# Chapter 8

# *Bonding:*
# *General Concepts*

# Chapter 8: Bonding and General Concepts Objectives

- Draw Lewis electron dot structures for small molecules and ions.
- Use the VSEPR theory to predict the shapes of simple molecules and ions and to explain the structures of more complex molecules.
- Use electronegativity and formal charge to predict the charge distribution in molecules and ions, to define bond polarity, and to predict molecular polarity.
- Define and predict trends in bond order, bond length and bond enthalpies.
- Distinguish how sigma and pi bonds arise and their consequences.
- Identify the hybridization of an atom in a molecule or ion.

# Chapter 8: Bonding and General Concepts
# Table of Contents

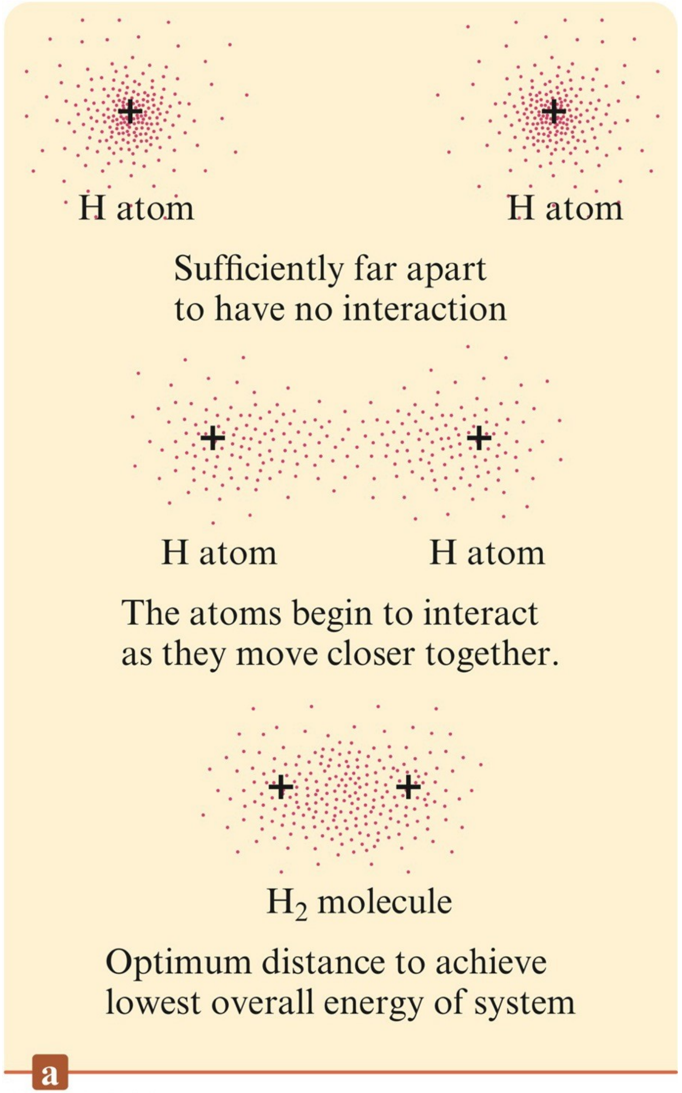
## Questions to Consider

- What is meant by the term “chemical bond”?
- Why do atoms bond with each other to form compounds?
- How do atoms bond with each other to form compounds?

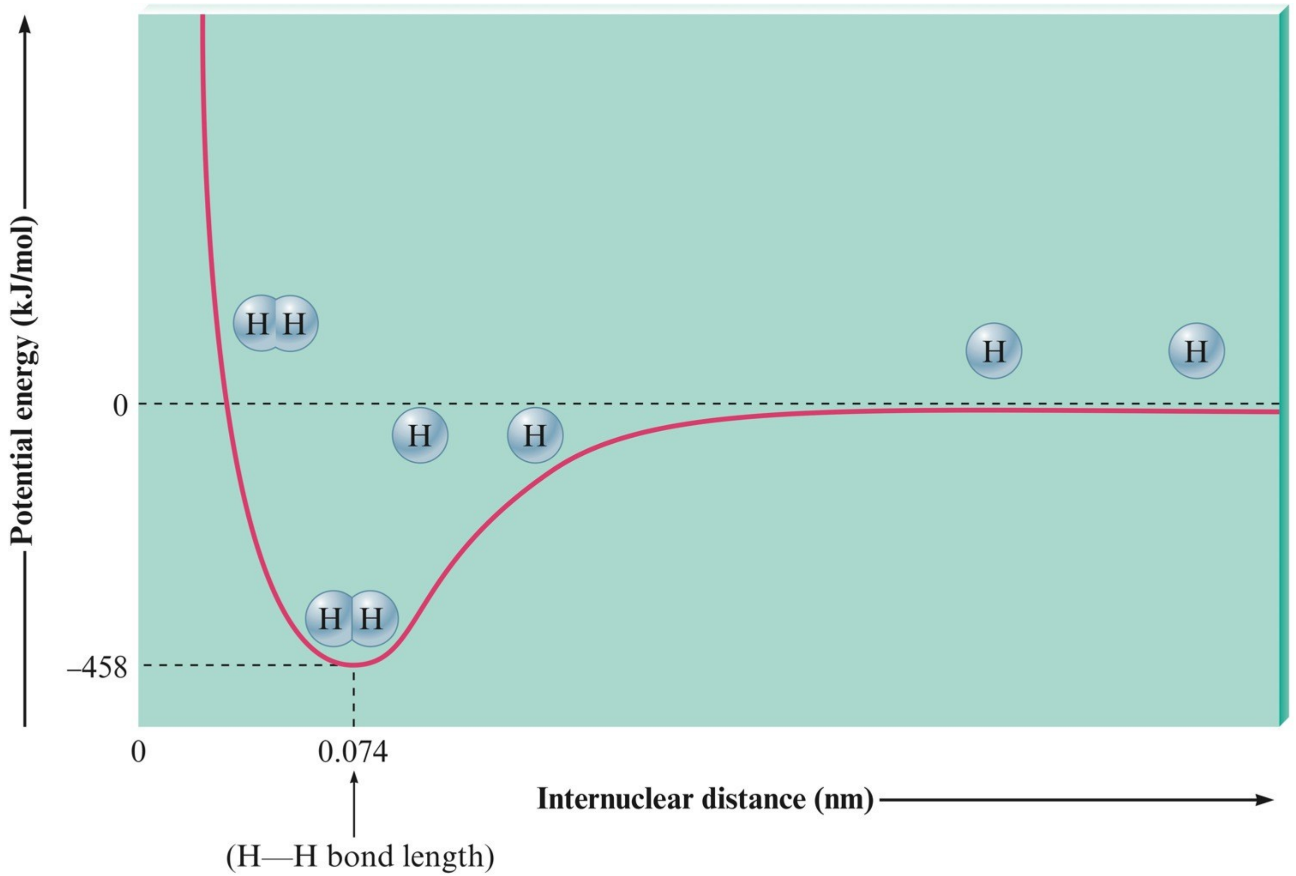
## A Chemical Bond

- No simple, and yet complete, way to define this.
- Forces that hold groups of atoms together and make them function as a unit.
- A bond will form if the energy of the aggregate is lower than that of the separated atoms.

# The Interaction of Two Hydrogen Atoms



# The Interaction of Two Hydrogen Atoms



## Key Ideas in Bonding

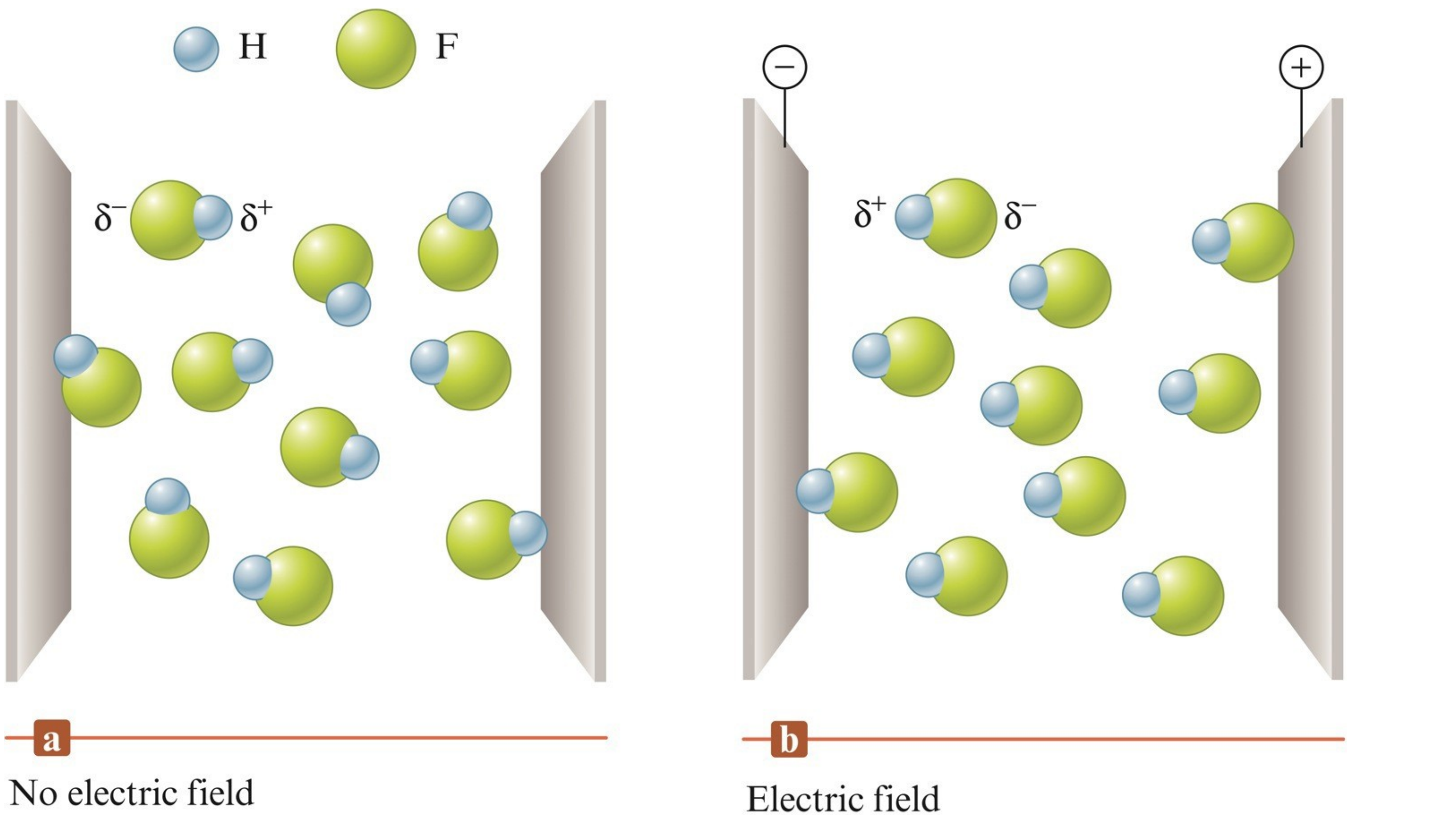
- Ionic Bonding – electrons are transferred
- Covalent Bonding – electrons are shared equally by nuclei
- What about intermediate cases?

## Polar Covalent Bond

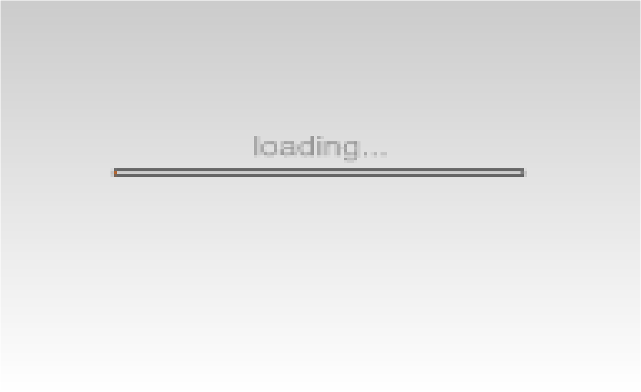
- Unequal sharing of electrons between atoms in a molecule.
- Results in a charge separation in the bond (partial positive and partial negative charge).

## The Effect of an Electric Field on Hydrogen Fluoride Molecules

$\delta^-$ or $\delta^+$ indicates a positive or negative fractional charge.



# Polar Molecules

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## CONCEPT CHECK!

What is meant by the term “chemical bond?”

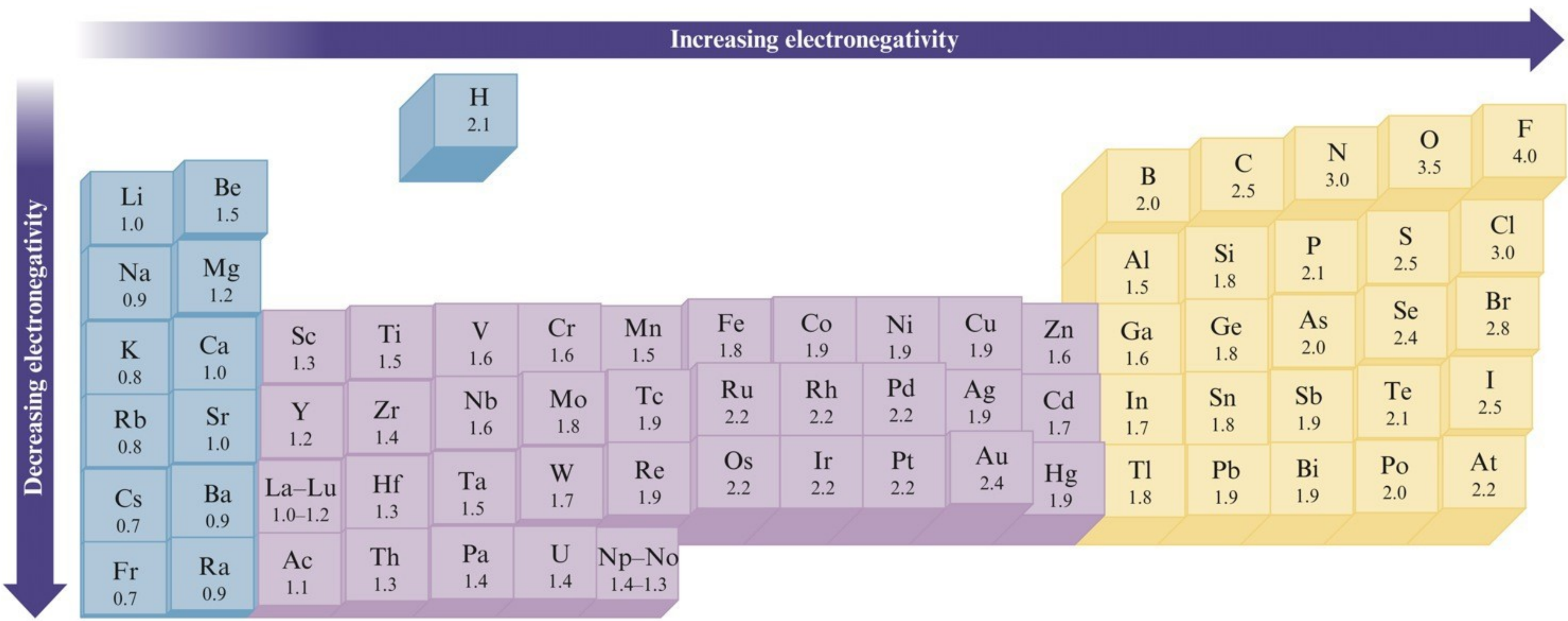
Why do atoms bond with each other to form molecules?

How do atoms bond with each other to form molecules?

- The ability of an atom in a molecule to attract shared electrons to itself.
- For a molecule HX, the relative electronegativities of the H and X atoms are determined by comparing the measured H–X bond energy with the "expected" H–X bond energy.

- On the periodic table, electronegativity generally increases across a period and decreases down a group.
- The range of electronegativity values is from 4.0 for fluorine (the most electronegative) to 0.7 for cesium (the least electronegative).

# The Pauling Electronegativity Values



**CONCEPT CHECK!**

If lithium and fluorine react, which has more attraction for an electron? Why?

In a bond between fluorine and iodine, which has more attraction for an electron? Why?

## CONCEPT CHECK!

What is the general trend for electronegativity across rows and down columns on the periodic table?

Explain the trend.

## Table 8.1 | The Relationship Between Electronegativity and Bond Type

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

**EXERCISE!**

Arrange the following bonds from most to least polar:

a) N–F O–F C–F
b) C–F N–O Si–F
c) Cl–Cl B–Cl S–Cl

a) C–F, N–F, O–F
b) Si–F, C–F, N–O
c) B–Cl, S–Cl, Cl–Cl

**CONCEPT CHECK!**

Which of the following bonds would be the least polar yet still be considered polar covalent?

Mg–O C–O O–O Si–O **N–O**

## CONCEPT CHECK!

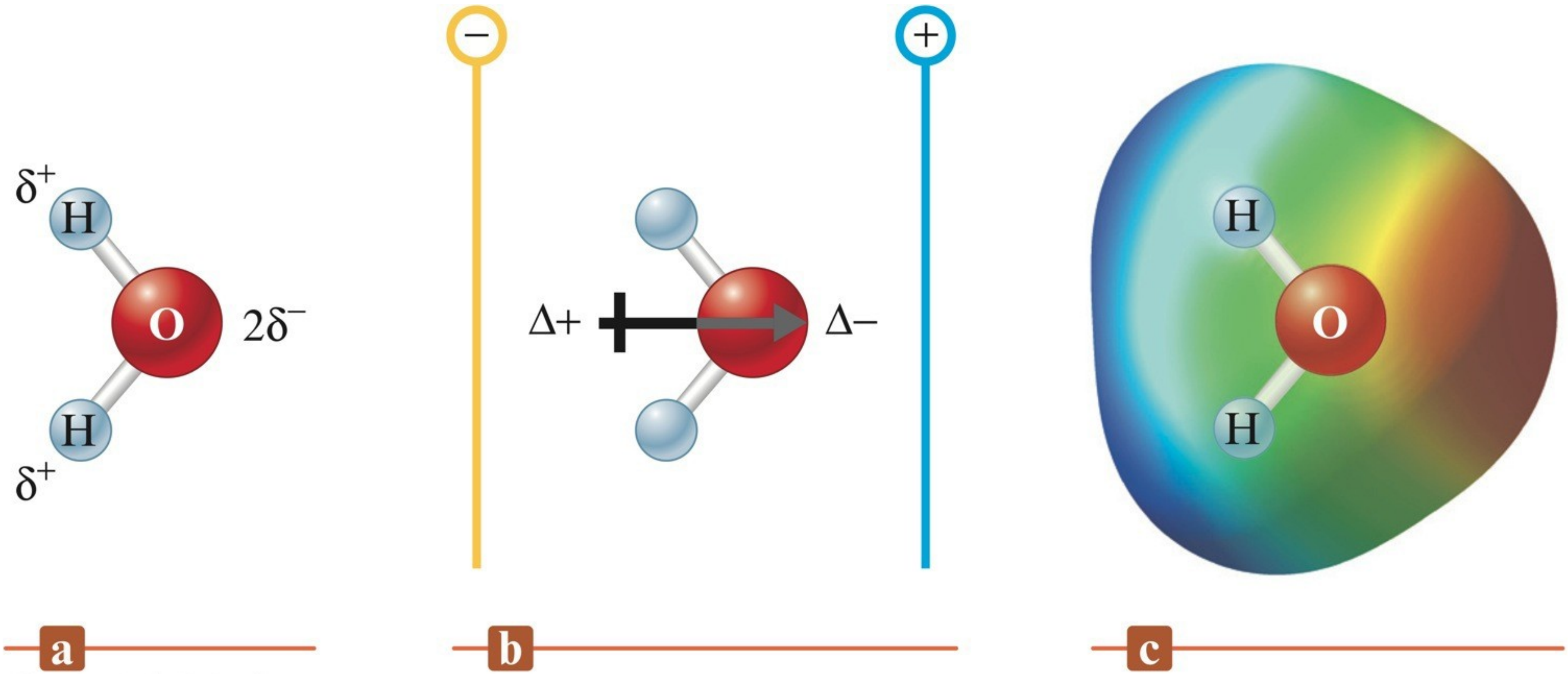
Which of the following bonds would be the most polar without being considered ionic?

Mg–O C–O O–O Si–O N–O

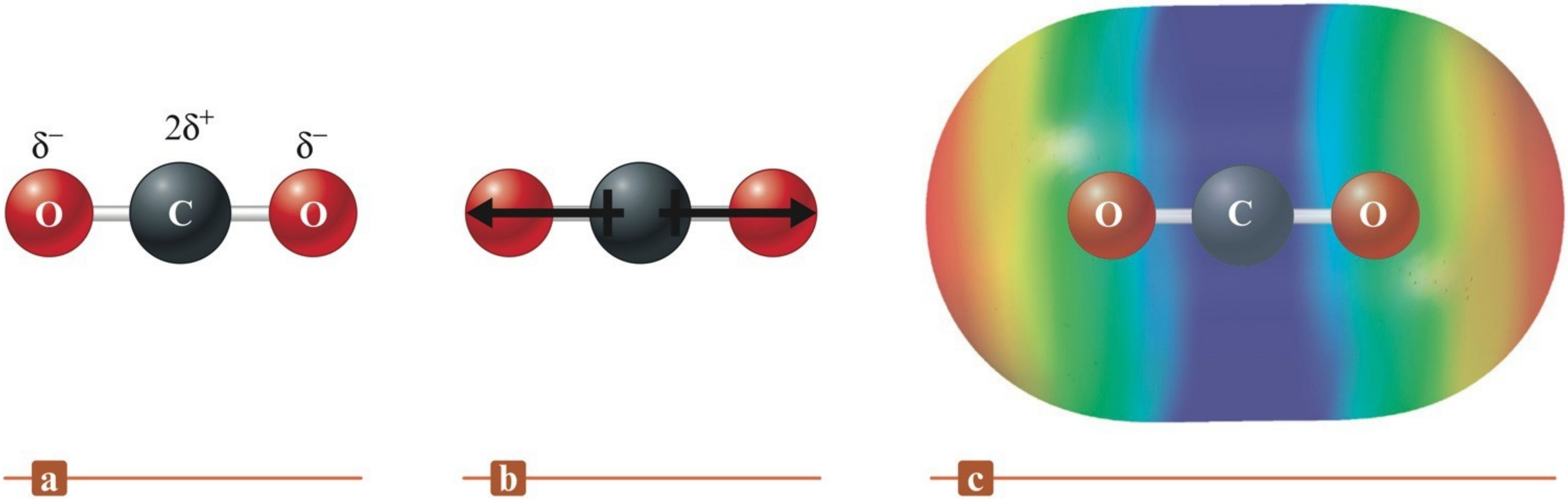
## Dipole Moment

- Property of a molecule whose charge distribution can be represented by a center of positive charge and a center of negative charge.
- Use an arrow to represent a dipole moment.
  - Point to the negative charge center with the tail of the arrow indicating the positive center of charge.

# Dipole Moment



# No Net Dipole Moment (Dipoles Cancel)



## Stable Compounds

- Atoms in stable compounds usually have a noble gas electron configuration.

## Electron Configurations in Stable Compounds

- When *two nonmetals* react to form a covalent bond, they share electrons in a way that completes the valence electron configurations of both atoms.
- When a *nonmetal and a representative-group metal* react to form a binary ionic compound, the ions form so that the valence electron configuration of the nonmetal achieves the electron configuration of the next noble gas atom. The valence orbitals of the metal are emptied.

## Isoelectronic Series

- A series of ions/atoms containing the same number of electrons.

$O^{2-}$, $F^{-}$, Ne, $Na^{+}$, $Mg^{2+}$, and $Al^{3+}$

## Ionic Radii

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## CONCEPT CHECK!

Choose an alkali metal, an alkaline earth metal, a noble gas, and a halogen so that they constitute an isoelectronic series when the metals and halogen are written as their most stable ions.

- What is the electron configuration for each species?
- Determine the number of electrons for each species.
- Determine the number of protons for each species.

## Periodic Table Allows Us to Predict Many Properties

- Trends for:
  - Atomic size, ion radius, ionization energy, electronegativity
- Electron configurations
- Formula prediction for ionic compounds
- Covalent bond polarity ranking

- What are the factors that influence the stability and the structures of solid binary ionic compounds?
- How strongly the ions attract each other in the solid state is indicated by the lattice energy.

## Lattice Energy

- The change in energy that takes place when separated gaseous ions are packed together to form an ionic solid.

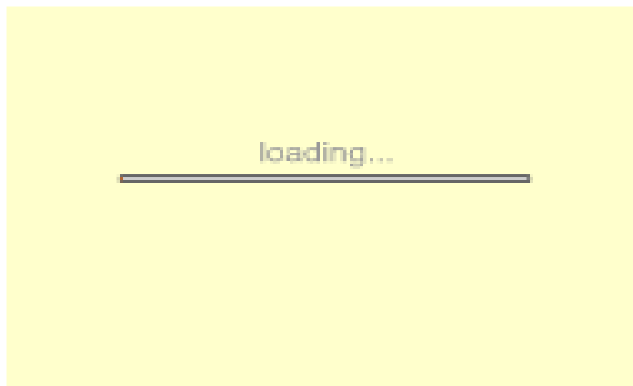
$$\text{Lattice energy} = k\left(\frac{Q_1 Q_2}{r}\right)$$

*k* = proportionality constant

$Q_1$ and $Q_2$ = charges on the ions

*r* = shortest distance between the centers of the cations and anions

# Born-Haber Cycle for NaCl

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## Formation of an Ionic Solid

Sublimation of the solid metal.

- $M(s) \rightarrow M(g)$ [endothermic]

Ionization of the metal atoms.

- $M(g) \rightarrow M^{+}(g) + e^{-}$ [endothermic]

Dissociation of the nonmetal.

- $^{1}/_{2}X_2(g) \rightarrow X(g)$ [endothermic]

## Formation of an Ionic Solid (continued)

Formation of nonmetal ions in the gas phase.

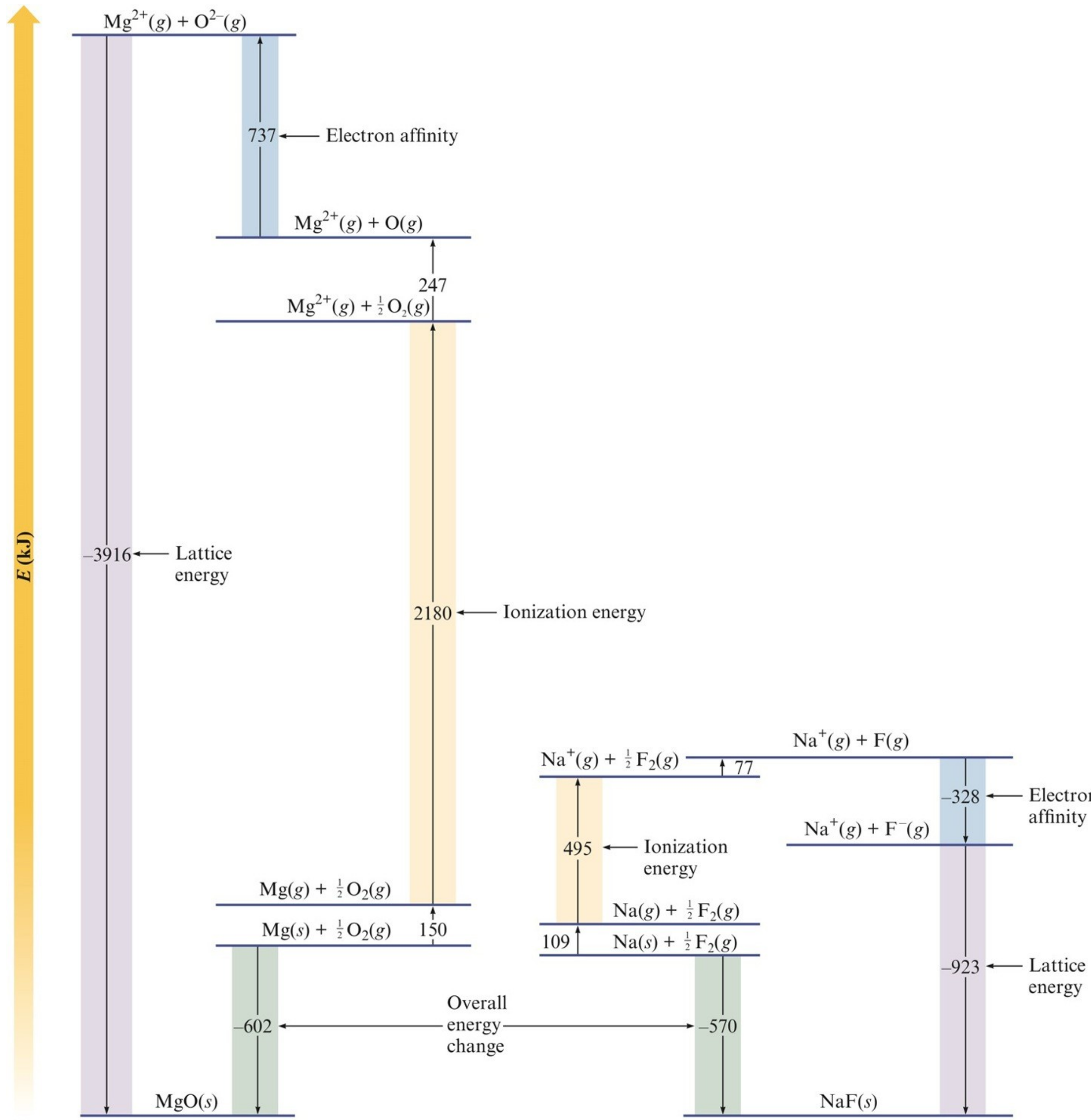
- $X(g) + e^- \rightarrow X^-(g)$ [exothermic]

Formation of the solid ionic compound.

- $M^+(g) + X^-(g) \rightarrow MX(s)$

  [quite exothermic]

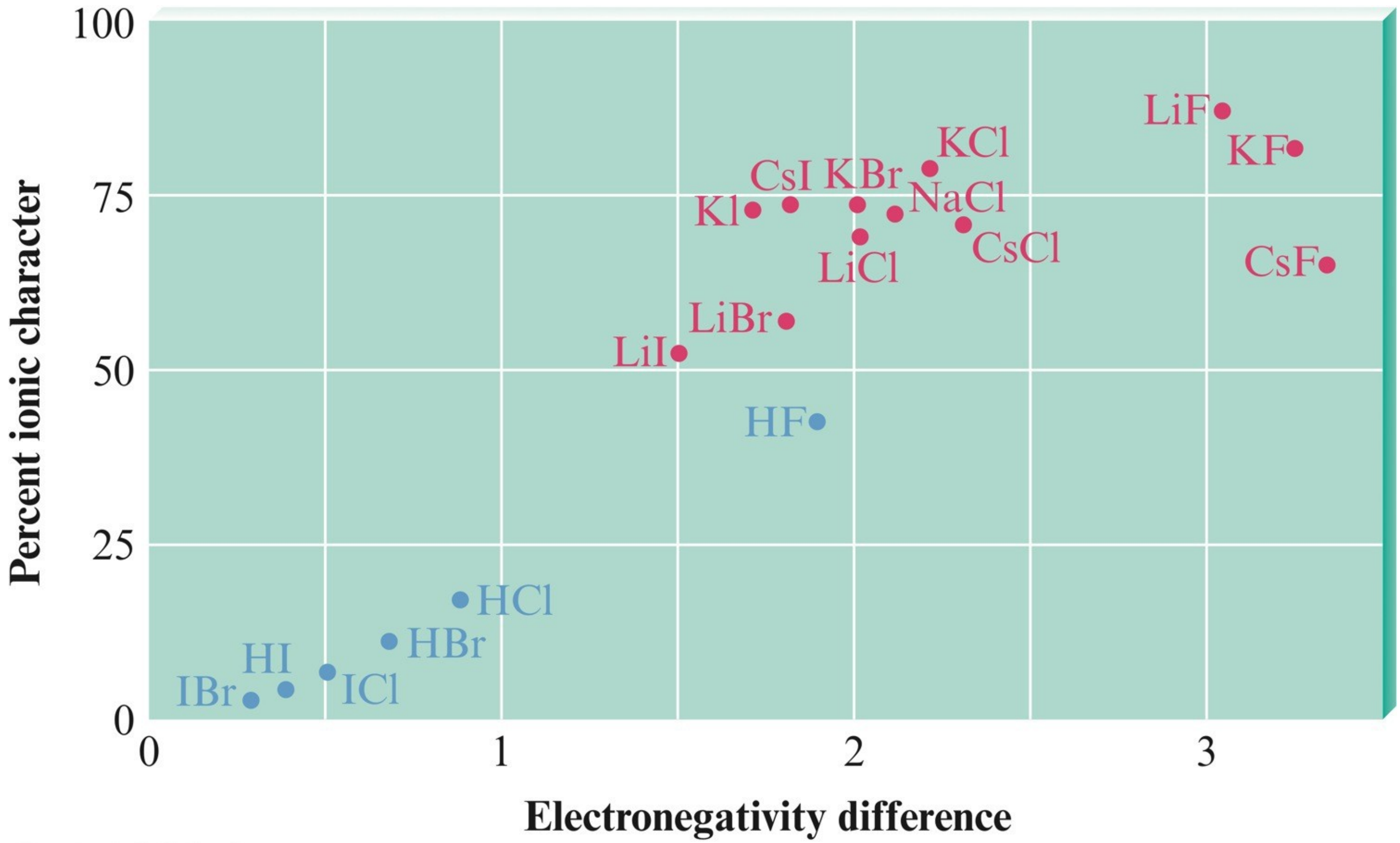
## Comparing Energy Changes



- No bonds reach 100% ionic character even with compounds that have the maximum possible electronegativity difference.

$$\% \text{ ionic character of a bond} = \left( \frac{\text{measured dipole moment of X} - \text{Y}}{\text{calculated dipole moment of X}^{+}\text{Y}^{-}} \right) \times 100\%$$

The relationship between the ionic character of a covalent bond and the electronegativity difference of the bonded atoms



## Operational Definition of Ionic Compound

- Any compound that conducts an electric current when melted will be classified as ionic.

## Models

- Models are attempts to explain how nature operates on the microscopic level based on experiences in the macroscopic world.

## Fundamental Properties of Models

1. A model does not equal reality.
2. Models are oversimplifications, and are therefore often wrong.
3. Models become more complicated and are modified as they age.
4. We must understand the underlying assumptions in a model so that we don’t misuse it.
5. When a model is wrong, we often learn much more than when it is right.

## Bond Energies

- To break bonds, energy must be *added* to the system (endothermic, energy term carries a positive sign).
- To form bonds, energy is *released* (exothermic, energy term carries a negative sign).

## Bond Energies

$$\Delta H = \Sigma n \times D(\text{bonds broken}) - \Sigma n \times D(\text{bonds formed})$$

*D* represents the bond energy per mole of bonds (always has a positive sign).

**CONCEPT CHECK!**

Predict $\Delta H$ for the following reaction:

$$CH_3N\equiv C(g) \rightarrow CH_3C\equiv N(g)$$

Given the following information:

| | **Bond Energy (kJ/mol)** |
|---|---|
| C–H | 413 |
| C–N | 305 |
| C–C | 347 |
| $C\equiv N$ | 891 |

$\Delta H = -42$ kJ

# Localized Electron Model

- A molecule is composed of atoms that are bound together by sharing pairs of electrons using the atomic orbitals of the bound atoms.

## Localized Electron Model

- Electron pairs are assumed to be localized on a particular atom or in the space between two atoms:
  - *Lone pairs* – pairs of electrons localized on an atom
  - *Bonding pairs* – pairs of electrons found in the space between the atoms

## Localized Electron Model

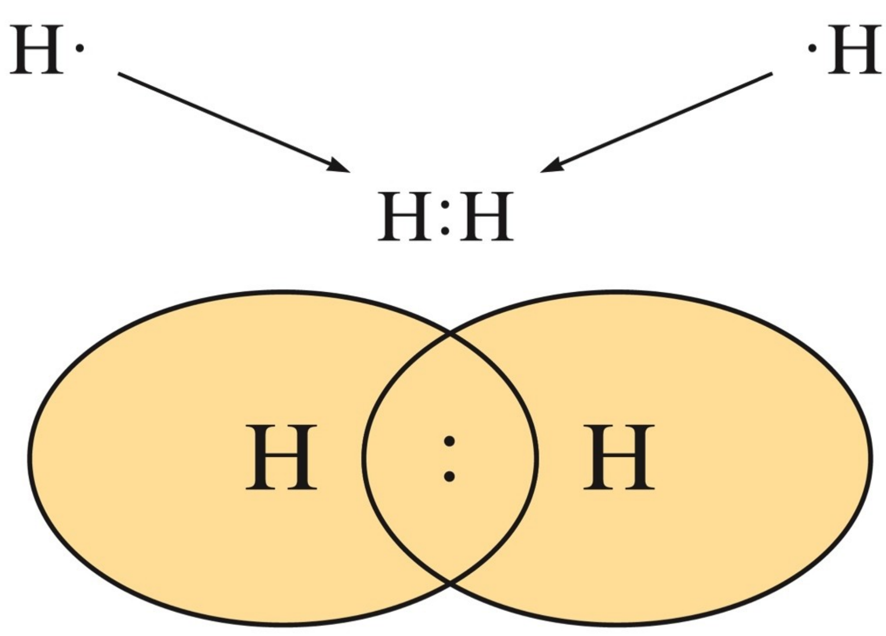
1. Description of valence electron arrangement (Lewis structure).
2. Prediction of geometry (VSEPR model).
3. Description of atomic orbital types used by atoms to share electrons or hold lone pairs.

## Lewis Structure

- Shows how valence electrons are arranged among atoms in a molecule.
- Reflects central idea that stability of a compound relates to noble gas electron configuration.

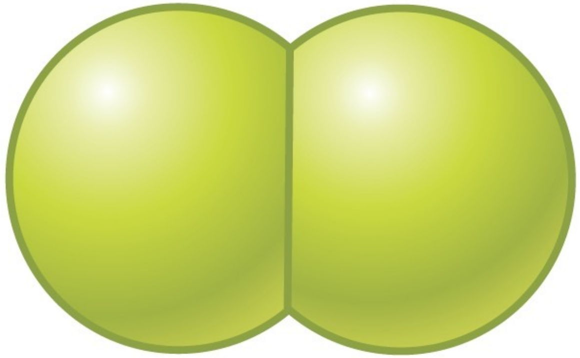
## Duet Rule

- Hydrogen forms stable molecules where it shares two electrons.



## Octet Rule

- Elements form stable molecules when surrounded by eight electrons.



$F_2$

## Single Covalent Bond

- A covalent bond in which two atoms share one pair of electrons.

H–H

## Double Covalent Bond

- A covalent bond in which two atoms share two pairs of electrons.

O=C=O

## Triple Covalent Bond

- A covalent bond in which two atoms share three pairs of electrons.

$$N \equiv N$$

## 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. Atoms usually have noble gas configurations. Arrange the remaining electrons to satisfy the octet rule (or duet rule for hydrogen).

## Steps for Writing Lewis Structures

1. Sum the valence electrons from all the atoms. (Use the periodic table.)

Example: $H_2O$

$2\ (1\ e^-) + 6\ e^- = 8\ e^-$ total

## Steps for Writing Lewis Structures

2. Use a pair of electrons to form a bond between each pair of bound atoms.

   Example: $H_2O$

$$\mathrm{H{-}O{-}H}$$

## Steps for Writing Lewis Structures

3. Atoms usually have noble gas configurations. Arrange the remaining electrons to satisfy the octet rule (or duet rule for hydrogen).

Examples: $H_2O$, $PBr_3$, and HCN

## CONCEPT CHECK!

Draw a Lewis structure for each of the following molecules:

$H_2$
$F_2$
HF

**CONCEPT CHECK!**

Draw a Lewis structure for each of the following molecules:

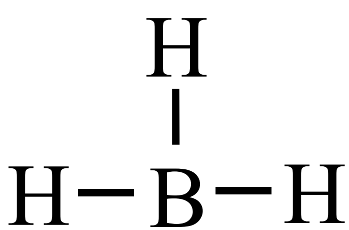
$NH_3$

$CO_2$

$CCl_4$

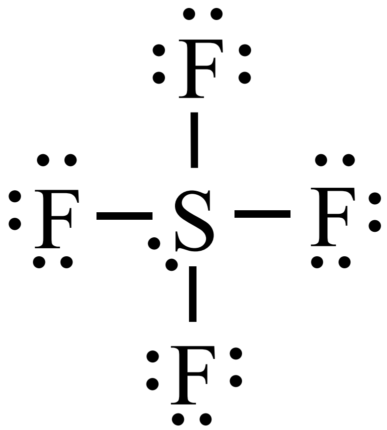
- Boron tends to form compounds in which the boron atom has fewer than eight electrons around it (it does not have a complete octet).

$BH_3 = 6e^-$

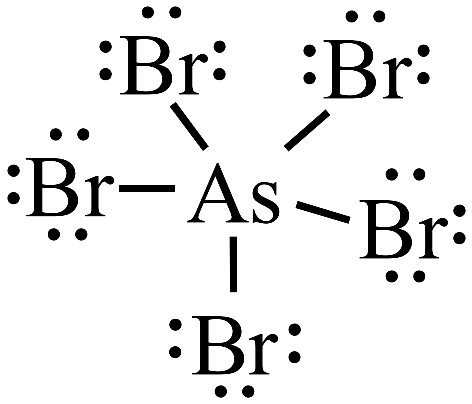


- When it is necessary to exceed the octet rule for one of several third-row (or higher) elements, place the extra electrons on the central atom.

$SF_4 = 34e^-$




$AsBr_5 = 40e^-$



**CONCEPT CHECK!**

Draw a Lewis structure for each of the following molecules:

$BF_3$

$PCl_5$

$SF_6$

## Let's Review

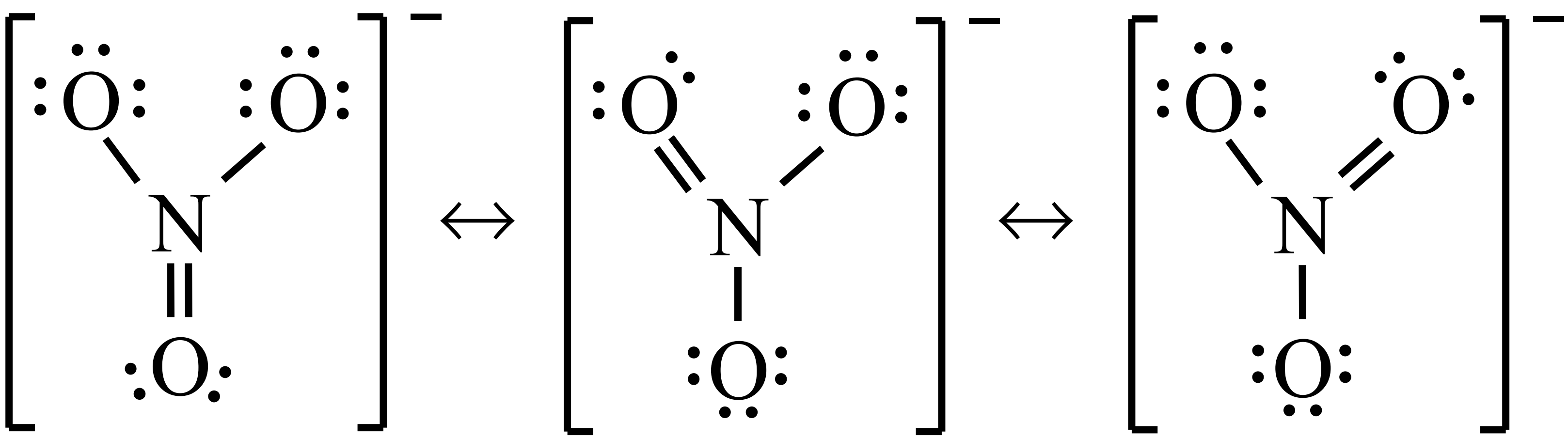
- C, N, O, and F should always be assumed to obey the octet rule.
- B and Be often have fewer than 8 electrons around them in their compounds.
- Second-row elements never exceed the octet rule.
- Third-row and heavier elements often satisfy the octet rule but can exceed the octet rule by using their empty valence *d* orbitals.

## Let's Review

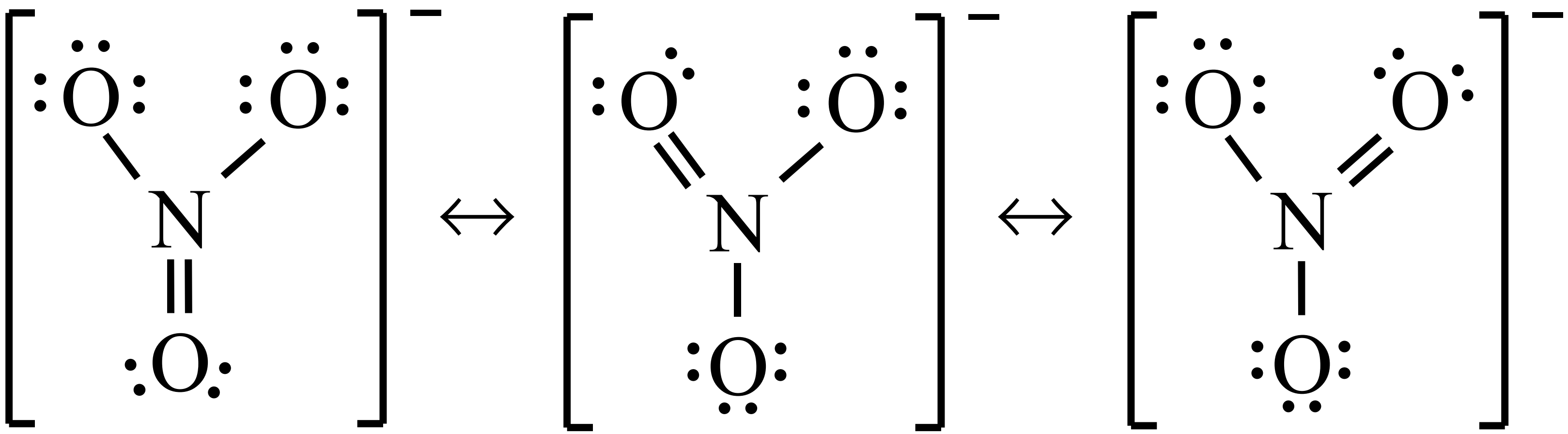
- When writing the Lewis structure for a molecule, satisfy the octet rule for the atoms first. If electrons remain after the octet rule has been satisfied, then place them on the elements having available *d* orbitals (elements in Period 3 or beyond).

- More than one valid Lewis structure can be written for a particular molecule.

$NO_3^- = 24e^-$



- Actual structure is an average of the resonance structures.
- Electrons are really delocalized – they can move around the entire molecule.



**CONCEPT CHECK!**

Draw a Lewis structure for each of the following molecules:

$CO$ $CO_2$

$CH_3OH$ $OCN^-$

## Formal Charge

- Used to evaluate nonequivalent 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.

## Formal Charge

- Formal charge = (# valence $e^-$ on free neutral atom) – (# valence $e^-$ assigned to the atom in the molecule).
- Assume:
  - Lone pair electrons belong entirely to the atom in question.
  - Shared electrons are divided equally between the two sharing 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.
  2. Subtract the number of assigned electrons from the number of valence electrons on the free, neutral atom.

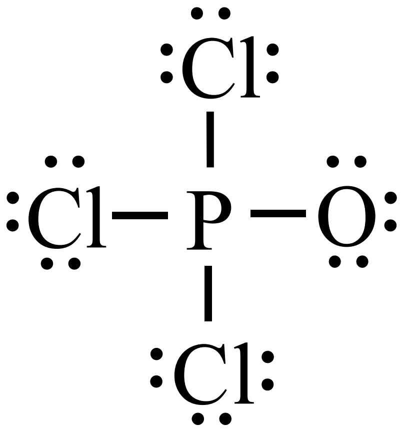
## CONCEPT CHECK!

Consider the Lewis structure for $POCl_3$. Assign the formal charge for each atom in the molecule.

P: 5 – 4 = +1

O: 6 – 7 = –1

Cl: 7 – 7 = 0

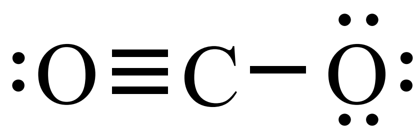


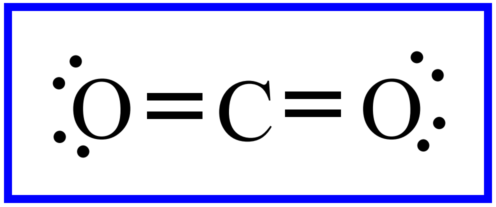
## Rules Governing Formal Charge

- The sum of the formal charges of all atoms in a given molecule or ion must equal the overall charge on that species.

## Rules Governing Formal Charge

- If nonequivalent Lewis structures exist for a species, those 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.





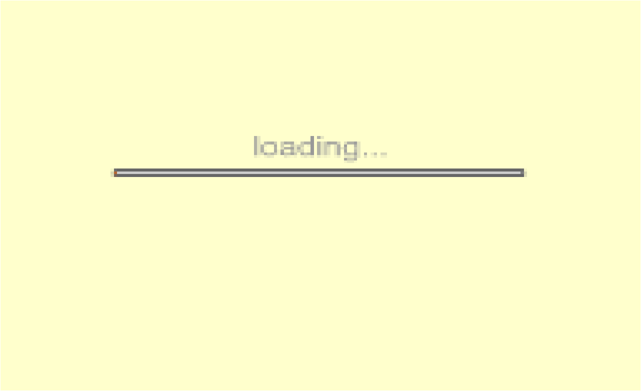
## VSEPR Model

- VSEPR: Valence Shell Electron-Pair Repulsion.
- The structure around a given atom is determined principally by minimizing electron pair repulsions.

## 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 (put the pairs as far apart as possible.
3. Determine the positions of the atoms from the way electron pairs are shared (how electrons are shared between the central atom and surrounding atoms).
4. Determine the name of the molecular structure from positions of the atoms.

# VSEPR

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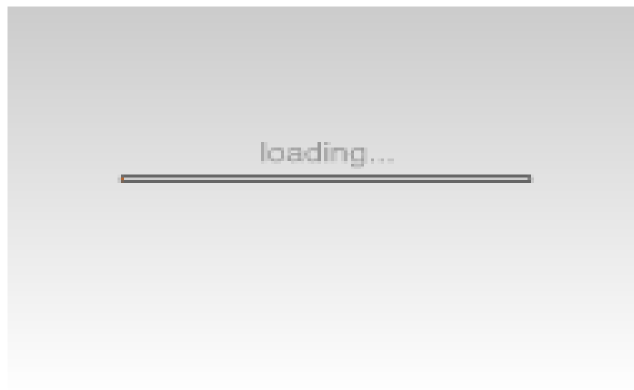
# VSEPR: Two Electron Pairs

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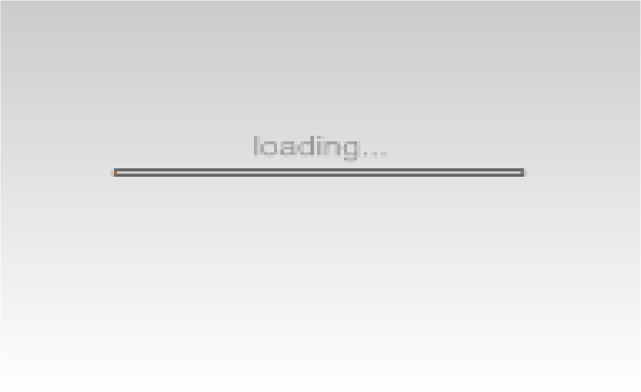
# VSEPR: Three Electron Pairs

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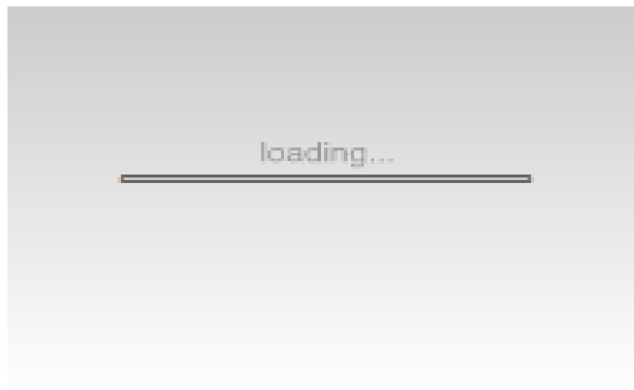
## VSEPR: Four Electron Pairs

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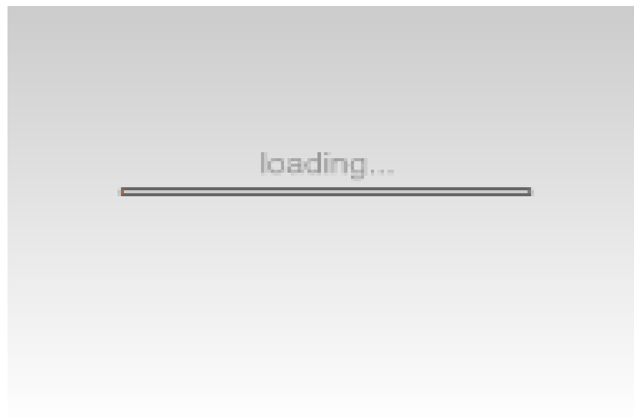
# VSEPR: Iodine Pentafluoride

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**CONCEPT CHECK!**

Determine the shape for each of the following molecules, and include bond angles:

HCN

$PH_3$

$SF_4$

HCN – linear, $180^0$

$PH_3$ – trigonal pyramid, $109.5^0$ ($107^0$)

$SF_4$ – see saw, $90^0$, $120^0$

## CONCEPT CHECK!

Determine the shape for each of the following molecules, and include bond angles:

$O_3$

$KrF_4$

$O_3$ – bent, $120^{0}$

$KrF_4$ – square planar, $90^{0}$, $180^{0}$

## CONCEPT CHECK!

True or false:

A molecule that has polar bonds will always be polar.

-If true, explain why.

-If false, provide a counter-example.

## *Let's Think About It*

- Draw the Lewis structure for $CO_2$.
- Does $CO_2$ contain polar bonds?
- Is the molecule polar or nonpolar overall? Why?

**CONCEPT CHECK!**

True or false:

Lone pairs make a molecule polar.

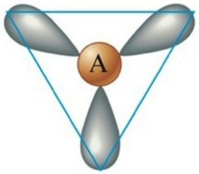
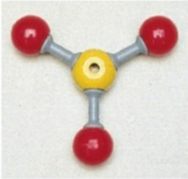
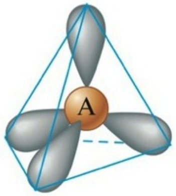
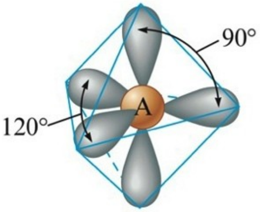
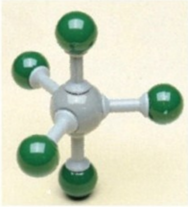
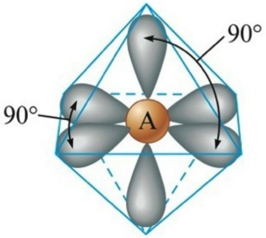
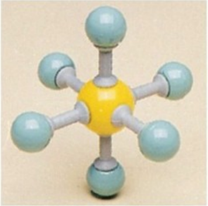
-If true, explain why.

-If false, provide a counter-example.

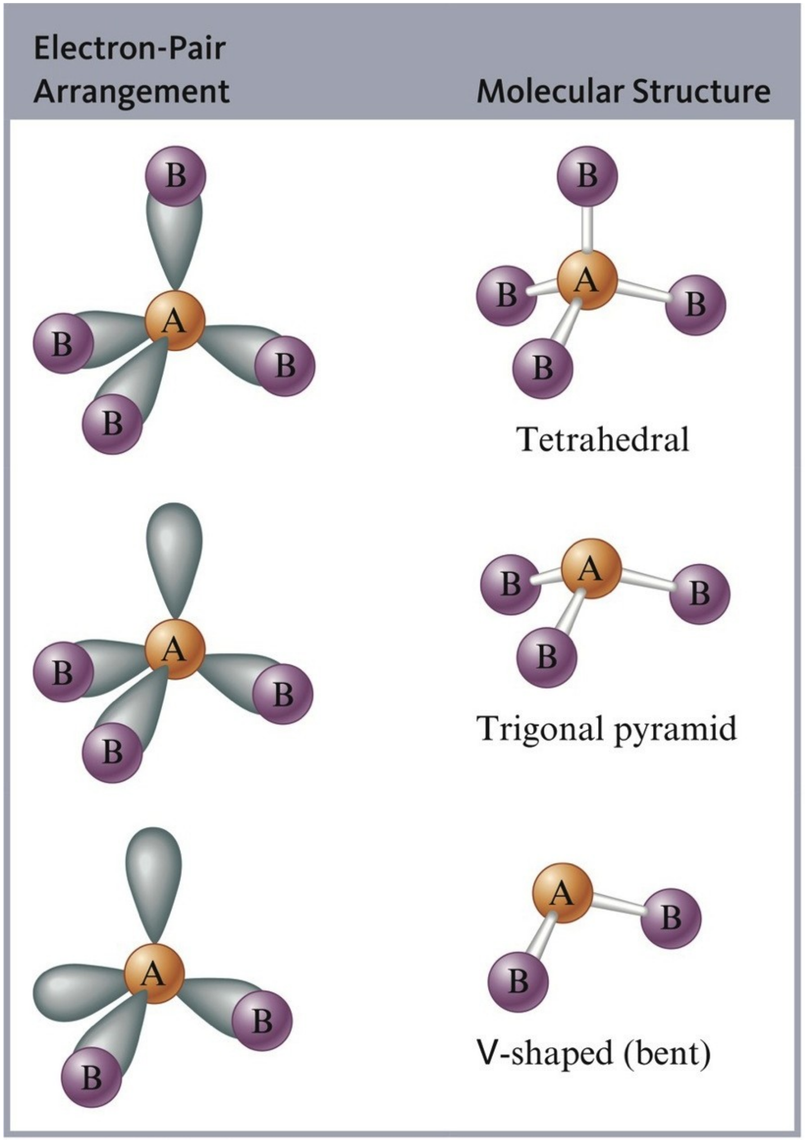
## *Let's Think About It*

- Draw the Lewis structure for $XeF_4$.
- Does $XeF_4$ contain lone pairs?
- Is the molecule polar or nonpolar overall? Why?

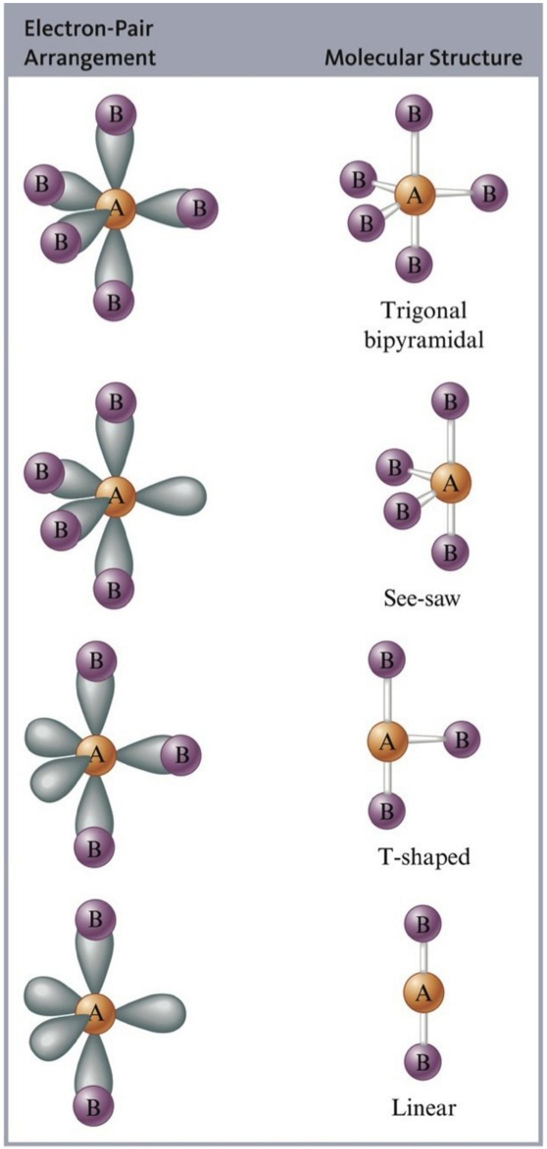
# Arrangements of Electron Pairs Around an Atom Yielding Minimum Repulsion

| Number of Electron Pairs | Arrangement of Electron Pairs | | Example |
|---|---|---|---|
| 2 | Linear |  |  |
| 3 | Trigonal planar |  |  |
| 4 | Tetrahedral |  |  |
| 5 | Trigonal bipyramidal |  |  |
| 6 | Octahedral |  |  |

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



## Structures of Molecules with Five Electron Pairs Around the Central Atom



## *EXERCISE!*

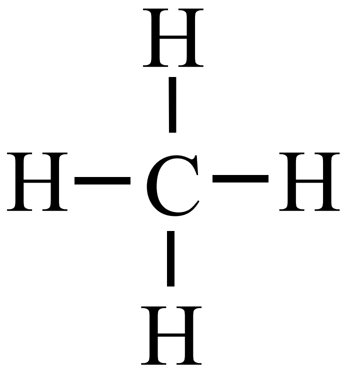
Draw the Lewis structure for methane, $CH_4$.

- What is the shape of a methane molecule?

  tetrahedral

- What are the bond angles?

  $109.5^{0}$



**CONCEPT CHECK!**

What is the valence electron configuration of a carbon atom?

$s^2p^2$

Why can't the bonding orbitals for methane be formed by an overlap of atomic orbitals?

## Bonding in Methane

- Assume that the carbon atom has four equivalent atomic orbitals, arranged tetrahedrally.

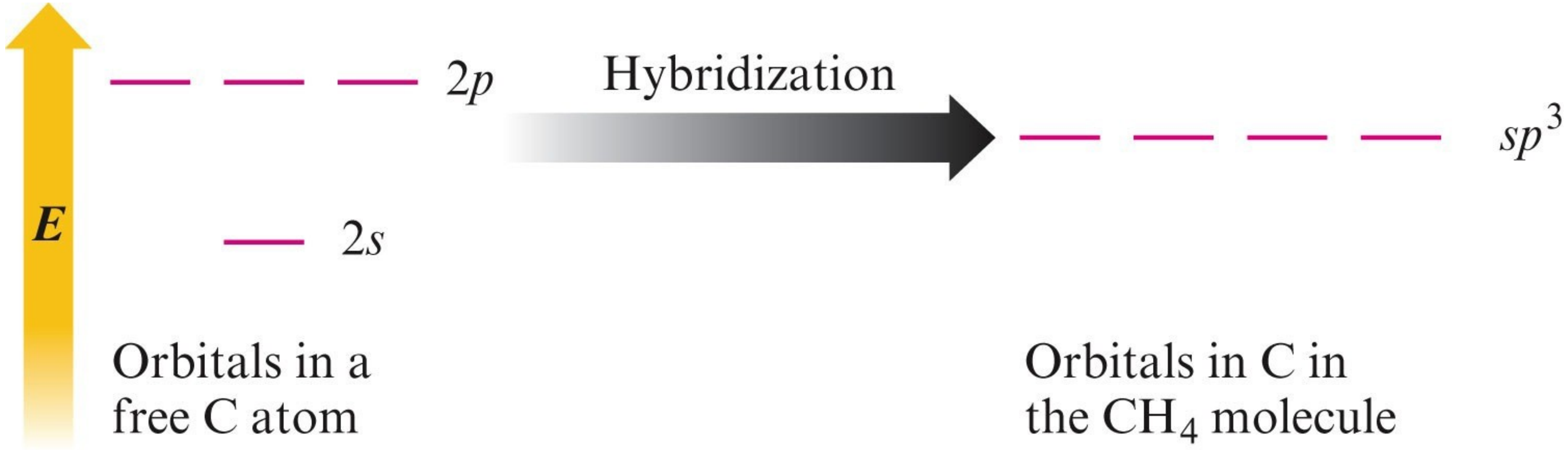
## Hybridization

- Mixing of the native atomic orbitals to form special orbitals for bonding.

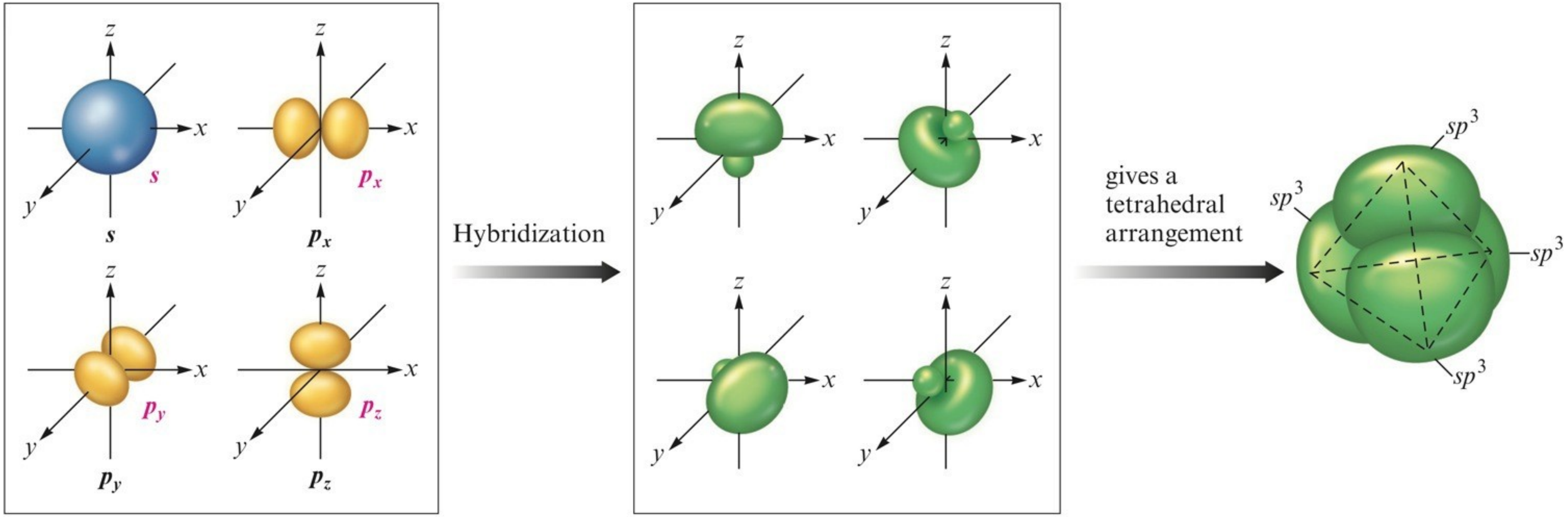
## *sp*³ Hybridization

- Combination of one *s* and three *p* orbitals.
- Whenever a set of equivalent tetrahedral atomic orbitals is required by an atom, the localized electron model assumes that the atom adopts a set of $sp^3$ orbitals; the atom becomes $sp^3$ hybridized.
- The four orbitals are identical in shape.

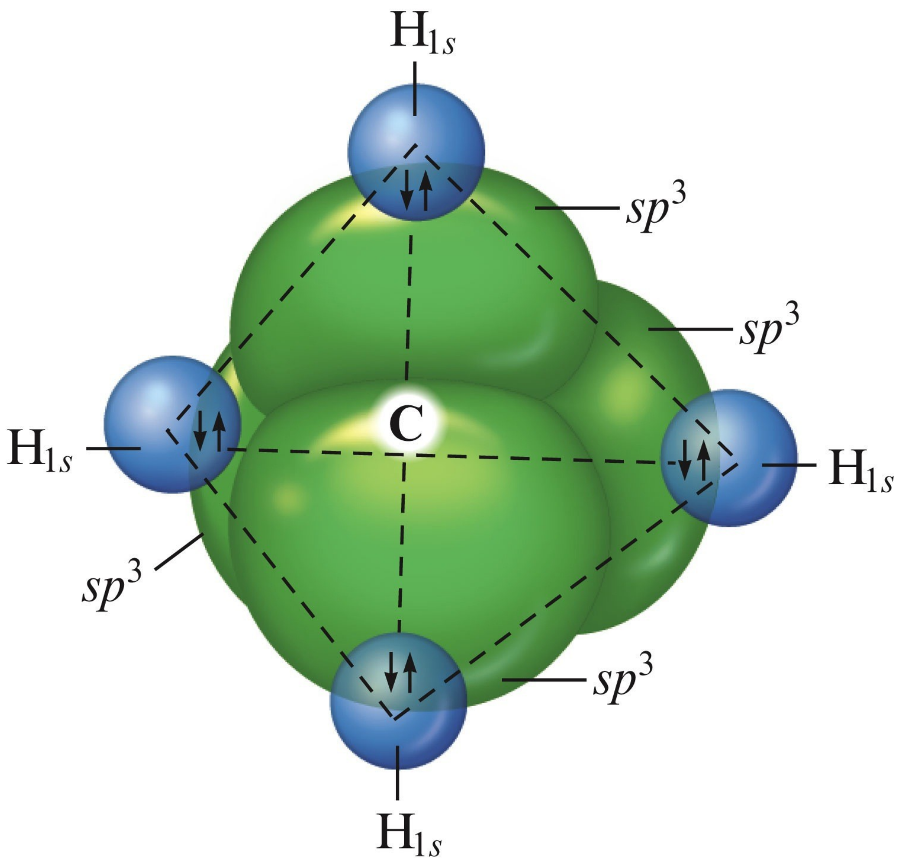
## An Energy-Level Diagram Showing the Formation of Four *sp³* Orbitals



## The Formation of *sp*³ Hybrid Orbitals



# Tetrahedral Set of Four *sp*³ Orbitals



**EXERCISE!**

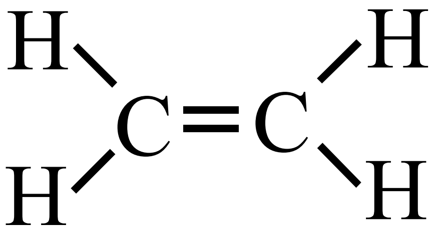
Draw the Lewis structure for $C_2H_4$ (ethylene)?

- What is the shape of an ethylene molecule?

  trigonal planar around each carbon atom

- What are the approximate bond angles around the carbon atoms?

  $120^0$



**CONCEPT CHECK!**

Why can't *sp*$^3$ hybridization account for the ethylene molecule?

## *sp*$^2$ Hybridization

- Combination of one *s* and two *p* orbitals.
- Gives a trigonal planar arrangement of atomic orbitals.
- One *p* orbital is not used.
  - Oriented perpendicular to the plane of the *sp*$^2$ orbitals.

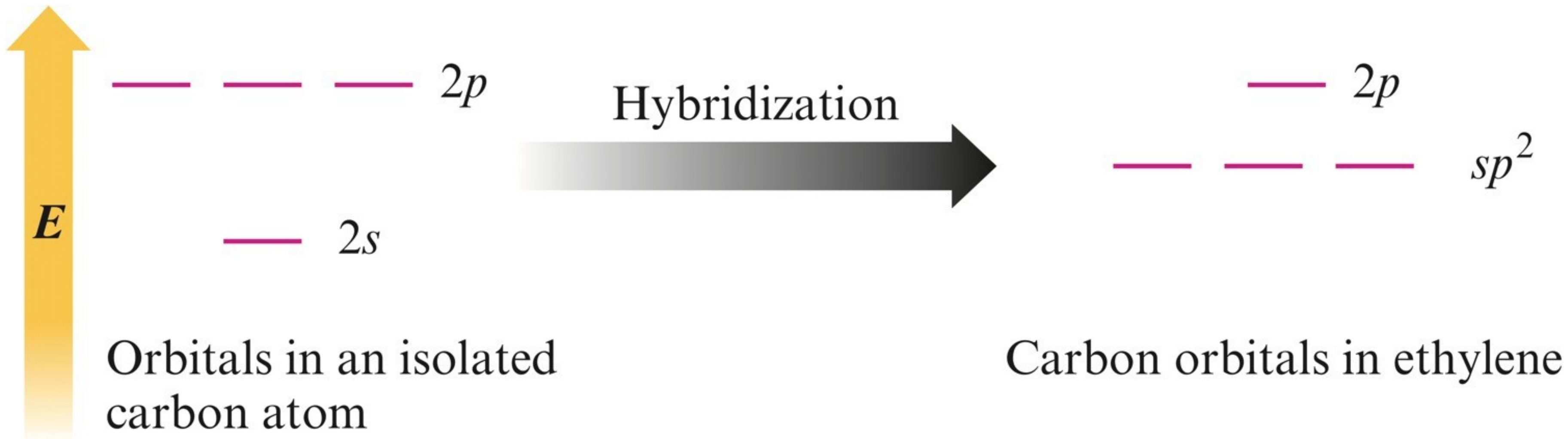
## Sigma (Σ) Bond

- Electron pair is shared in an area centered on a line running *between* the atoms.

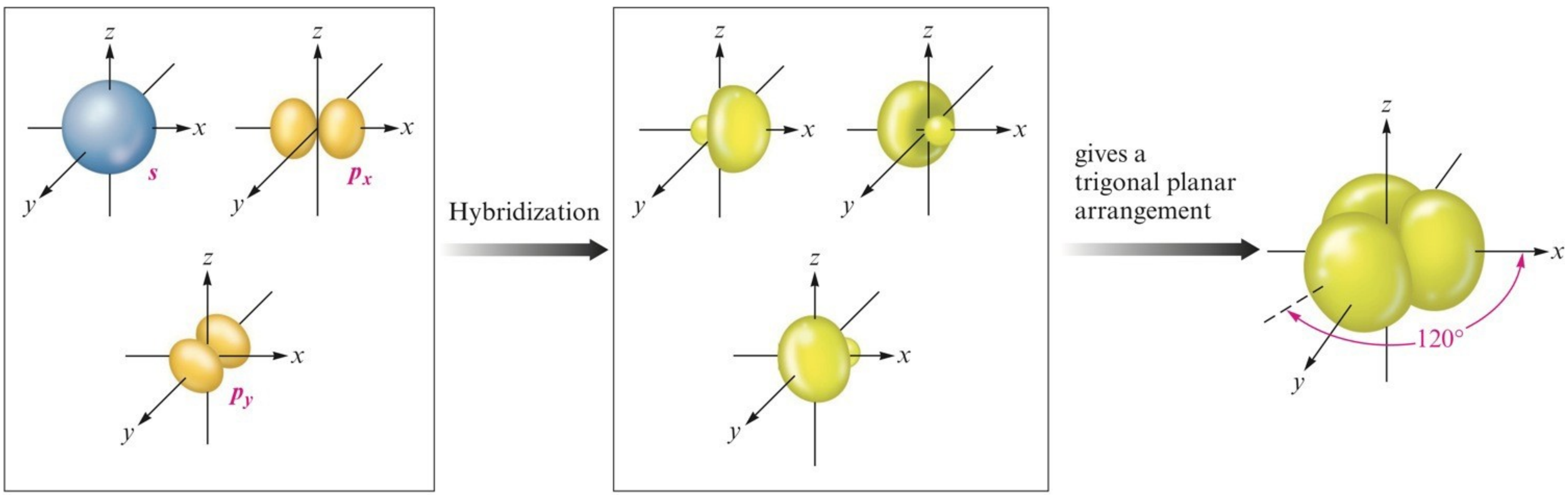
## Pi (Π) Bond

- Forms double and triple bonds by sharing electron pair(s) in the space above and below the σ bond.
- Uses the unhybridized *p* orbitals.

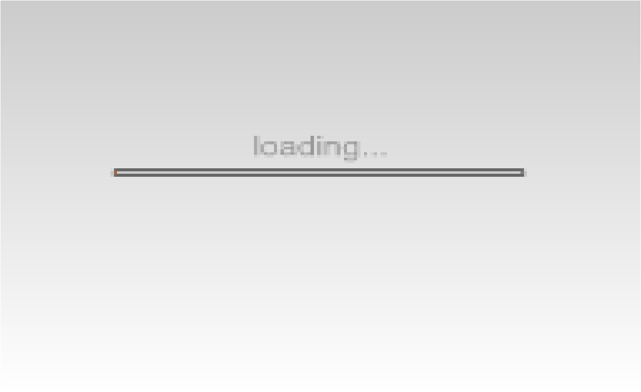
# An Orbital Energy-Level Diagram for *sp*² Hybridization



# The Hybridization of the *s*, $p_x$, and $p_y$ Atomic Orbitals



# Formation of C=C Double Bond in Ethylene

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## *EXERCISE!*

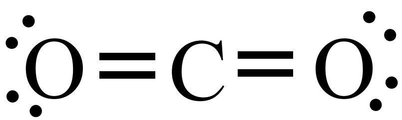
Draw the Lewis structure for $CO_2$.

- What is the shape of a carbon dioxide molecule?

  linear

- What are the bond angles?

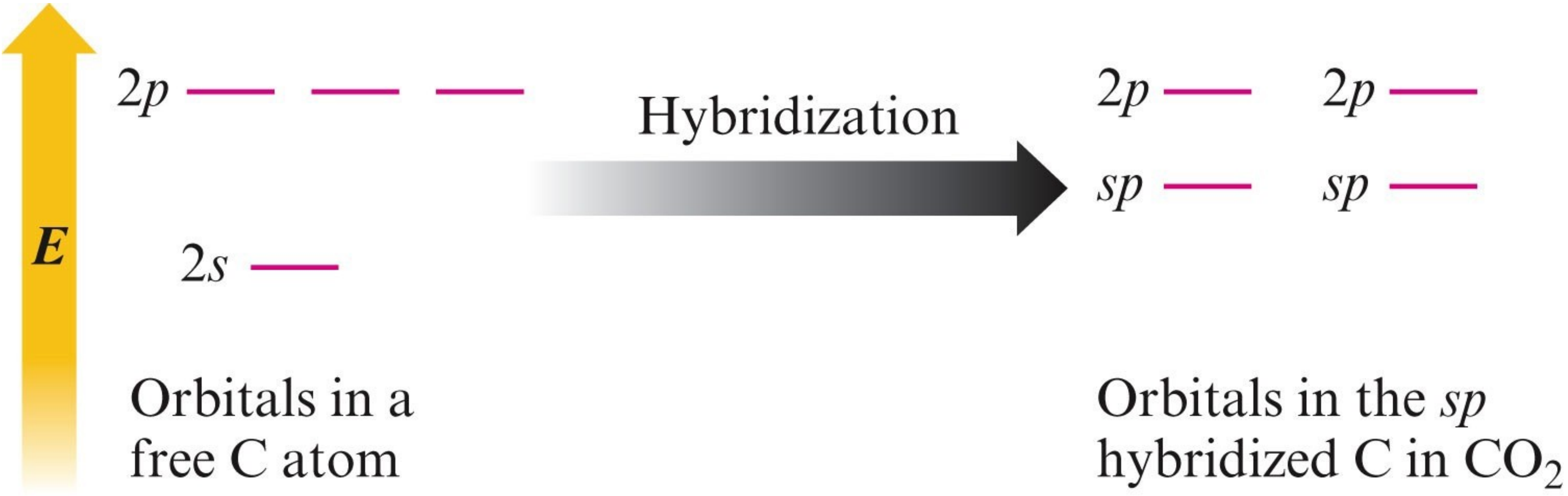
  $180^0$



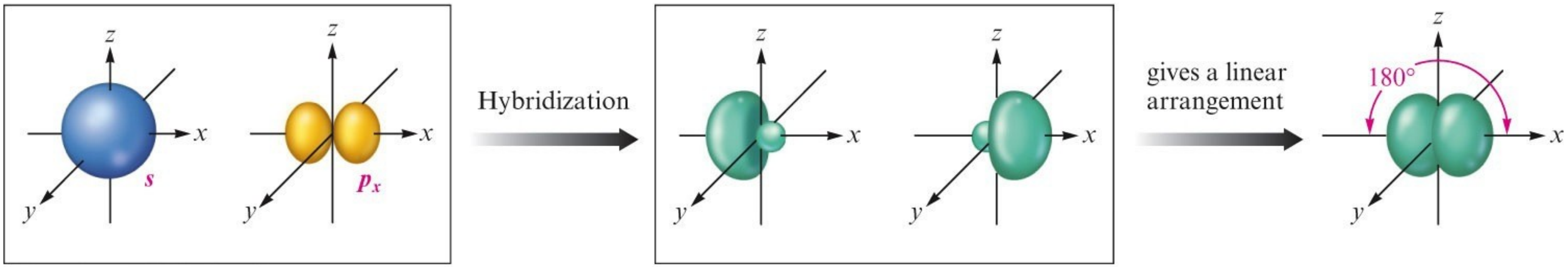
## *sp* Hybridization

- Combination of one *s* and one *p* orbital.
- Gives a linear arrangement of atomic orbitals.
- Two *p* orbitals are not used.
  - Needed to form the π bonds.

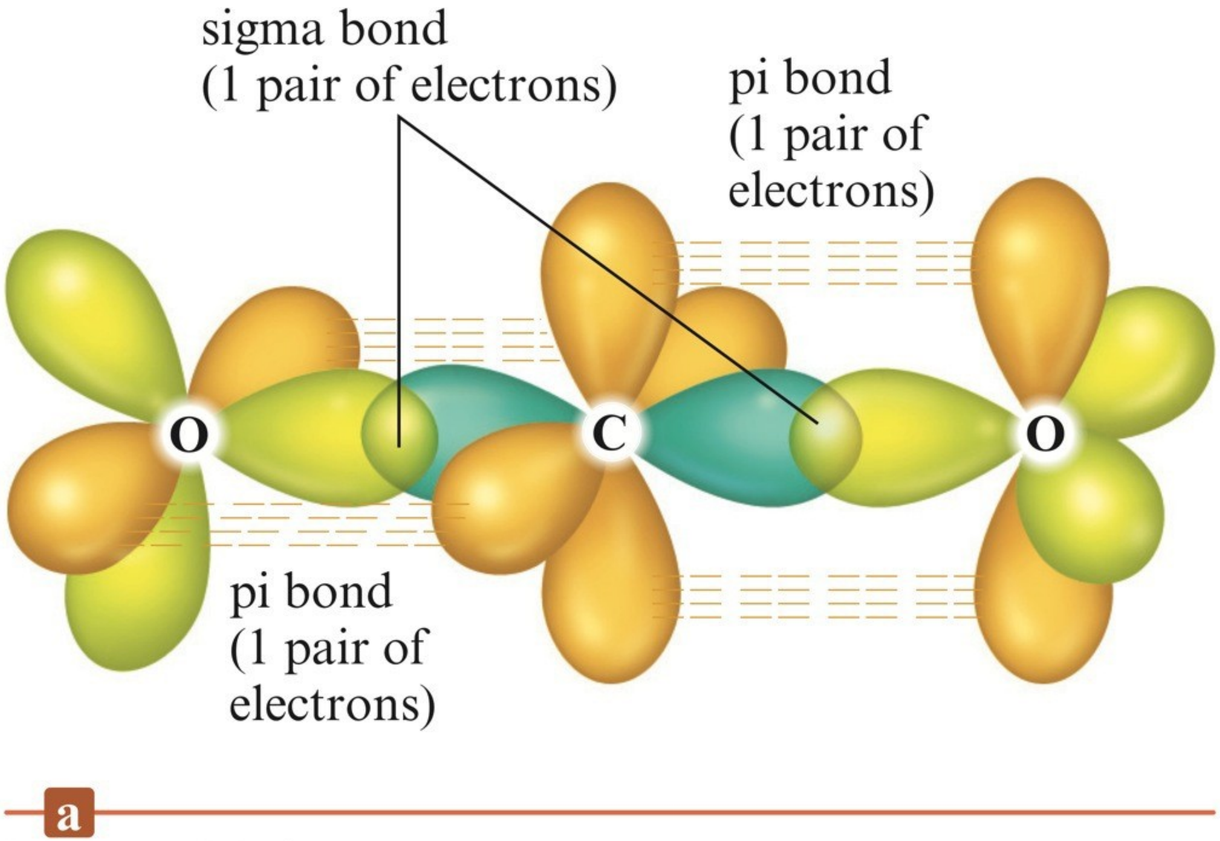
# The Orbital Energy-Level Diagram for the Formation of *sp* Hybrid Orbitals on Carbon



## When One *s* Orbital and One *p* Orbital are Hybridized, a Set of Two *sp* Orbitals Oriented at 180 Degrees Results



# The Orbitals for $CO_2$




**EXERCISE!**

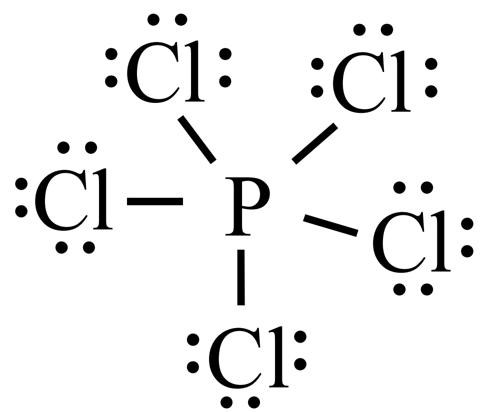
Draw the Lewis structure for $PCl_5$.

- What is the shape of a phosphorus pentachloride molecule?

  trigonal bipyramidal

- What are the bond angles?

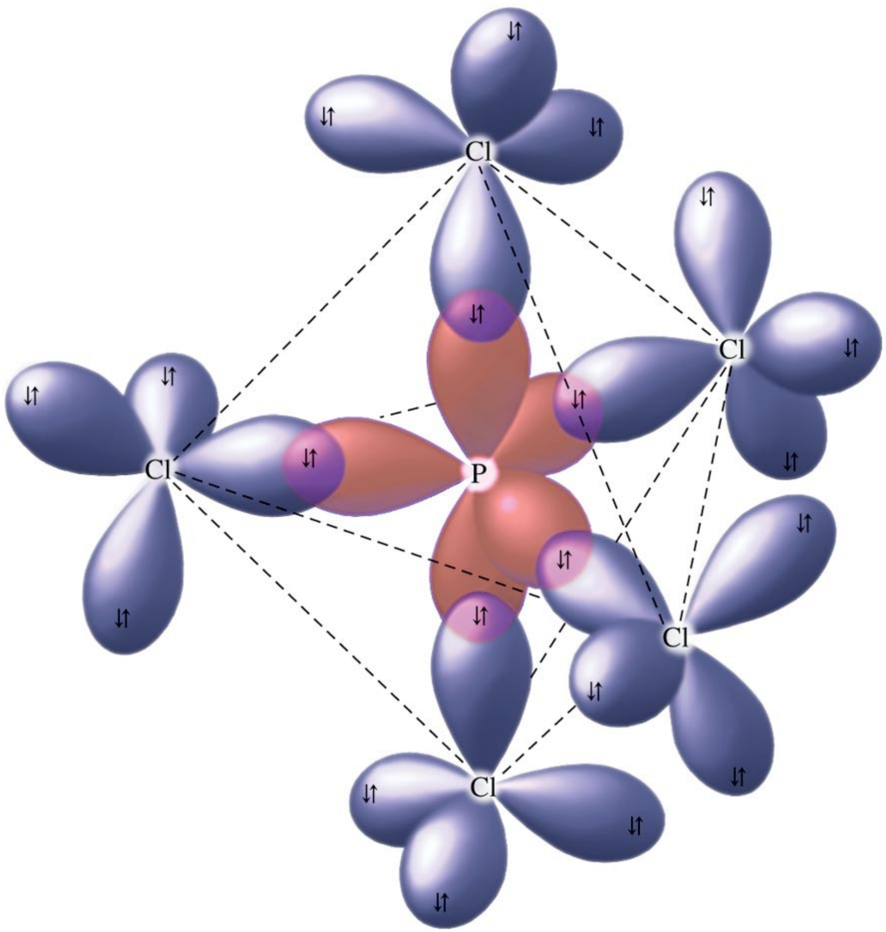
  $90^{0}$ and $120^{0}$



## *dsp*$^3$ Hybridization

- Combination of one *d*, one *s*, and three *p* orbitals.
- Gives a trigonal bipyramidal arrangement of five equivalent hybrid orbitals.

# The Orbitals Used to Form the Bonds in $PCl_5$



## EXERCISE!

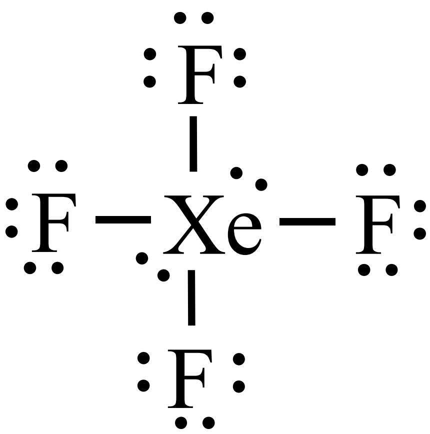
Draw the Lewis structure for $XeF_4$.

- What is the shape of a xenon tetrafluoride molecule?

  octahedral

- What are the bond angles?

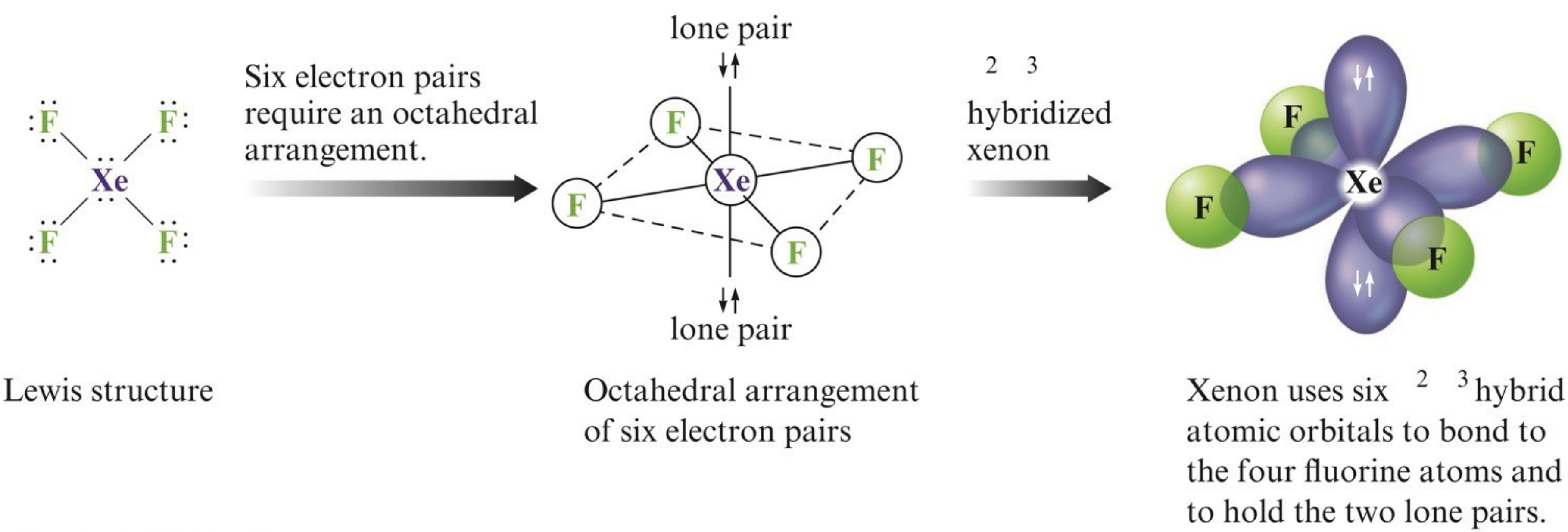
  $90^0$ and $180^0$



## $d^2sp^3$ Hybridization

- Combination of two *d*, one *s*, and three *p* orbitals.
- Gives an octahedral arrangement of six equivalent hybrid orbitals.

# How is the Xenon Atom in $XeF_4$ Hybridized?



**CONCEPT CHECK!**

Draw the Lewis structure for HCN.

Which hybrid orbitals are used?

Draw HCN:

- Showing all bonds between atoms.
- Labeling each bond as σ or π.

## CONCEPT CHECK!

Determine the bond angle and expected hybridization of the central atom for each of the following molecules:

$NH_3$ $SO_2$ $KrF_2$

$CO_2$ $ICl_5$

$NH_3$ – $109.5^0$, $sp^3$

$SO_2$ – $120^0$, $sp^2$

$KrF_2$ – $90^0$, $120^0$, $dsp^3$

$CO_2$ – $180^0$, sp

$ICl_5$ – $90^0$, $180^0$, $d^2sp^3$

## Using the Localized Electron Model

- Draw the Lewis structure(s).
- Determine the arrangement of electron pairs using the VSEPR model.
- Specify the hybrid orbitals needed to accommodate the electron pairs.