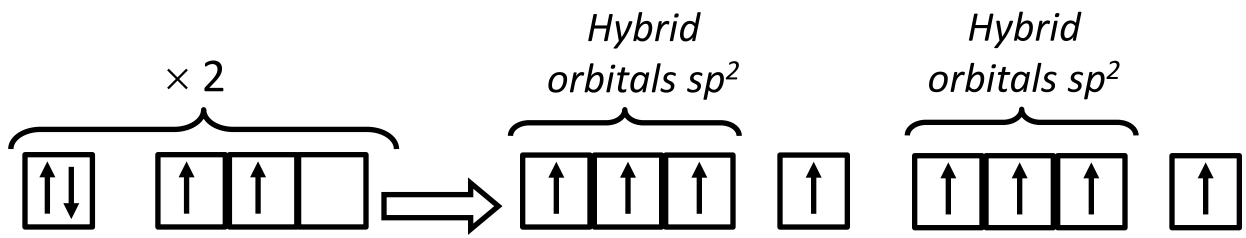

**Figure 14.7**

The four electron pairs around the nitrogen atom require a tetrahedral arrangement. We have seen that a tetrahedral set of $sp^3$ hybrid orbitals is obtained by combining the 2*s* and three 2*p* orbitals. In the $NH_3$ molecule three of the $sp^3$ orbitals are used to form bonds to the three hydrogen atoms, and the fourth $sp^3$ orbital is used to hold the lone pair, as shown in Fig. 14.7.

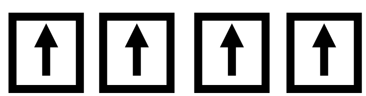
# $sp^2$ *Hybridization*



$2 \times ({}_{6}C : 1s^2 / \underline{2s^2\ 2p^2}) \Rightarrow$




$4 \times ({}_{1}H : 1s^1) \Rightarrow$



One 2s and two 2p orbitals are used to form three $sp^2$ hybrid orbitals on each carbon.

In forming the $sp^2$ orbitals, one 2p orbital on carbon has not been used.

# *$sp^2$ Hybridization*

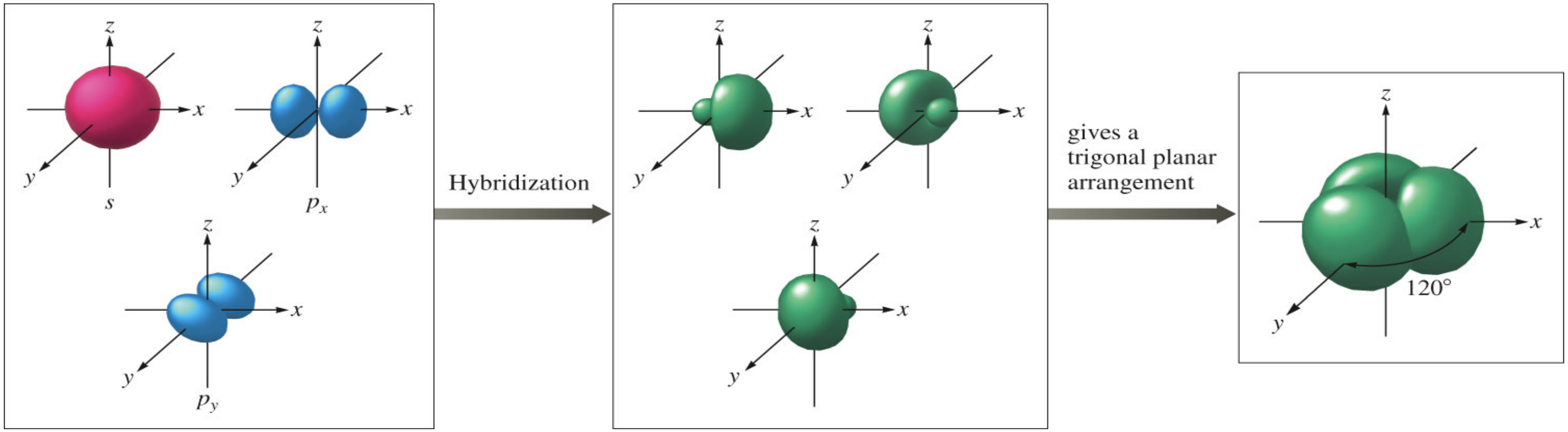



**Figure 14.8 - The hybridization of the *s*, $p_x$, and $p_y$ atomic orbitals results in the formation of three $sp^2$ orbitals centered in the *xy* plane. The large lobes of the orbitals lie in the plane at angles of 120 degrees and point toward the corners of a triangle.**

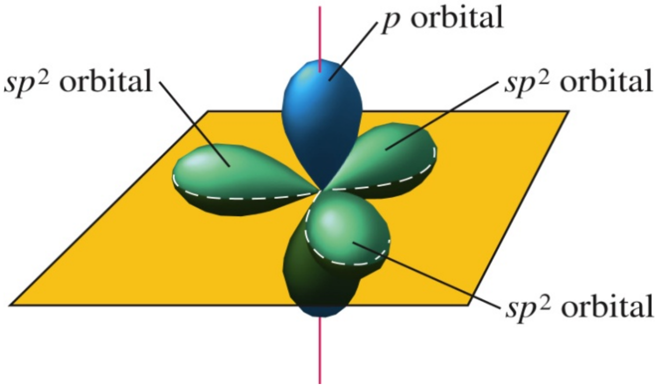



**Figure 14.10 - When one *s* and two *p* orbitals are mixed to form a set of three $sp^2$ orbitals, one *p* orbital remains unchanged and is perpendicular to the plane of the hybrid orbitals. Note that in this figure and those that follow, the hybrid orbitals are drawn with narrowed lobes to show their orientations more clearly.**

# *sp*$^2$ Hybridization

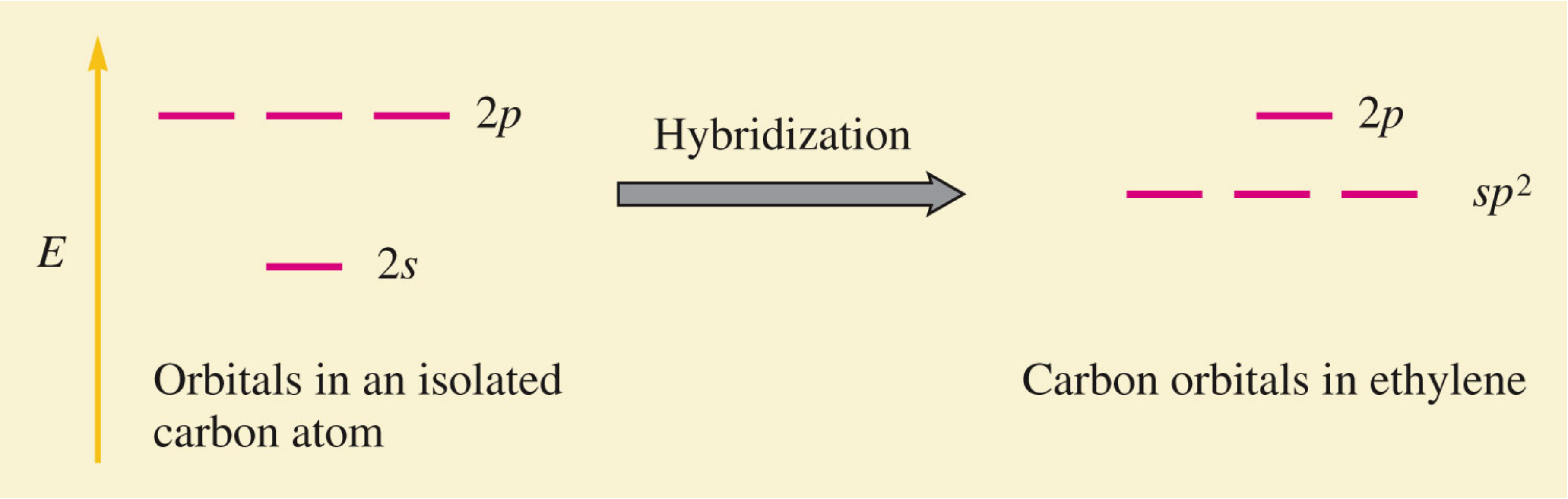
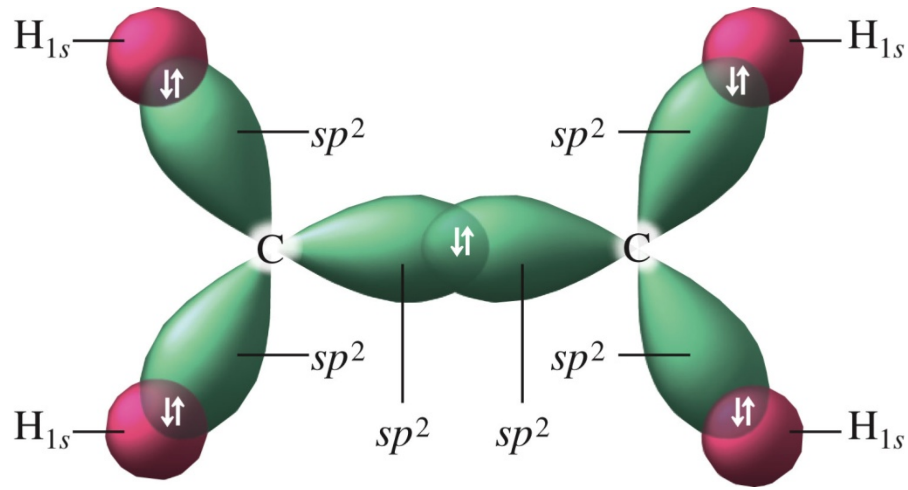



**Figure 14.9 - An orbital energy-level diagram for *sp*$^2$ hybridization. Note that one *p* orbital remains unchanged.**

# *sp² Hybridization*

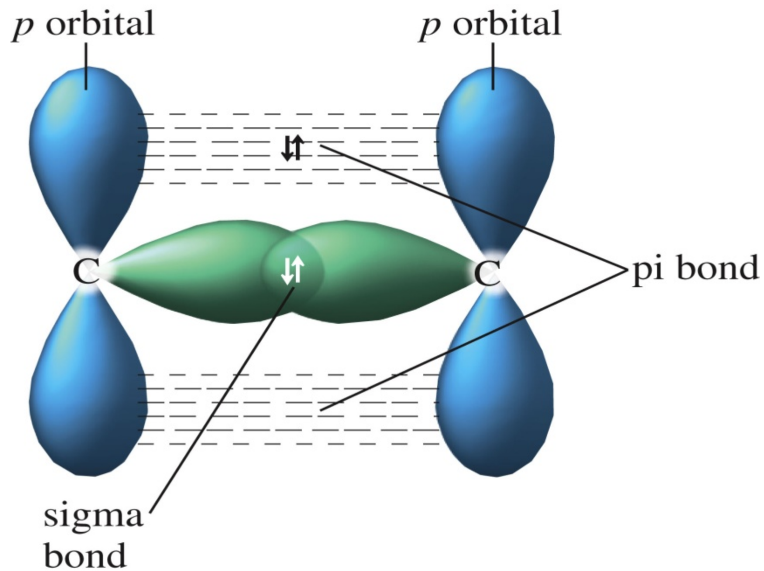



The three $sp^2$ orbitals on each carbon atom can be used to share electrons with hydrogen 1s orbitals.

The electron pair is shared in an area centered on a line running between the atoms, this type of covalent bond is called a sigma (σ) bond.

The remaining p orbital on each carbon is oriented perpendicular to the plane of the $sp^2$ orbitals.

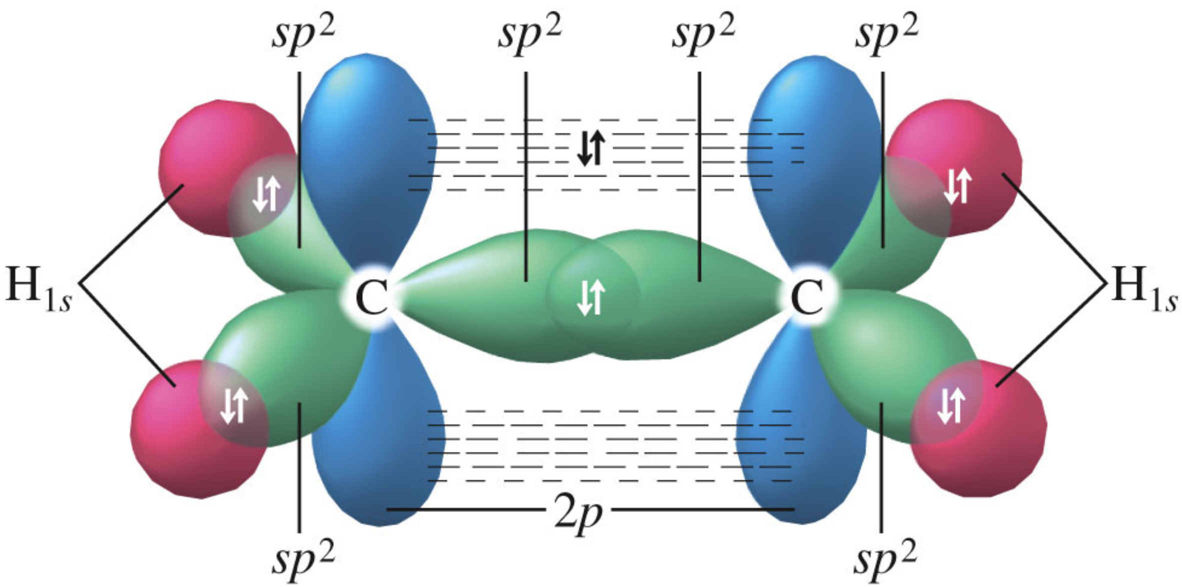
# $sp^2$ Hybridization



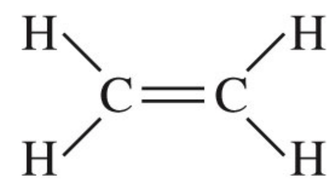

The second C–C bond is formed using the 2p orbitals on each carbon atom.

The parallel p orbitals share an electron pair which occupies the space above and below a line joining the atoms, to form a pi ($\pi$) bond.

# $sp^2$ *Hybridization*



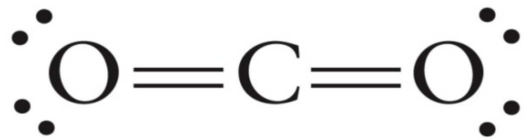

(a)




(b)

**A double bond always consists of one σ bond and one π bond.**

# *sp* Hybridization



The carbon atom has two effective pairs (two double bonds) that will be arranged at an angle of 180 degrees.

Carbon requires sp hybridization.

sp hybrid orbitals are used to form the σ bonds between the carbon and the oxygen atoms.

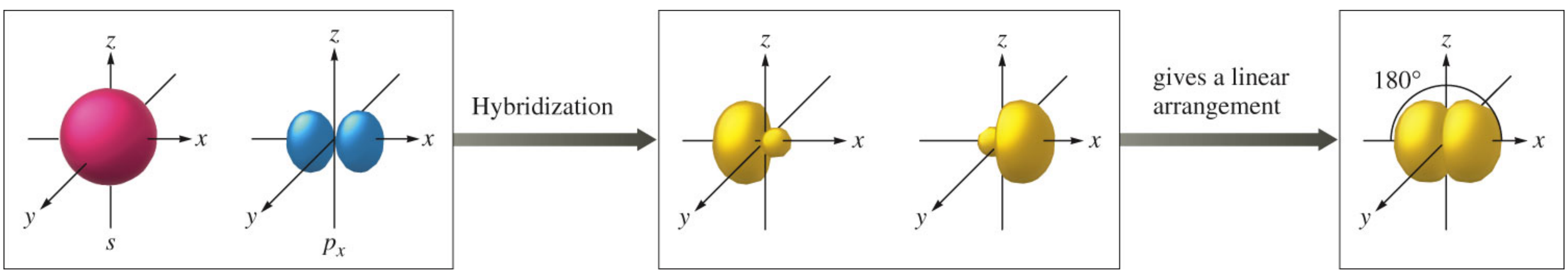
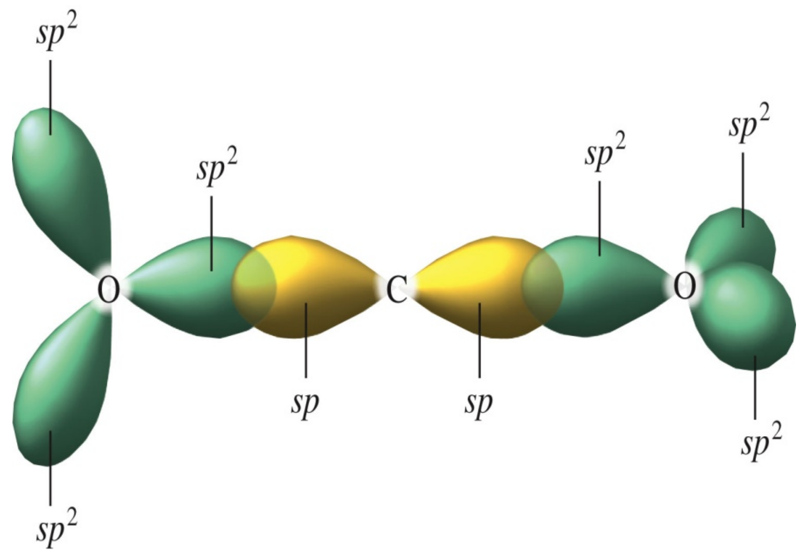
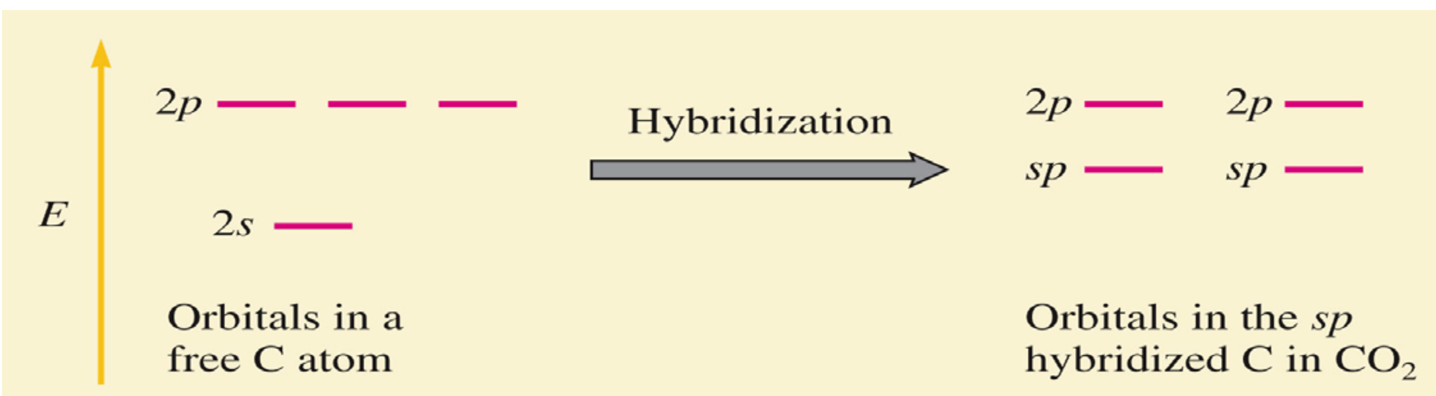



**Figure 14.14 - When one *s* orbital and one *p* orbital are hybridized, a set of two *sp* orbitals oriented at 180 degrees results.**

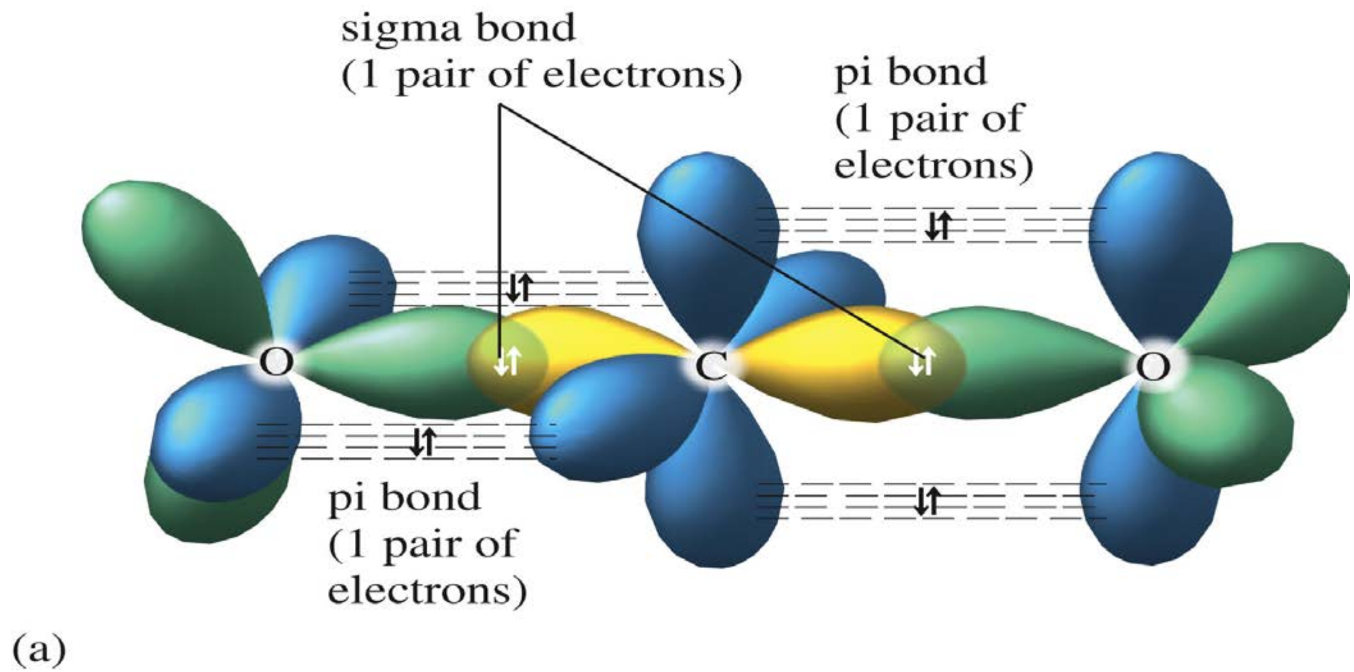
# *sp Hybridization*

- Each oxygen atom has three effective pairs around it (one double bond and two lone pairs), requiring $sp^2$ hybridization.
- One p orbital on each oxygen is unchanged and is used for the π bond with the carbon atom.



# *sp Hybridization*




- The sp orbitals on carbon for σ bonds with the $sp^2$ orbitals on the two oxygen atoms.
- The remaining $sp^2$ orbitals on the oxygen atoms hold lone pairs.
- The π bonds between the carbon atom and each oxygen atom are formed by the overlap of parallel 2p orbitals.
- The sp hybridized carbon atom has two unhybridized p orbitals, each of these p orbitals is used to form a π bond with an oxygen atom.

# Hybridization and the Localized Electron Model

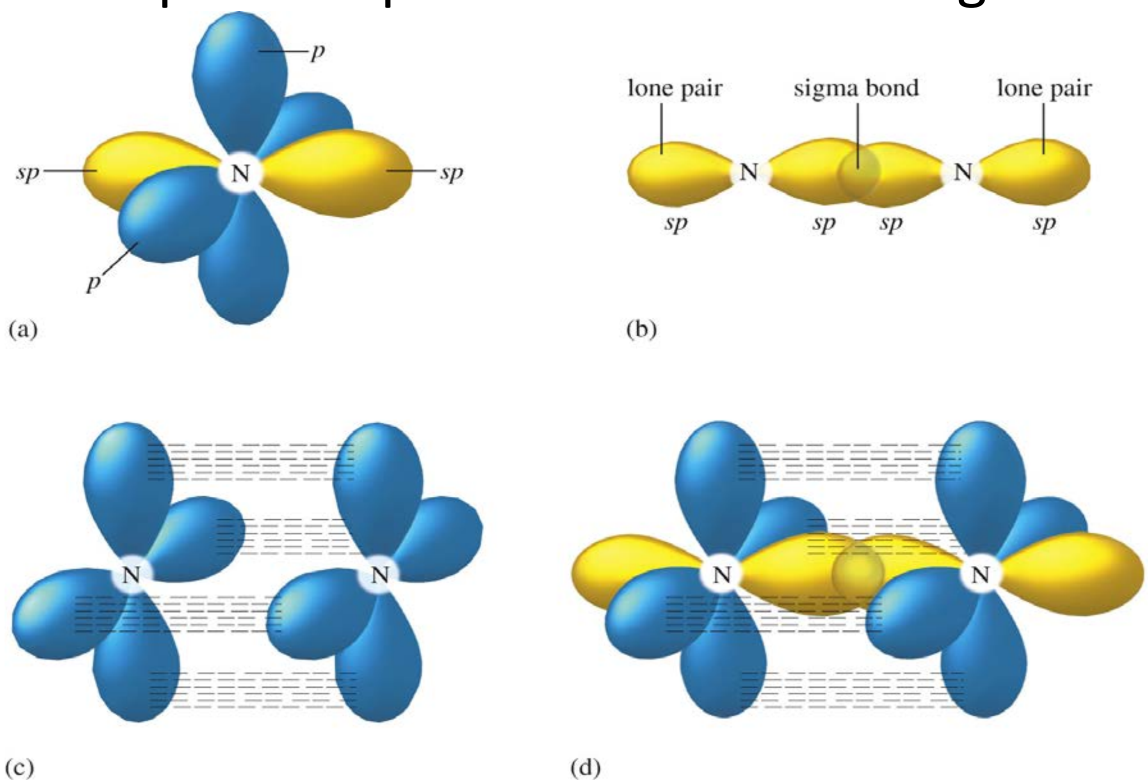
**Example 14.2**

Describe the bonding in the $N_2$ molecule.

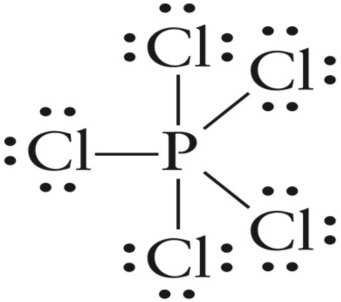
# Hybridization and the Localized Electron Model

**SOLUTION**

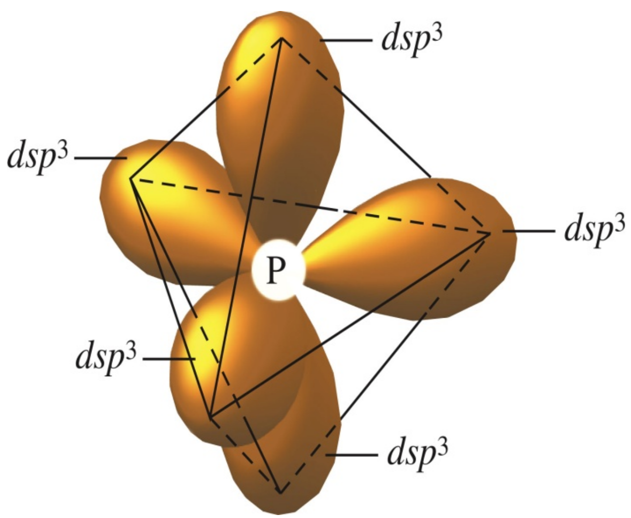
- sp hybridization.
- The sp orbitals are used to form the σ bond between the nitrogen atoms and to hold lone pairs.
- The p orbitals are used to form the two π bonds.
- A lone pair occupies an sp orbital on each nitrogen atom.



# *dsp³ Hybridization*

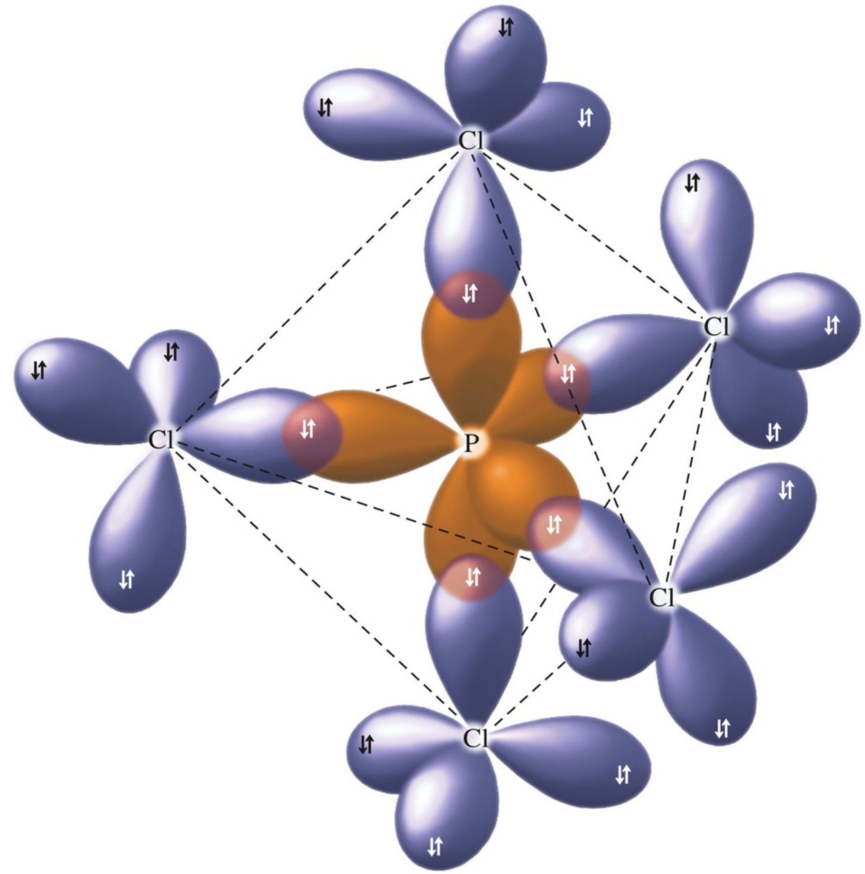



- For molecules in which the central atom exceeds the octet rule.
- $dsp^3$ formed from one d orbital, one s orbital, and three p orbitals.
- For $PCl_5$, five equivalent $dsp^3$ orbitals share electrons with the five chlorine atoms.



# *$dsp^3$ Hybridization*

- Each chlorine atom is surrounded by four electron pairs, requiring a set of four $sp^3$ orbitals on each chlorine atom.
- In $PCl_5$, the five P–Cl σ bonds are formed by sharing electrons between a $dsp^3$ orbital on the phosphorus atom and an $sp^3$ orbital on each chlorine. The other $sp^3$ orbitals on each chlorine hold lone pairs.



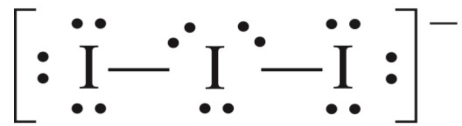
# Hybridization and the Localized Electron Model

**Example 14.3**

Describe the bonding in the triiodide ion ($I_3^-$).

# Hybridization and the Localized Electron Model

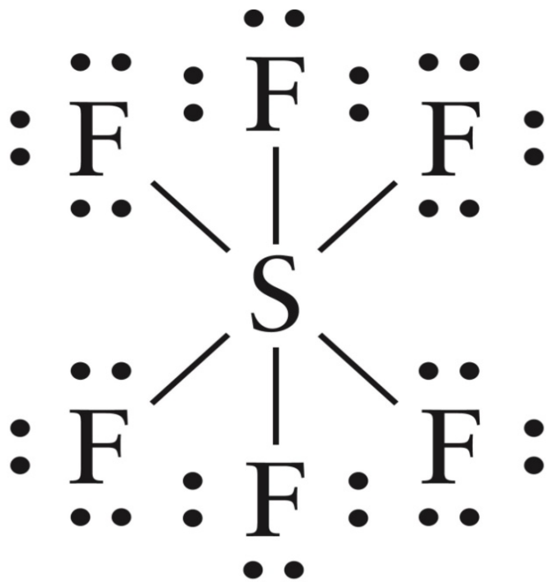
**SOLUTION**

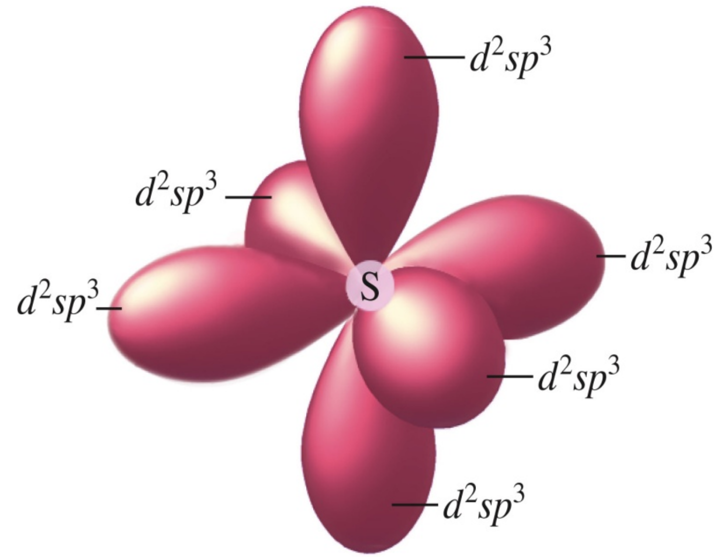


The central iodine atom has five pairs of electrons. A set of five pairs requires a trigonal bipyramidal arrangement, which in turn requires a set of $dsp^3$ orbitals. The outer iodine atoms, have four pairs of electrons, which calls for a tetrahedral arrangement and $sp^3$ hybridization.

Central iodine atom: $dsp^3$ hybridized
Three of these hybrid orbitals hold lone pairs and two of them overlap with $sp^3$ orbitals from the other two iodine atoms to form $\sigma$ bond.

# $d^2sp^3$ Hybridization




The sulfur in $SF_6$ requires an octahedral set of six equivalent $d^2sp^3$ hybrid orbitals in which two d orbitals, one s orbital, and three p orbitals are combined.

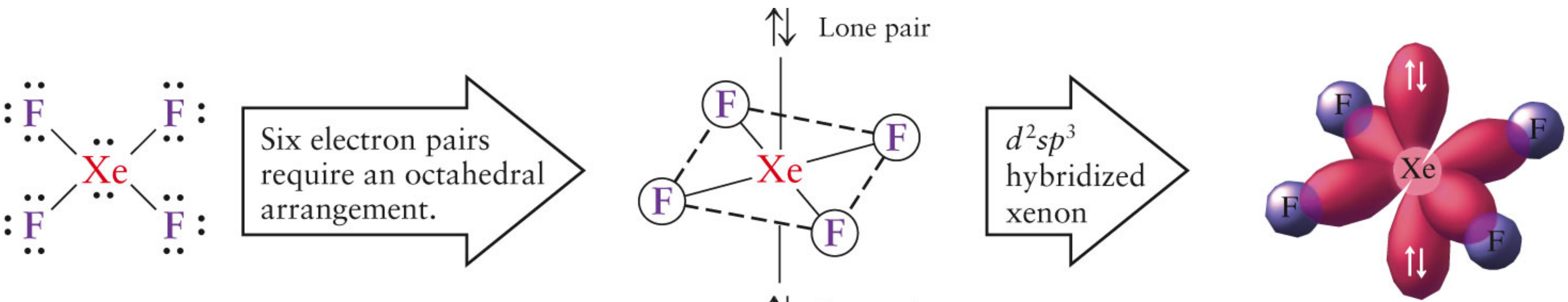
# Hybridization and the Localized Electron Model

**Example 14.4**

How is the xenon atom in $XeF_4$ hybridized?

# Hybridization and the Localized Electron Model

## SOLUTION




Lewis structure

Octahedral arrangement of six electron pairs.

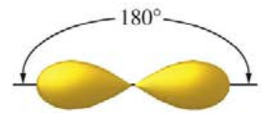
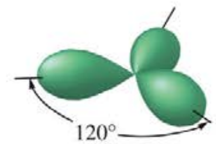
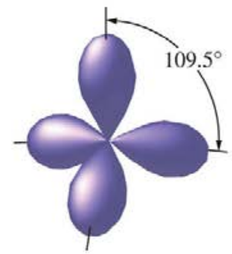
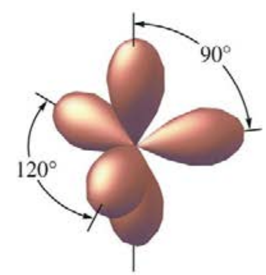
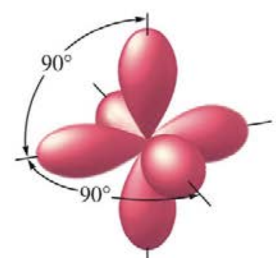
Xenon uses six $d^2sp^3$ hybrid atomic orbitals to bond to the four fluorine atoms and to hold the two lone pairs.

# Hybridization and the Localized Electron Model

**Describing a Molecule with the Localized Electron Model**

1. Draw the Lewis structure(s)
2. Determine the arrangement of electron pairs using the VSEPR model.
3. Specify the hybrid orbitals needed too accommodate the electron pairs.

# Hybridization and the Localized Electron Model

| Number of Effective Pairs | Arrangement of Pairs | | | Hybridization Required |
|---|---|---|---|---|
| 2 | | Linear | *sp* |   |
| 3 |  | Trigonal planar | $sp^2$ |   |
| 4 |  | Tetrahedral | $sp^3$ |   |
| 5 |  | Trigonal bipyramidal | $dsp^3$ |   |
| 6 |  | Octahedral | $d^2sp^3$ |   |

# Hybridization and the Localized Electron Model

**Example 14.5**

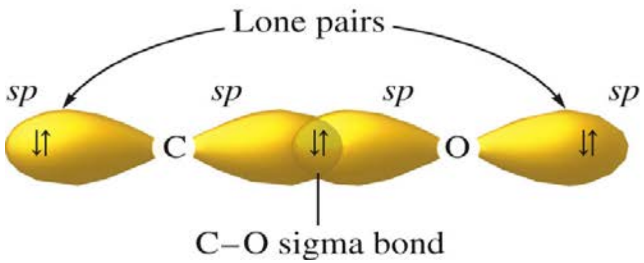
For each of the following molecules or ions, describe the molecular structure, and predict the hybridizarion of each atom.

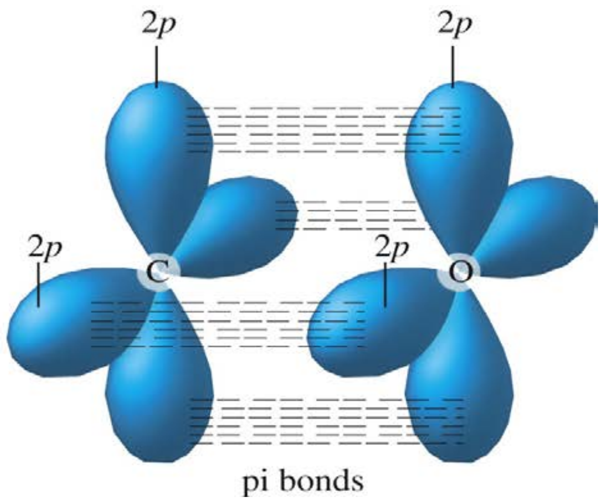
a. $CO$ b. $BF_4^-$ c. $XeF_2$

# Hybridization and the Localized Electron Model

**SOLUTION**

**a.** $:C\equiv O:$

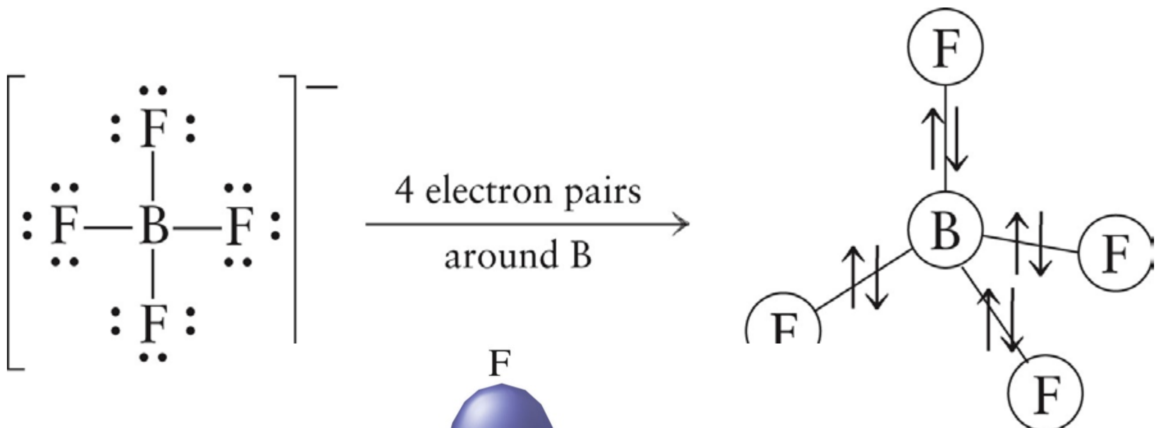


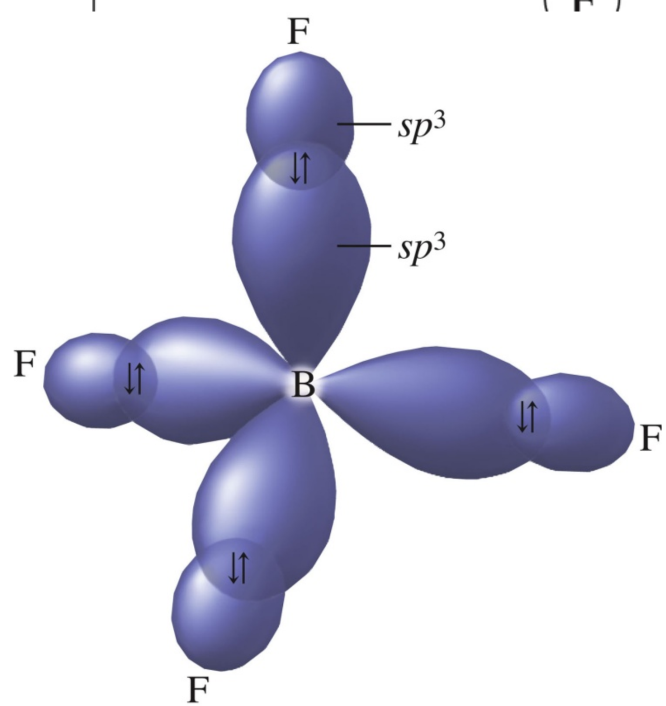



# Hybridization and the Localized Electron Model

**SOLUTION**

**b.**

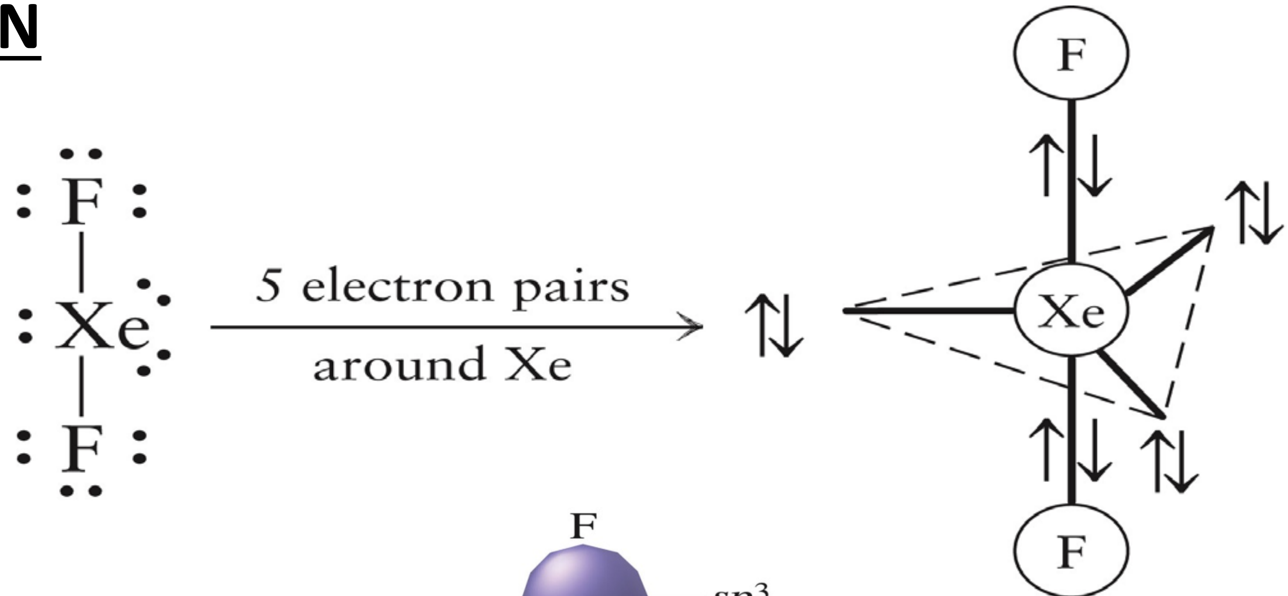


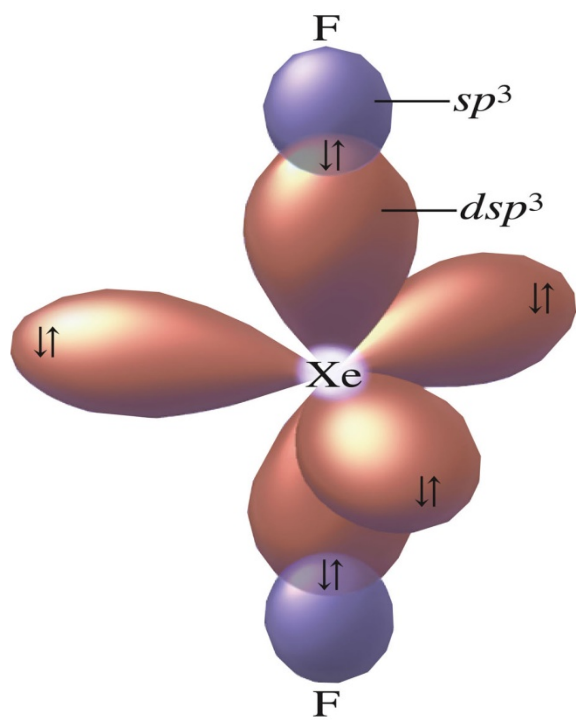



# Hybridization and the Localized Electron Model

**SOLUTION**

c.



# HOMEWORK

**<u>Chap.13:</u> 57-60-79-88-92-99**

**<u>Chap.14:</u> 19-31**

Write Lewis structures that obey the octet rule for each of the following. Except for HCN and $H_2CO$, the first atom listed is the central atom. For HCN and $H_2CO$, carbon is the central atom.

a. HCN
b. $PH_3$
c. $CHCl_3$
d. $NH_4^+$
e. $H_2CO$
f. $SeF_2$
g. $CO_2$
h. $O_2$
i. HBr

# 60

Draw Lewis structures for the following. Show all resonance structures, where applicable. Carbon is the central atom in $OCN^-$ and $SCN^-$.

a. $NO_2^-$, $NO_3^-$, $N_2O_4$($N_2O_4$ exists as $O_2N$—$NO_2$.)

b. $OCN^-$, $SCN^-$, $N_3^-$

# 79

Draw Lewis structures that obey the octet rule for the following species. Assign the formal charge to each central atom.

a) $POCl_3$
b) $SO_4^{2-}$
c) $ClO_4^-$
d) $PO_4^{3-}$
e) $SO_2Cl_2$
f) $XeO_4$
g) $ClO_3^-$
h) $NO_4^{3-}$

# 88

Predict the molecular structure and the bond angles for each of the following.

a. $SeO_3$ b. $SeO_2$ c. $PCl_3$ d. $SCl_2$ e. $SiF_4$

Predict the molecular structure and the bond angles for each of the following.

a. $ICl_5$ b. $XeCl_4$ c. $SeCl_6$

# 99

Draw Lewis structures, predict the molecular structures and indicate which of the following molecules have net dipole moments.

a) $OCl_2$, $KrF_2$, $BeH_2$, $SO_2$

b) $SO_3$, $NF_3$, $IF_3$

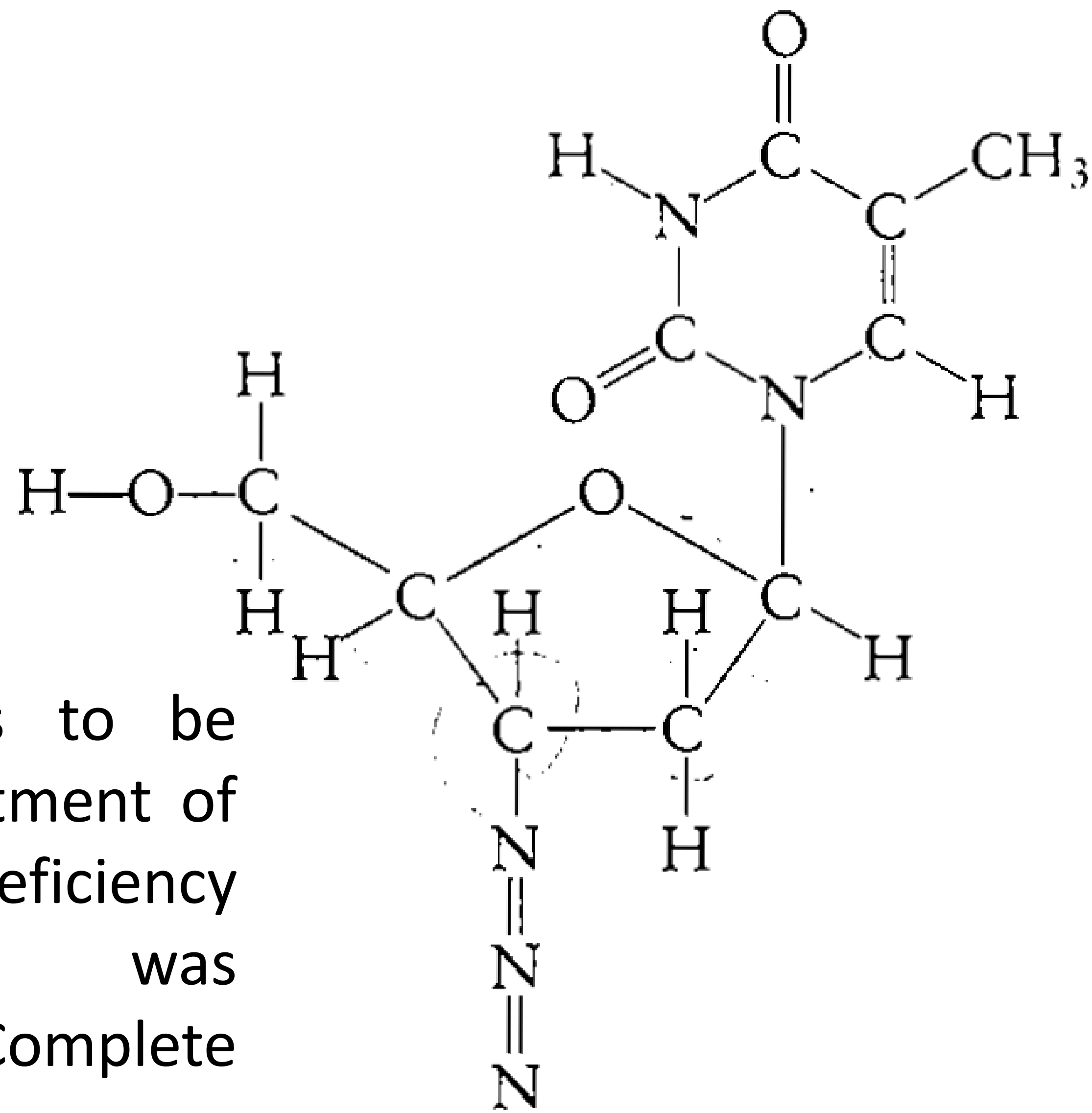
c) $CF_4$, $SeF_4$, $KrF_4$

d) $IF_5$, $AsF_5$

# 19

Give the expected hybridization of the central atom for the molecules or ions in Exercises 57 and 60 from Chapter 13.

# 31




One of the first drugs to be approved for use in treatment of acquired immune deficiency syndrome (AIDS) was azidothymidine (AZT). Complete the Lewis structure of AZT.

a. How many carbon atoms use $sp^3$ hybridization?
b. How many carbon atoms use $sp^2$ hybridization?
c. Which atom is *sp* hybridized?
d. How many $\sigma$ bonds are in the molecule?
e. How many $\pi$ bonds are in the molecule?
f. What is the N—N—N bond angle in the azide (—$N_3$) group?
g. What is the H—O—C bond angle in the side group attached to the five-membered ring?
h. What is the hybridization of the oxygen atom in the —$CH_2OH$ group?