# Chapter 9
# Molecular Geometries

## and Bonding Theories

# Coverage of Chapter 9

9.1 All

9.2 All

9.3 All

9.4 All

9.5 Omit Hybridization Involving d Orbitals

9.6 All

9.7 and 9.8 Omit ALL

# Molecular Shapes

- The shape of a molecule plays an important role in its reactivity.
- By knowing the number of bonding and nonbonding electron pairs we can predict the shape of the molecule.

# Two (2) Theories for
# MOLECULAR GEOMETRY

1. **V**alence **S**hell **E**lectron **P**air **R**epulsion
   *(VSEPR) THEORY*

**&**

2. The **V**alence **B**ond
   ***(VB) THEORY***

# Lewis Structures
# &
# Formal Charge

Formal charge is a charge assigned to each atom in a Lewis structure that helps to distinguish among competing structures.

What is the correct formula for
Hypo Chlorous Acid
$HClO$ (aq)

H – Cl – O

or

H – O – Cl

# Hypo chlorite ion
# $ClO^-$

| O – Cl |

| | O | Cl |
|---|---|---|
| Number of Valence $e^-$ | 6 | 7 |
| Number of Nonbonding $e^-$ | - 6 | - 6 |
| ½ Number of Bonding $e^-$ | - 1 | - 1 |
| Formal Charge | -1 | 0 |

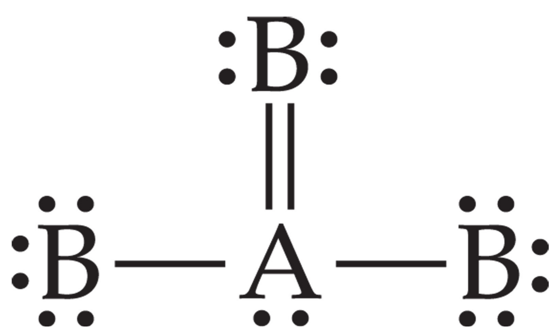
# Where does the H go on HClO?

| O – Cl – H     or     H – O – Cl |

| | O | Cl | O | Cl |
|---|---|---|---|---|
| Valence $e^-$ | 6 | 7 | 6 | 7 |
| Nonbonding $e^-$ | -6 | -4 | -4 | -6 |
| ½ Bonding $e^-$ | -1 | -2 | -2 | -1 |
| | -1 | -1 | 0 | 0 |

# Electron Domains

- Electron pairs are refered to as electron domains
- Single, double or triple bonds all count as one electron domain.



The atom A in this molecule, has four electron domains.

The First
***MOLECULAR GEOMETRY*** theory
(**VSEPR**)

**V**alence **S**hell **E**lectron **P**air
**R**epulsion theory

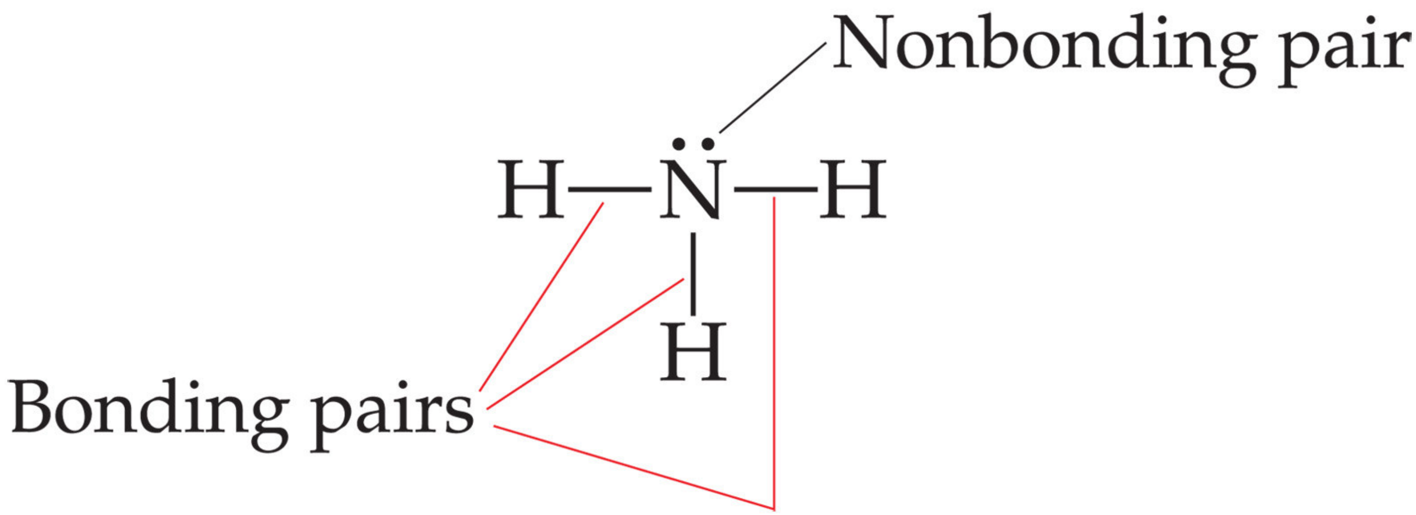
# VSEPR Theory

1. To predict molecular shape, assume the valence electrons repel each other

2. The electrons adopt an arrangement in space to minimize $e^-$ $e^-$ repulsion

3. The molecule adopts whichever 3D geometry minimized this repulsion.

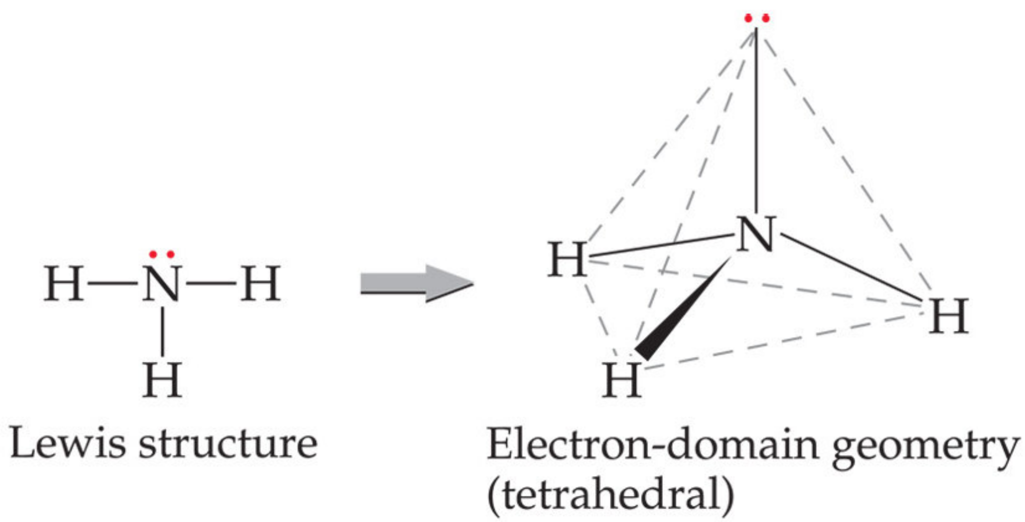
# What Determines the Shape of a Molecule?




Four electron domains on N

3 bonding and 1 nonbonding

# What Determines the Shape of a Molecule?




Electrons, whether they be bonding or non-bonding, repel each other. So electrons are placed as far as possible from each other

# Two (2) Different "Types" of Molecules

1. Molecules with NO nonBonding electrons on the central atom

2. Molecules with nonBonding electrons on the central atom

# Electron Domains & NonBonding Electrons

**Example 1** $CO_2$

| O = C = O |

How many electron domains on C 2

How many NonBonding electrons on C 0

# Electron Domains & NonBonding Electrons

Example 2 $H_2O$

$$H - \ddot{\underline{O}} - H$$

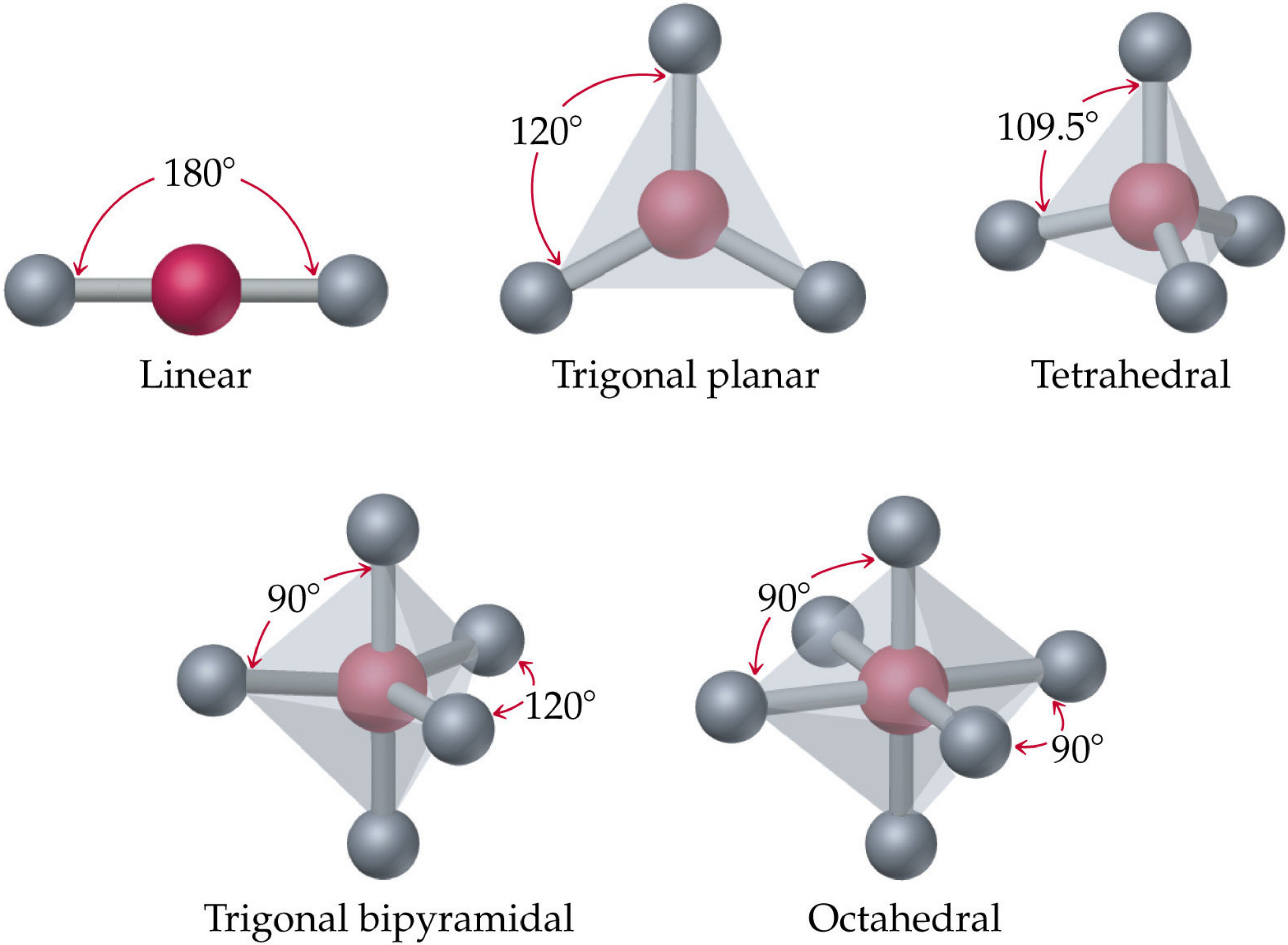
How many electron domains on O 4

How many NonBonding electrons on O 4

# Molecular Geometries for molecules with no nonbonding electrons on central atom

There are five fundamental geometries :

1. Linear
2. Trigonal Planar
3. Tetrahedral
4. Trigonal bepyramidal
5. Octahedral


180°
Linear
120°
Trigonal planar
109.5°
Tetrahedral
90°
120°
Trigonal bipyramidal
90°
90°
Octahedral

# Only consider Three in detail

1. Linear
2. Trigonal Planar
3. Tetrahedral

# In order to determine geometry

First Draw Lewis Dot Formula

# MOLECULES IN WHICH THE CENTRAL ATOM HAS NO LONE PAIRS

## ZINC CHLORIDE

$ZnCl_2$    Zn (30) [Ar] $3d^{10} 4s^2$

$$|\overline{\underline{Cl}} - Zn - \overline{\underline{Cl}}|$$

B – A – B

$AB_2$ = LINEAR

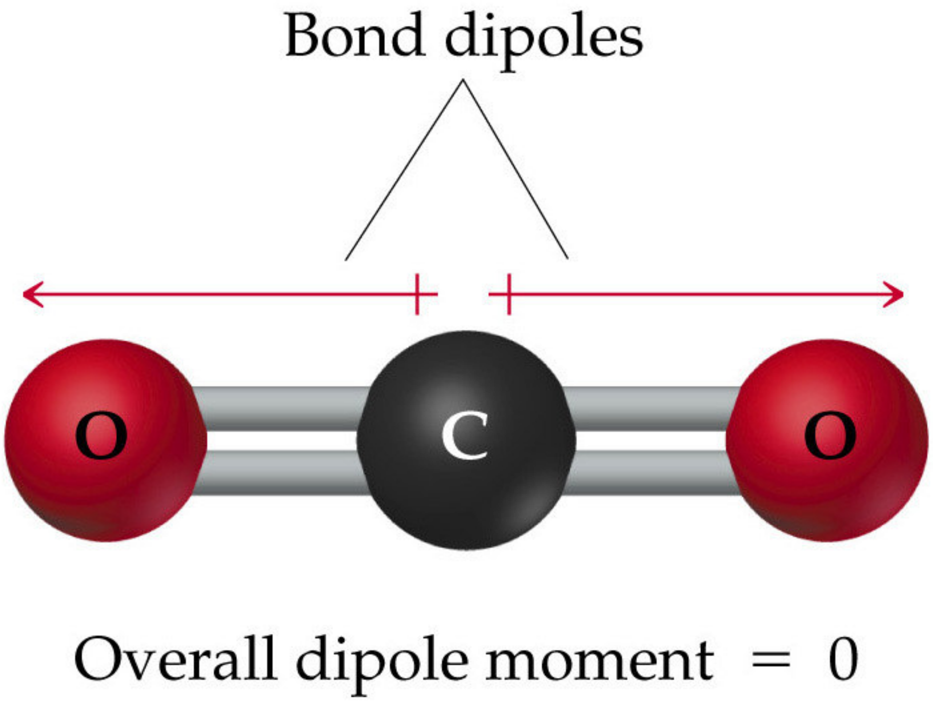
# $AB_2$ Molecules Such as $CO_2$ are ***<u>Linear</u>***

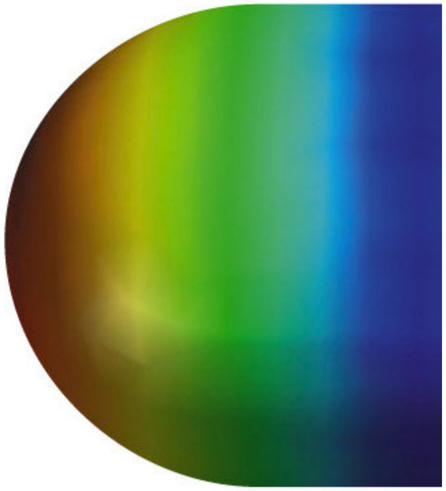
(Molecules With ***NO*** UnPaired Electrons On the Central Atom)

$$\overset{..}{:O} = C = \overset{..}{O:}$$

B – A – B

# Molecular Shape and Molecular Polarity



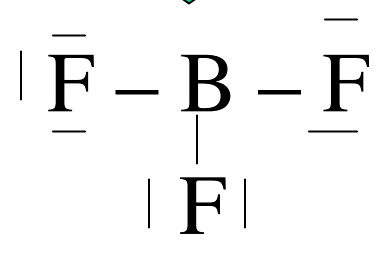
# $AB_3$ Molecules Such as $BF_3$ are ***Planar***

(Molecules With ***NO*** UnPaired Electrons On the Central Atom)

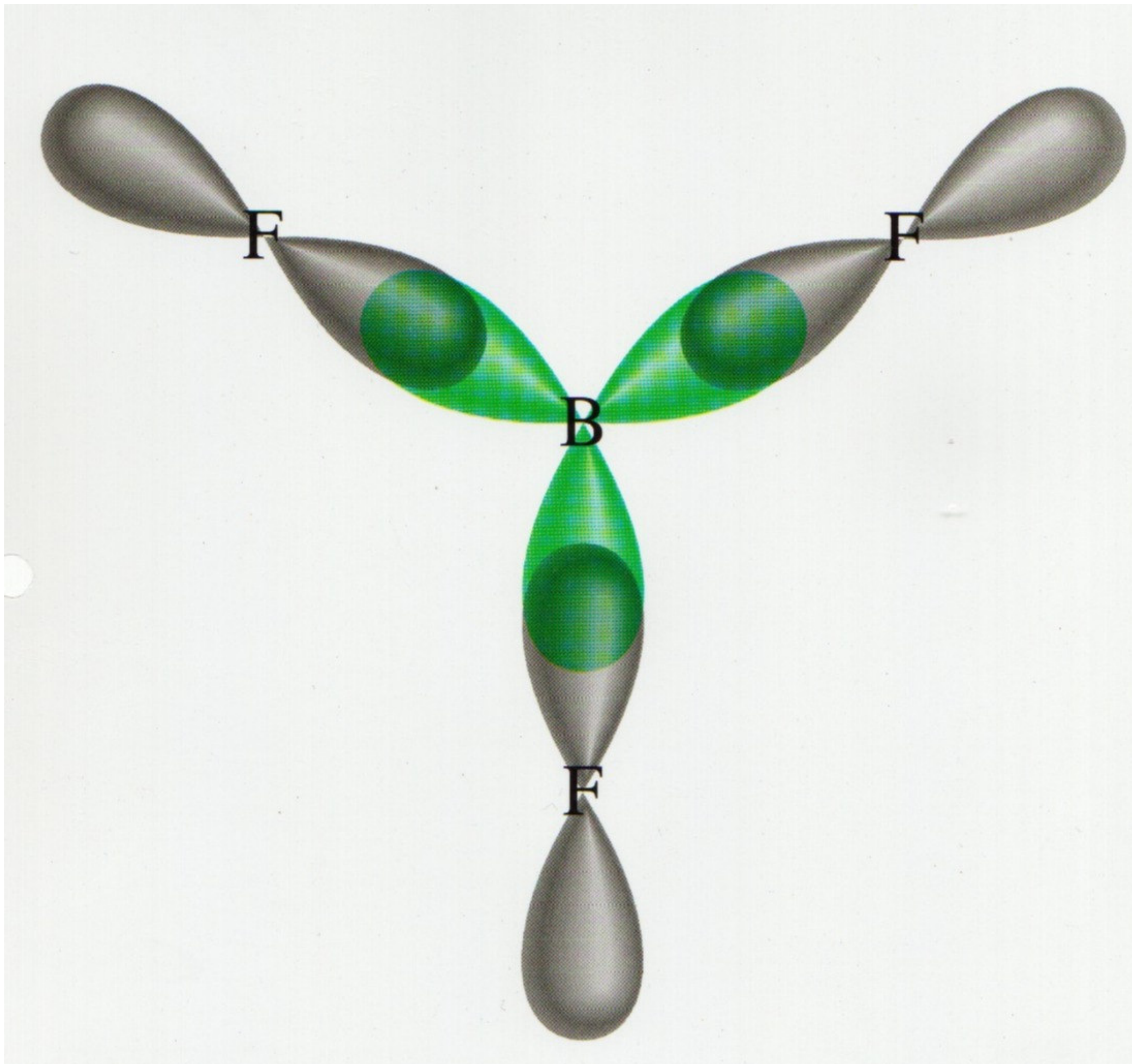
Formula B $F_3$

Number of Valence $e^-$ 3 21 = 24 total

- Lewis Structure



AB$_3$ (Molecules With NO UnPaired Electrons On the Central Atom) Such as BF$_3$ are Planar



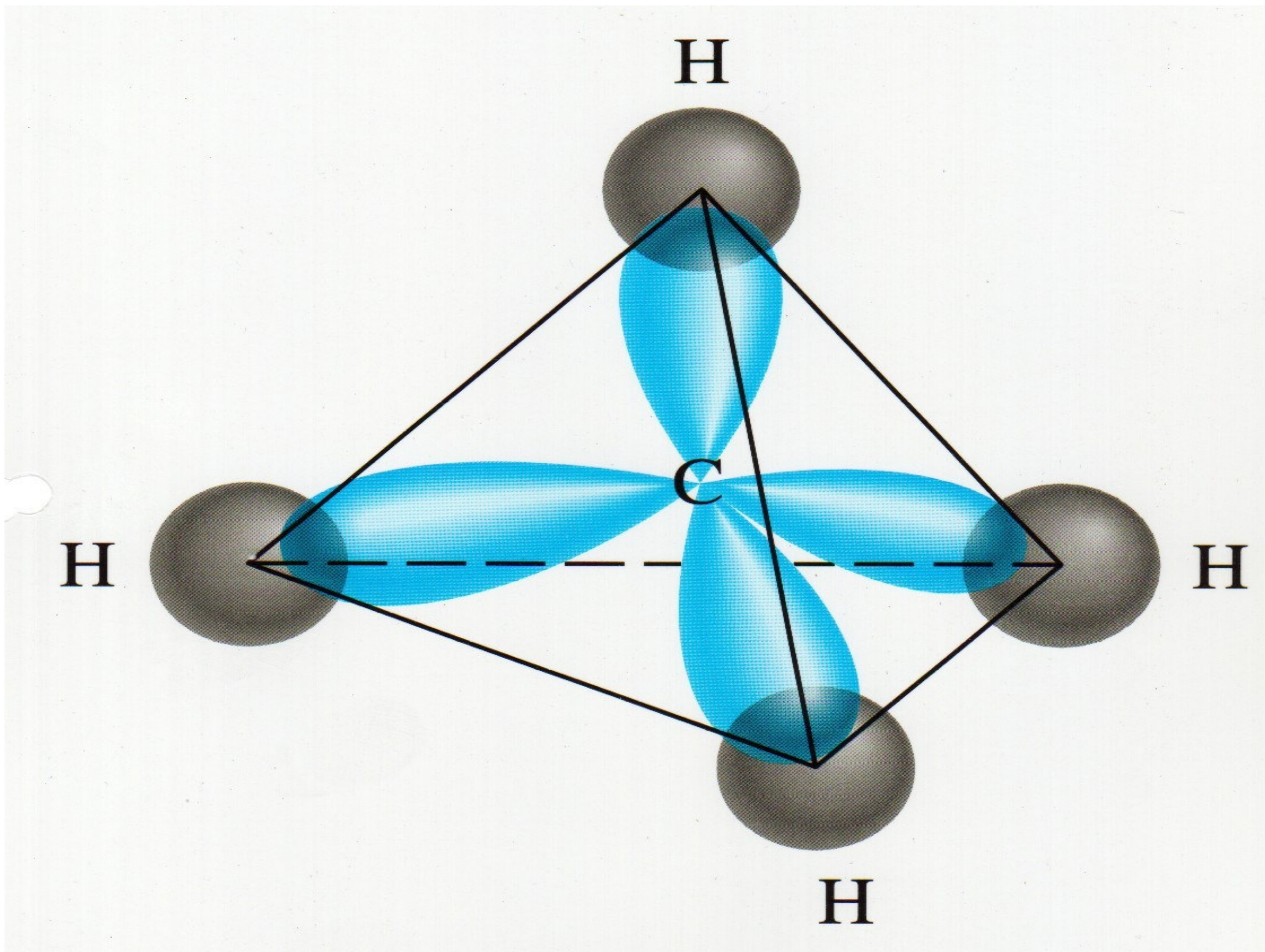
# $AB_4$ Molecules Such as $CH_4$ are Tetrahedral (Molecules With NO UnPaired Electrons On the Central Atom)

- Formula $C\ H_4$
- Number of Valence $e^-$ 4 4 = 8 total
- Lewis Structure

```
      H
      |
  H – C – H
      |
      H
```

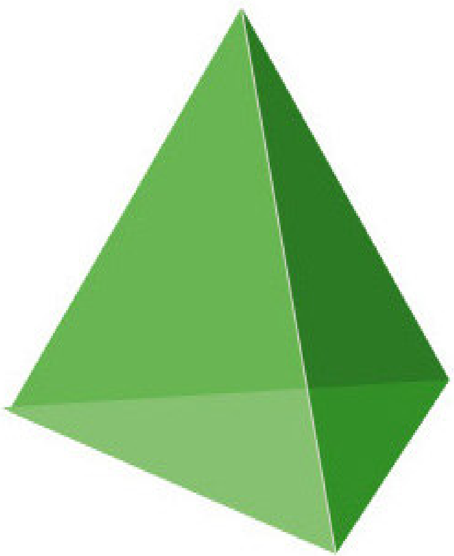
# $AB_4$ Such as $CH_4$ are Tetrahedral

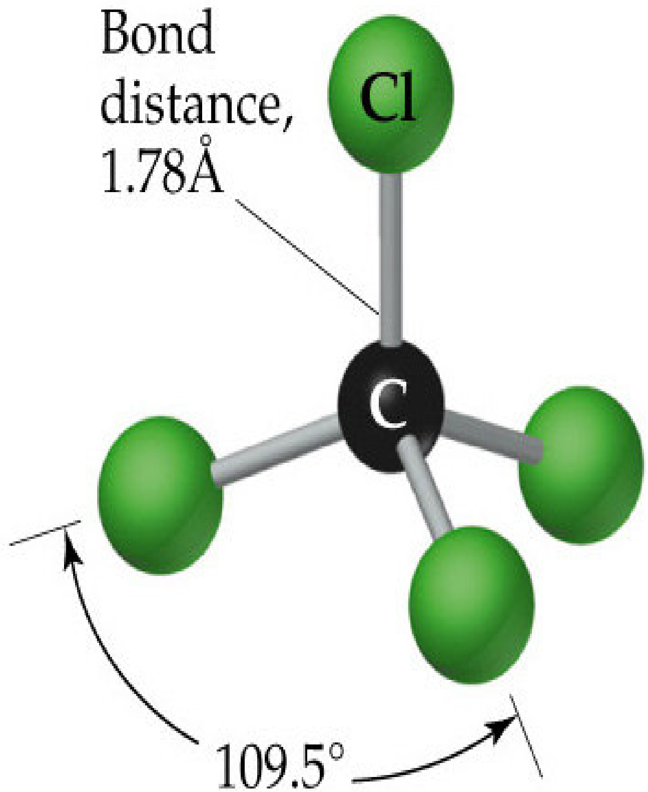
*(Molecules With NO UnPaired Electrons On the Central Atom)*

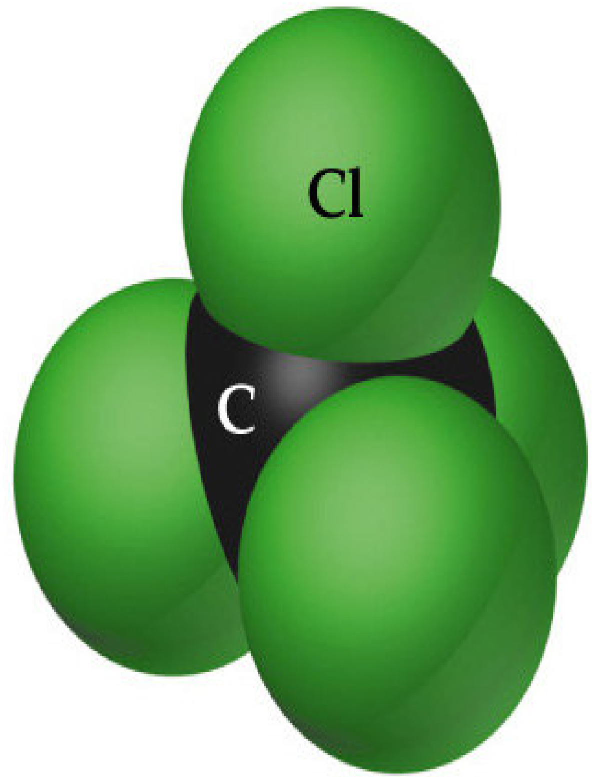


## $AB_4$ Molecules Such as $CCl_4$ are Tetrahedral

# **Carbon TetraChloride**

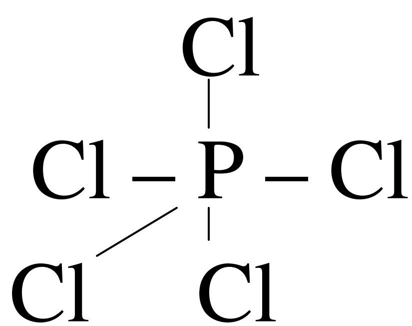




## $AB_5$ Such as $PCl_5$ are Triangular bipyramidal

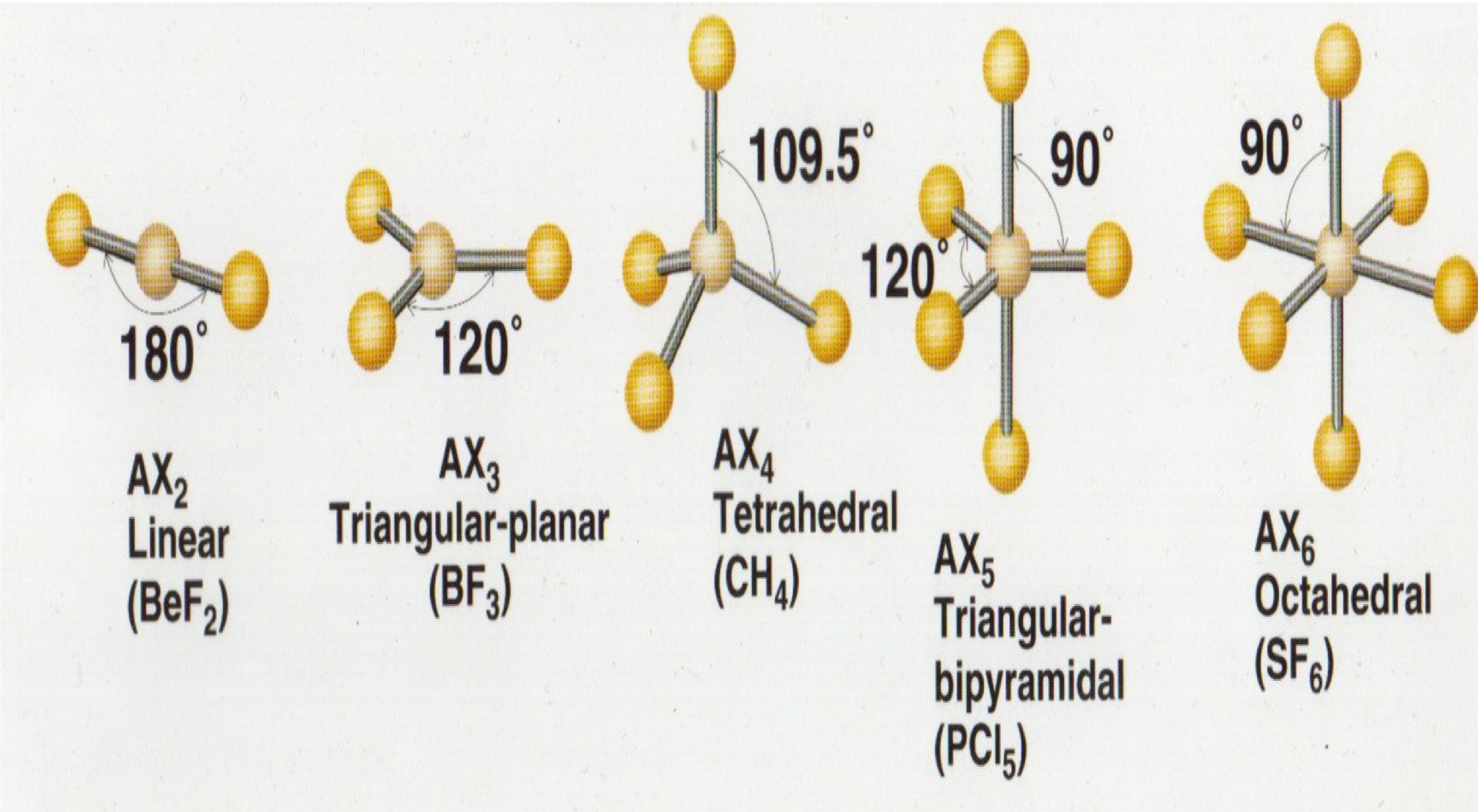
- Name ?
- Number of Bonds ?
- Lewis dot structure ?



# $AB_6$ Such as $SF_6$ are Octahedral

- Name ?
- Number of Bonds ?
- Lewis dot structure ?

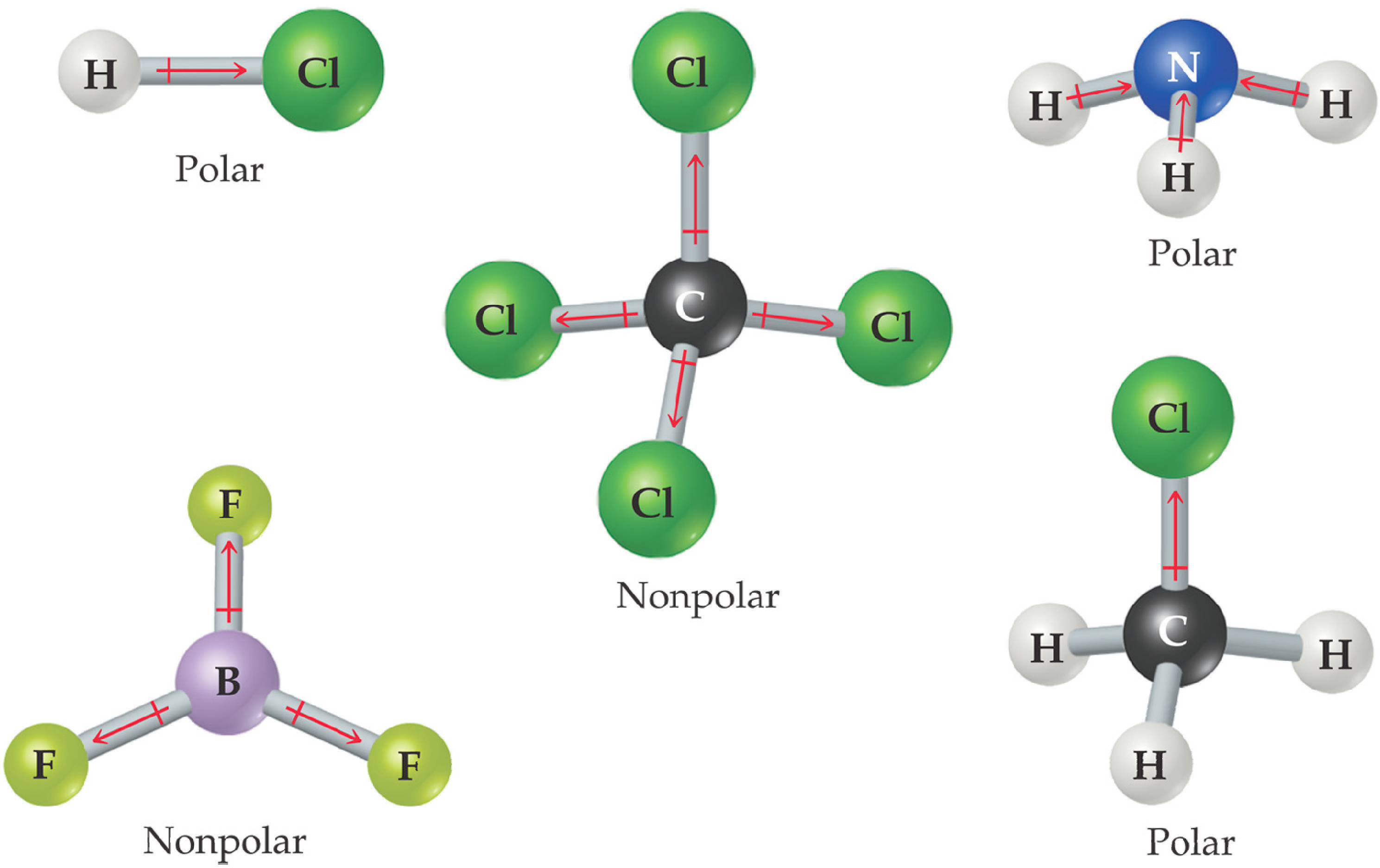
# Molecules With NO UNPaired $e^-$



# Molecules with NO unpaired $e^-$ on Central Atom

1. 2 Bonds ……….$AB_2$ or $AX_2$ e.g. $CO_2$
2. 3 Bonds ……... $AB_3$ or $AX_3$ e.g. $BF_3$
3. 4 Bonds ……….$AB_4$ or $AX_4$ e.g. $CH_4$
4. 5 Bonds ……... $AB_5$ or $AX_5$ e.g. $PCl_5$
5. 6 Bonds ……... $AB_6$ or $AX_6$ e.g. $SF_6$

# Polarity


H
Cl
Polar
Cl
Cl
C
Cl
Cl
Nonpolar
N
H
H
H
Polar
F
B
F
F
Nonpolar
Cl
C
H
H
H
Polar

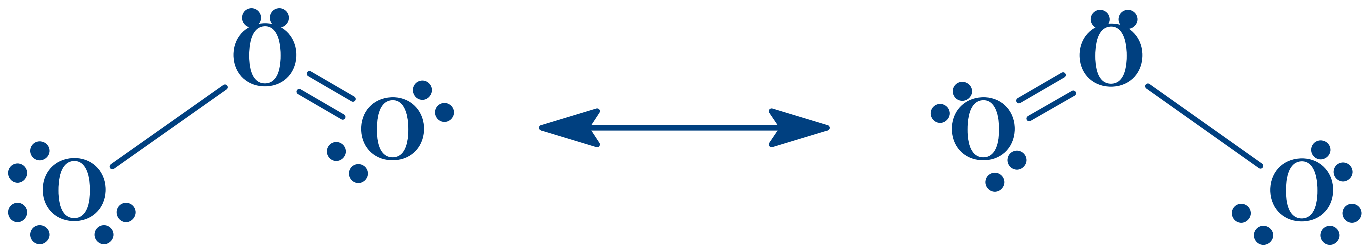
Part 2. of VSEPR Theory

# CENTRAL ATOM HAS LONE PAIRS

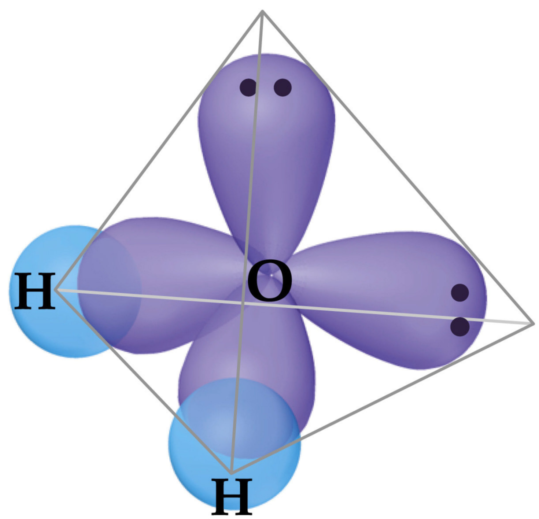
# Molecules With UnPaired Electrons On the Central Atom

| Class | Example | Geometry |
|---|---|---|
| • $AB_2E$ | $SO_2$ & $O_3$ | Bent |
| • $AB_2E_2$ | $H_2O$ | Bent |
| • $AB_3E$ | $NH_3$ | Trigonal pyramidal |

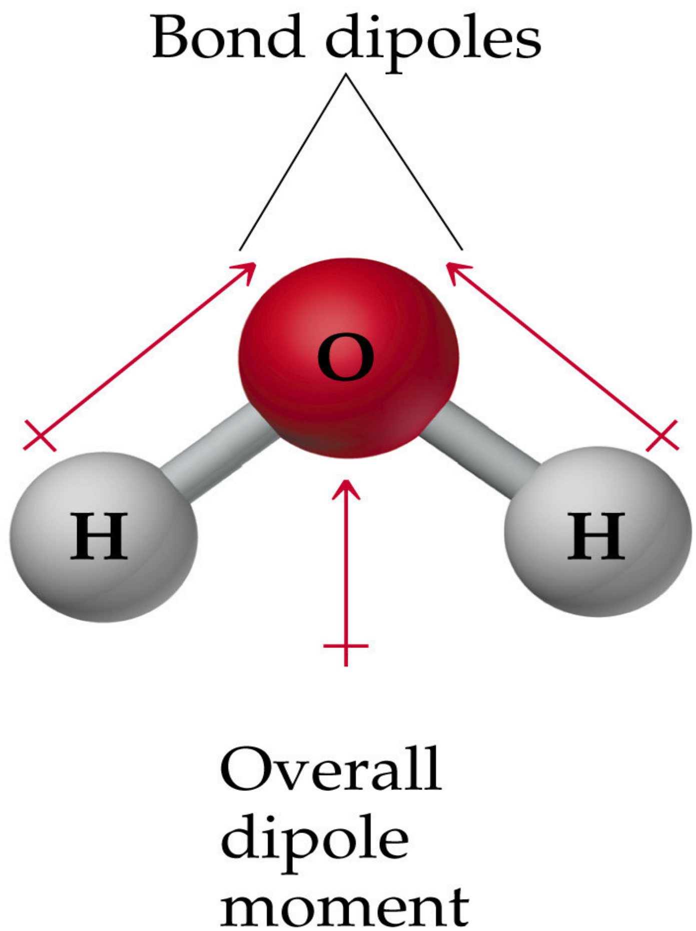
1. AB$_2$E OZONE

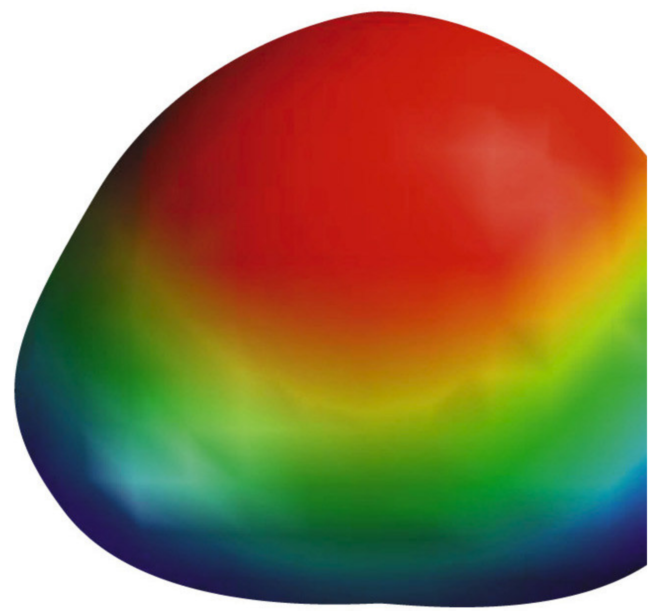



2. AB$_2$E$_2$ WATER

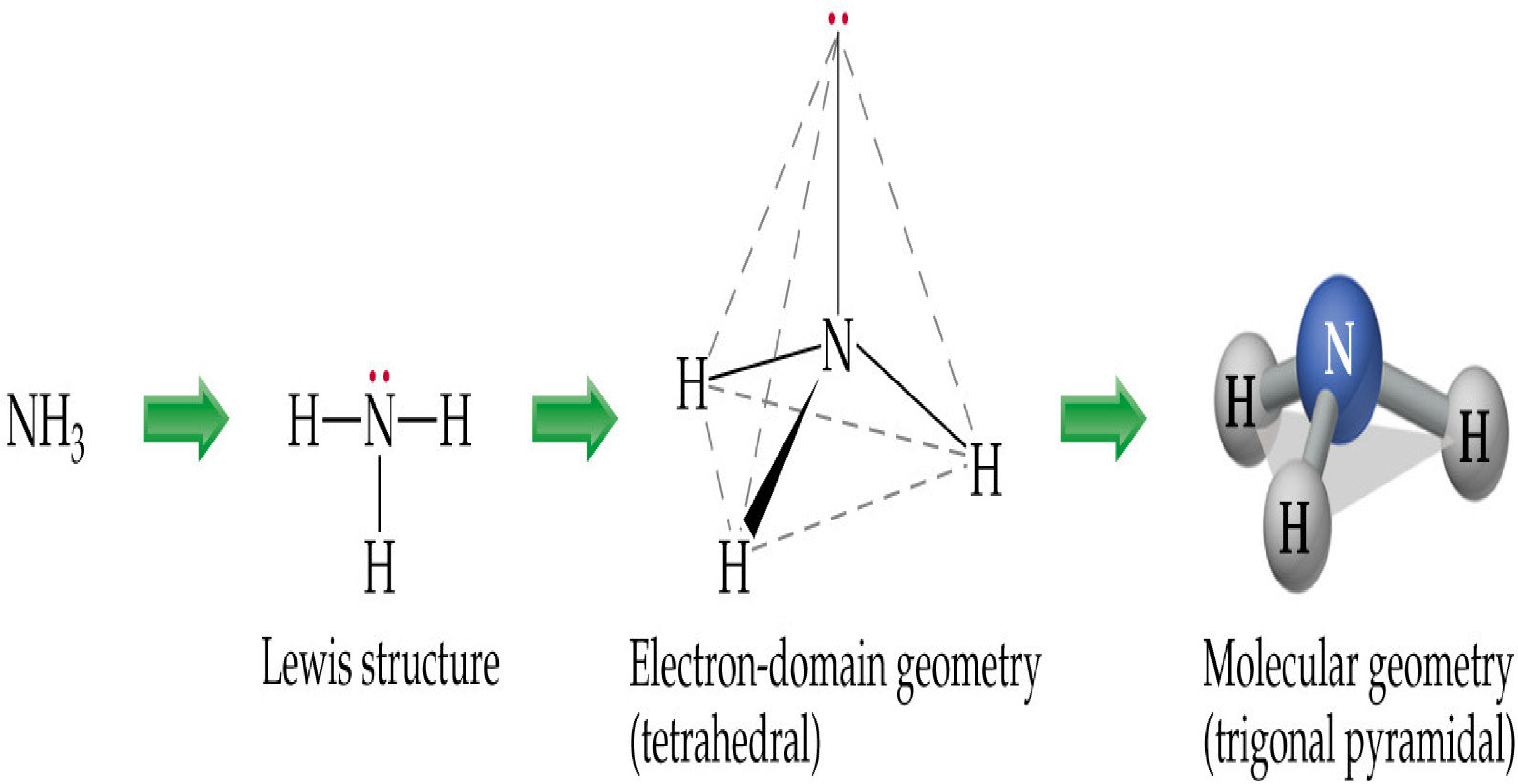


# $AB_2E_2$ (Molecules With UnPaired Electrons On the Central Atom) Such as $H_2O$ are Bent

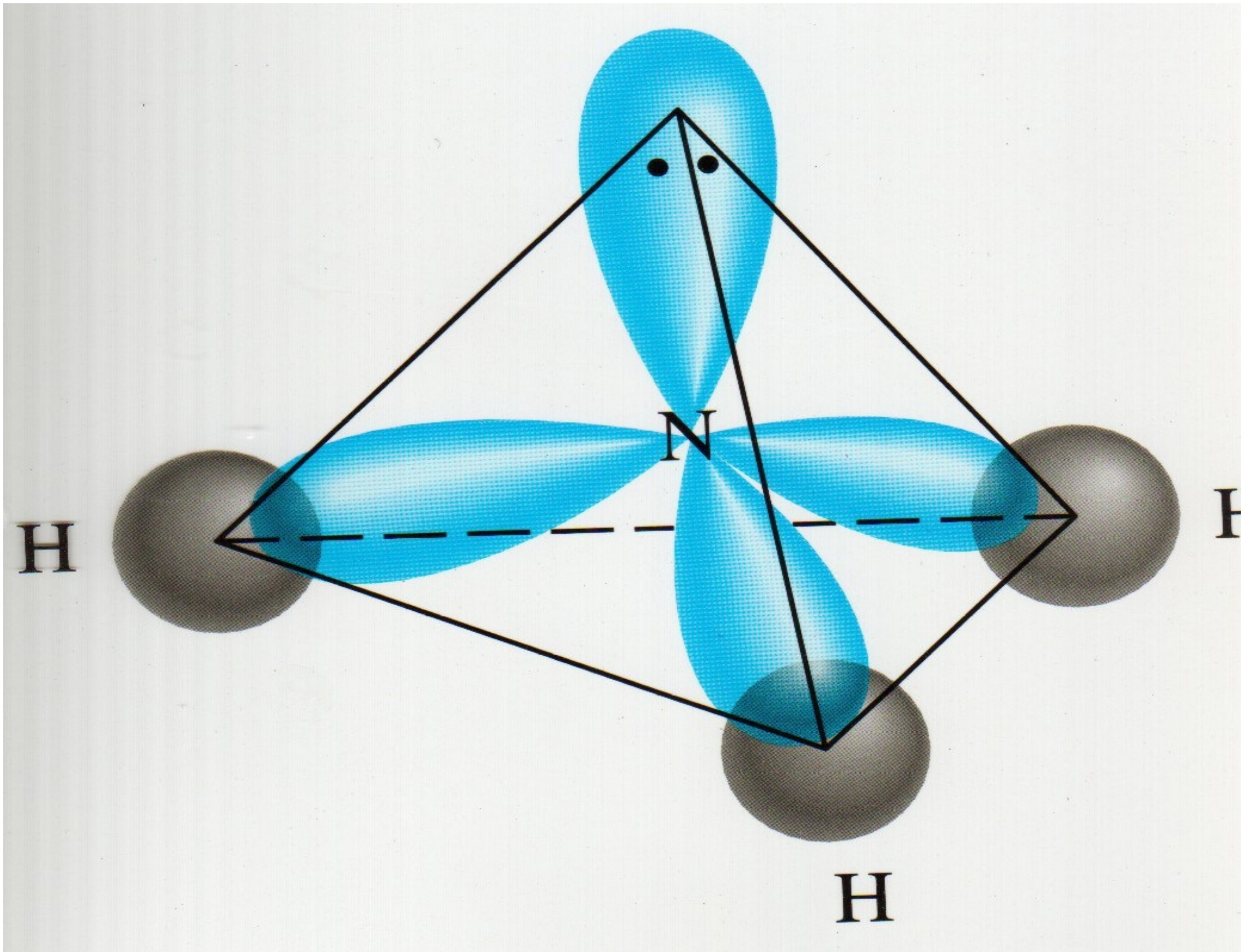


# 3. $AB_3E$ AMMONIA



AB$_3$E (Molecules With UnPaired Electrons On the Central Atom) Such as $NH_3$ are NOT Planar



# Predict Molecular Shapes

1. $SiCl_4$ ____________
2. $CH_2Cl_2$ ____________
3. $GeCl_2$ ____________
4. $OF_2$ ____________
5. $NH_3$ _____________
6. $PH_3$ ______________

Give the
electron domain and molecular geometries for

| | ***electron domain*** | ***molecular geometry*** |
|---|---|---|
| (a) $N_2O$ | ______________ | __________________ |
| (b) $SO_3$ | ______________ | __________________ |
| (c) $PCl_3$ | ______________ | __________________ |
| (d) $NH_2Cl$ | ______________ | __________________ |

# Examples of $AB_2$ molecules

- Linear $AB_2$ How many bonds

  $CO_2$
- Bent $AB_2E$ How many "bonds"

  $SO_2$ and $NO_2^-$
- Bent $AB_2E_2$ How many "bonds"

  $H_2O$

# Examples of $AB_3$ molecules

- Planar $AB_3$ How many bonds

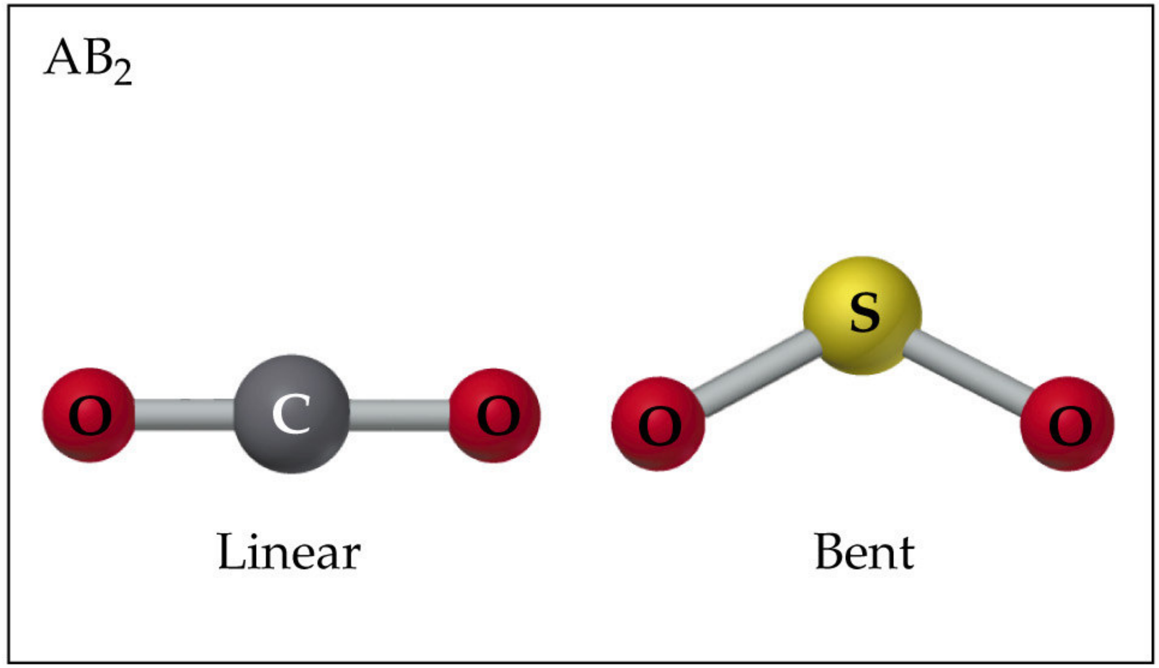
  $BF_3$

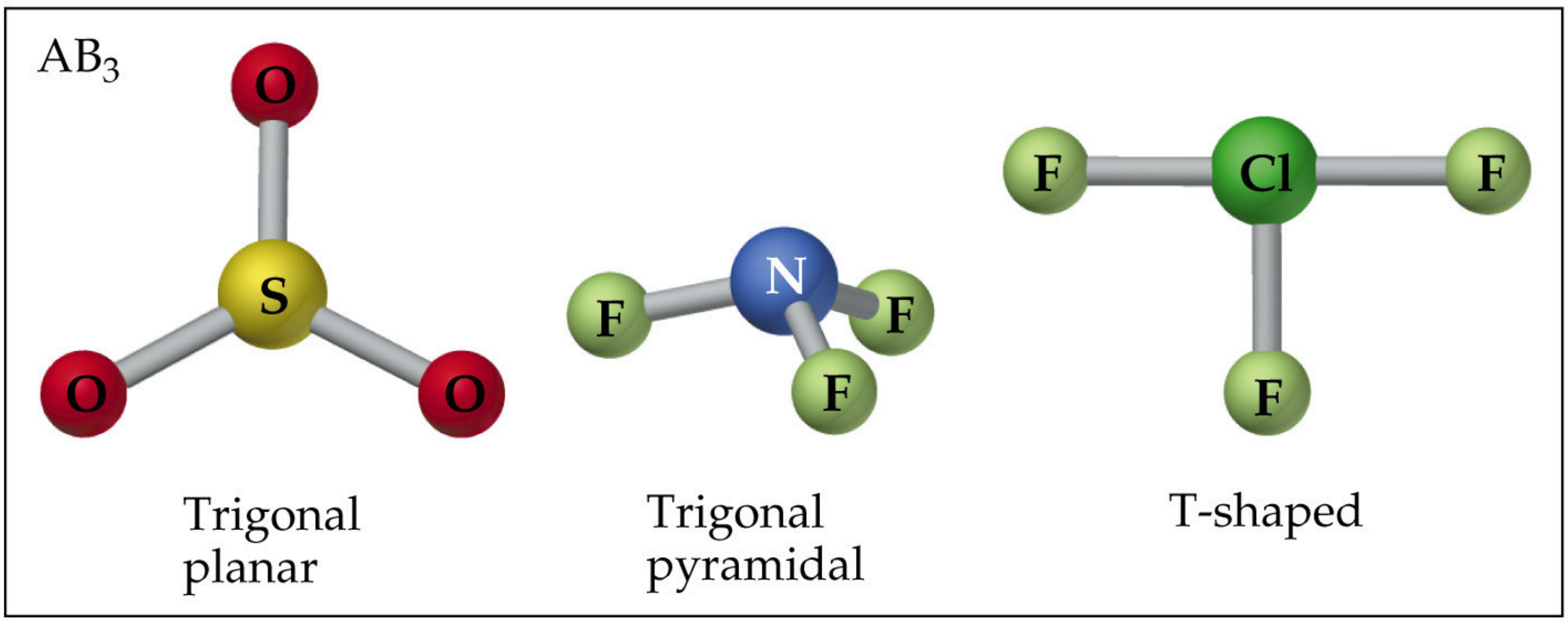
- Pyramidal $AB_3E$ How many "bonds"

  $NH_3$

- T shape $AB_3E_2$ How many "bonds"

  $ClF_3$


AB2
O
C
O
S
O
O
Linear
Bent


AB3
O
S
O
O
N
F
F
F
Cl
F
F
F
Trigonal planar
Trigonal pyramidal
T-shaped

# Two (2) Theories for
# MOLECULAR GEOMETRY

1. **V**alence **S**hell **E**lectron **P**air **R**epulsion

   *(VSEPR)* THEORY

*Now consider*

2. The **V**alence **B**ond

   ***(VB) THEORY***

# Valence bond Method

uses molecular orbitals

not Atomic Orbitals

## What is a molecular orgital?

Orbitals used in bonding of Molecules

# $CH_4$ as an EXAMPLE

Ground State Electron Configuration

C (6 $e^-$ ) $1s^2\ 2s^2\ 2p^2$ = ( ↑↓) (↑↓) (↑) (↑ ) ( )

*Only place for two bonds to form* ⬆ ⬆

*Therefore would predict $CH_2$ formation and not $CH_4$*

*But $CH_2$ does not exist while $CH_4$ does*

C (6 $e^-$) $1s^2\ 2s^2\ 2p^2$ = (↑↓) (↑↓)  (↑) (↑) ( )

*Only place for two bonds to form*

Excited State Electron Configuration

C (6 $e^-$) $1s^2\ 2s^1\ 2p^3$ = (↑↓) (↑)  (↑) (↑) (↑)

Now a place for four bonds

One electron from H goes into an s orbital

and Three from H go into the p orbitals

The **BONDS** in $CH_4$ are **ALL** the **SAME!**

One electron in an s orbital and Three in p orbitals would create different bonds.

Since All the Bonds are Equal, this cannot be correct

**INTRODUCE THE CONCEPT OF HYBRIDIZATION**

# Hybridization

**In order to made All Bonding sites equal, we must create NEW Orbitals.**

**s, p, d, f are ATOMIC ORBITALS**

**MOLECULAR ORBITALS are formed from Atomic orbitals**

# VALENCE BOND THEORY

**VALENCE SHELL ORBITALS**

***<u>HYBRIDIZE</u>***

**THE <u>ORIENTATION</u> OF ALL HYBRID VALENCE SHELL ORBITALS <u>DETERMINES</u> THE GEOMETRY OF THE MOLECULE**

# MOLECULAR ORBITALS
## are formed from
# ATOMIC ORBITALS

| Atomic Orbitals | Molecular Orbitals |
|---|---|
| one S + one P | Two (2) SP |
| one S + two P | Three (3) $SP^2$ |
| one S + three P | Four (4) $SP^3$ |

# MOLECULAR ORBITALS

**They are called**

SP

$SP^2$

$SP^3$

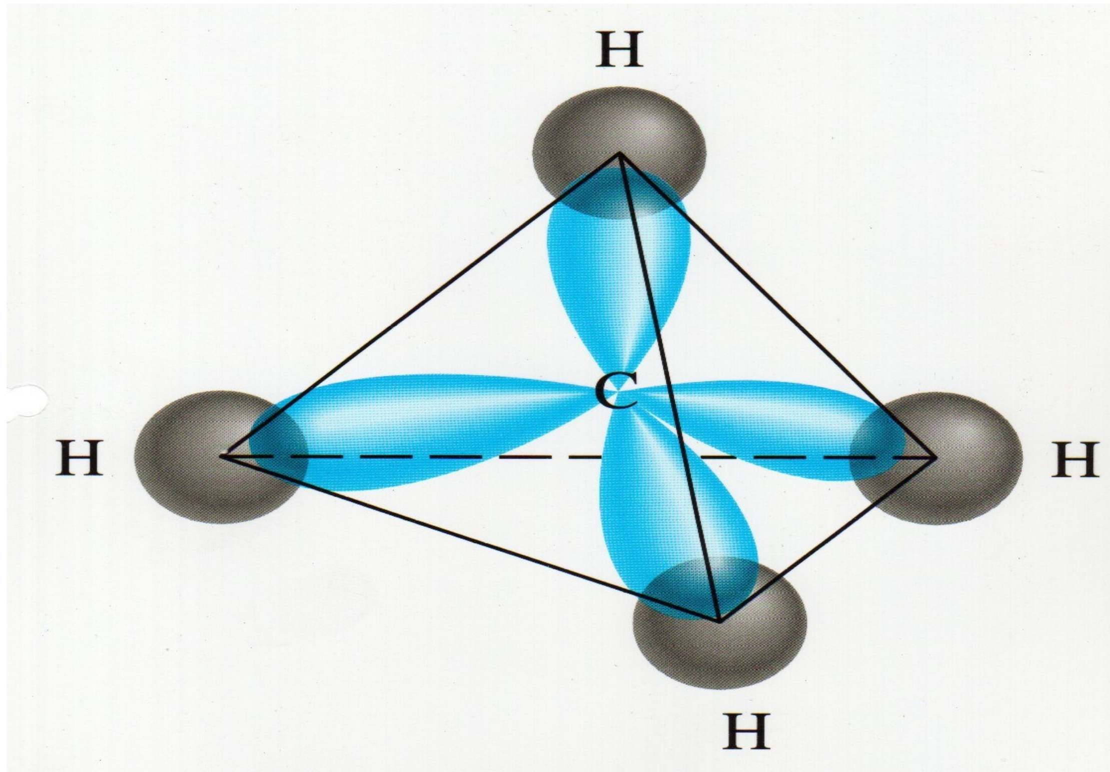
$SP^3d$ and

$SP^3d^2$

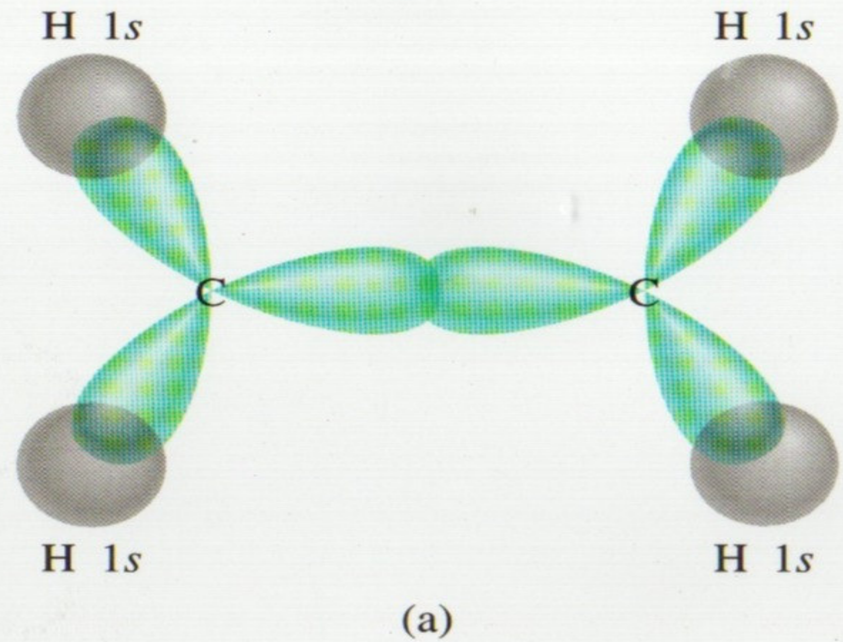
# $sp^3$ HYBRIDIZATION

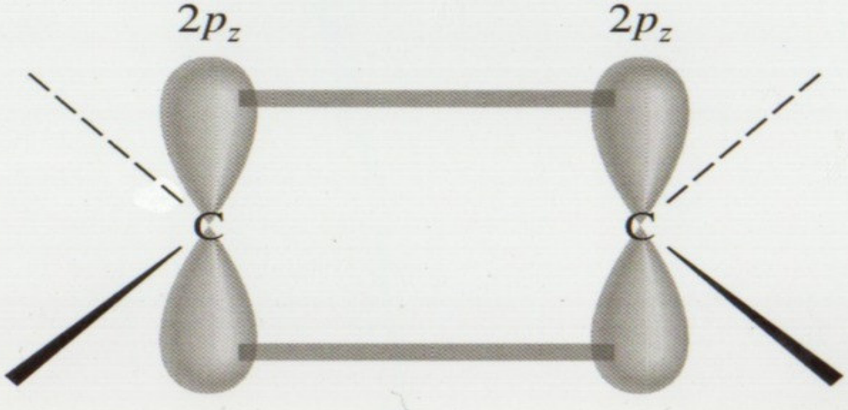
TETRAHEDRAL
Bond Angles
109½°

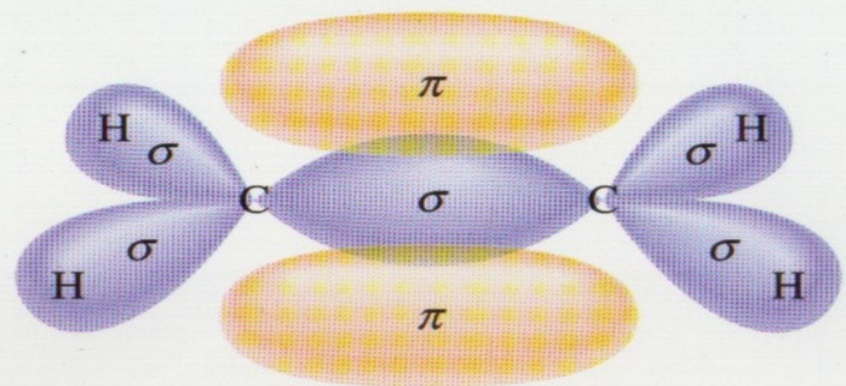
Methane $CH_4$
Four σ Bonds
on C



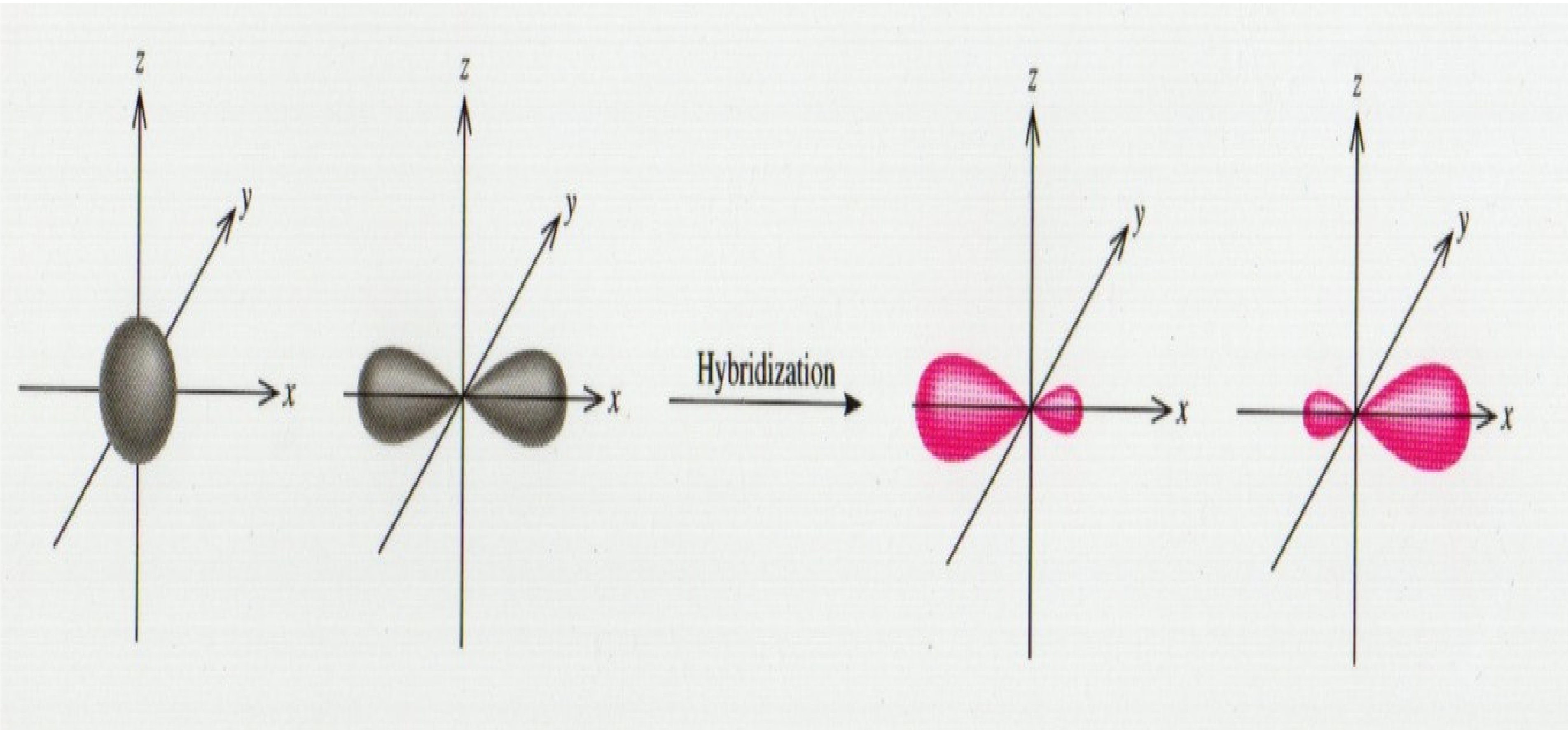
# $sp^2$ HYBRIDIZATION



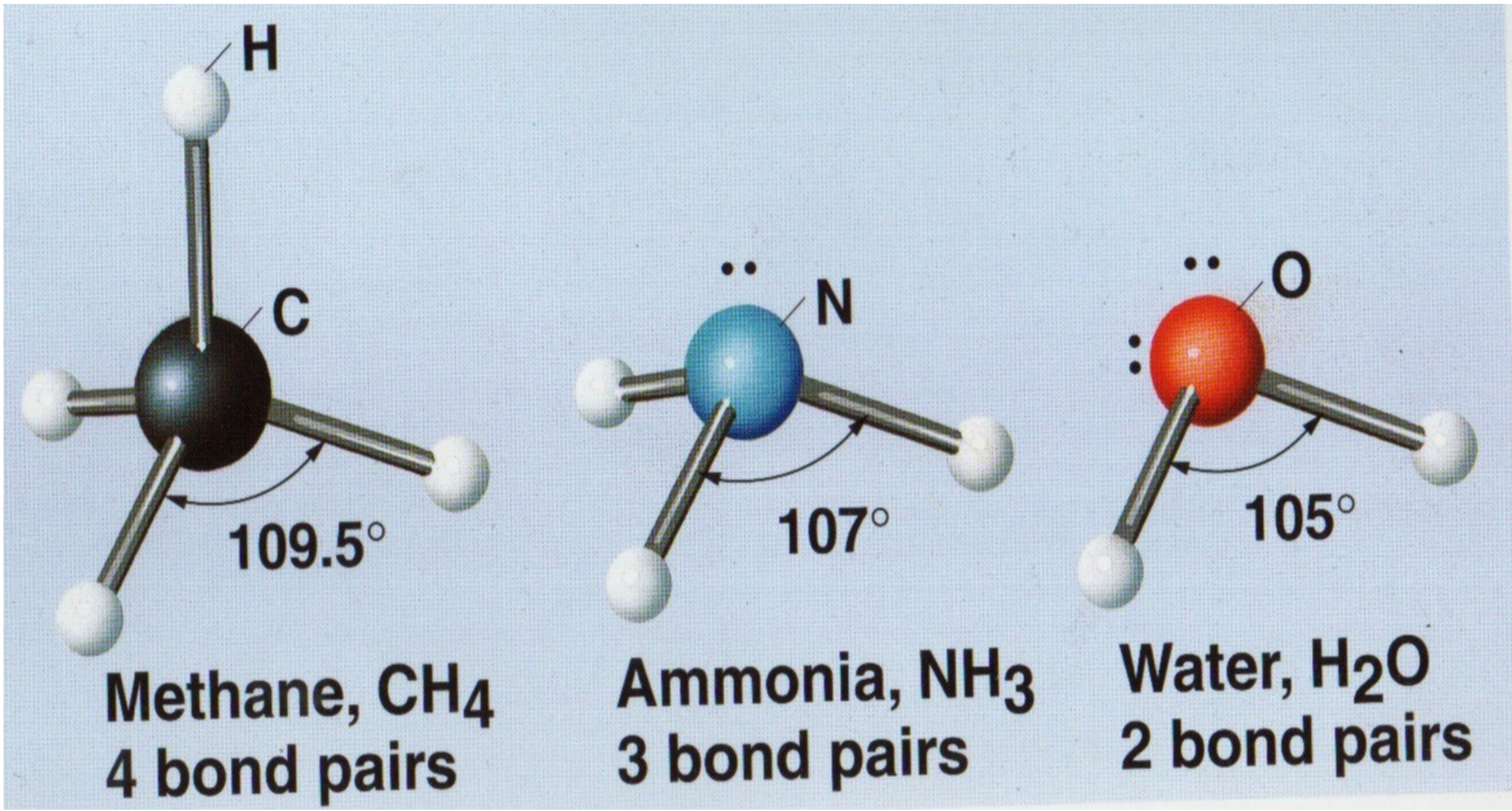



# sp HYBRIDIZATION
# one S orbital + one P orbital



# Carbon is NOT The Only Element That Undergoes $sp^3$ HYBRIDIZATION



In $CH_3COOH$, there are three (3) hybridized atoms.

Geometry is assign about each hybridized atom separately.