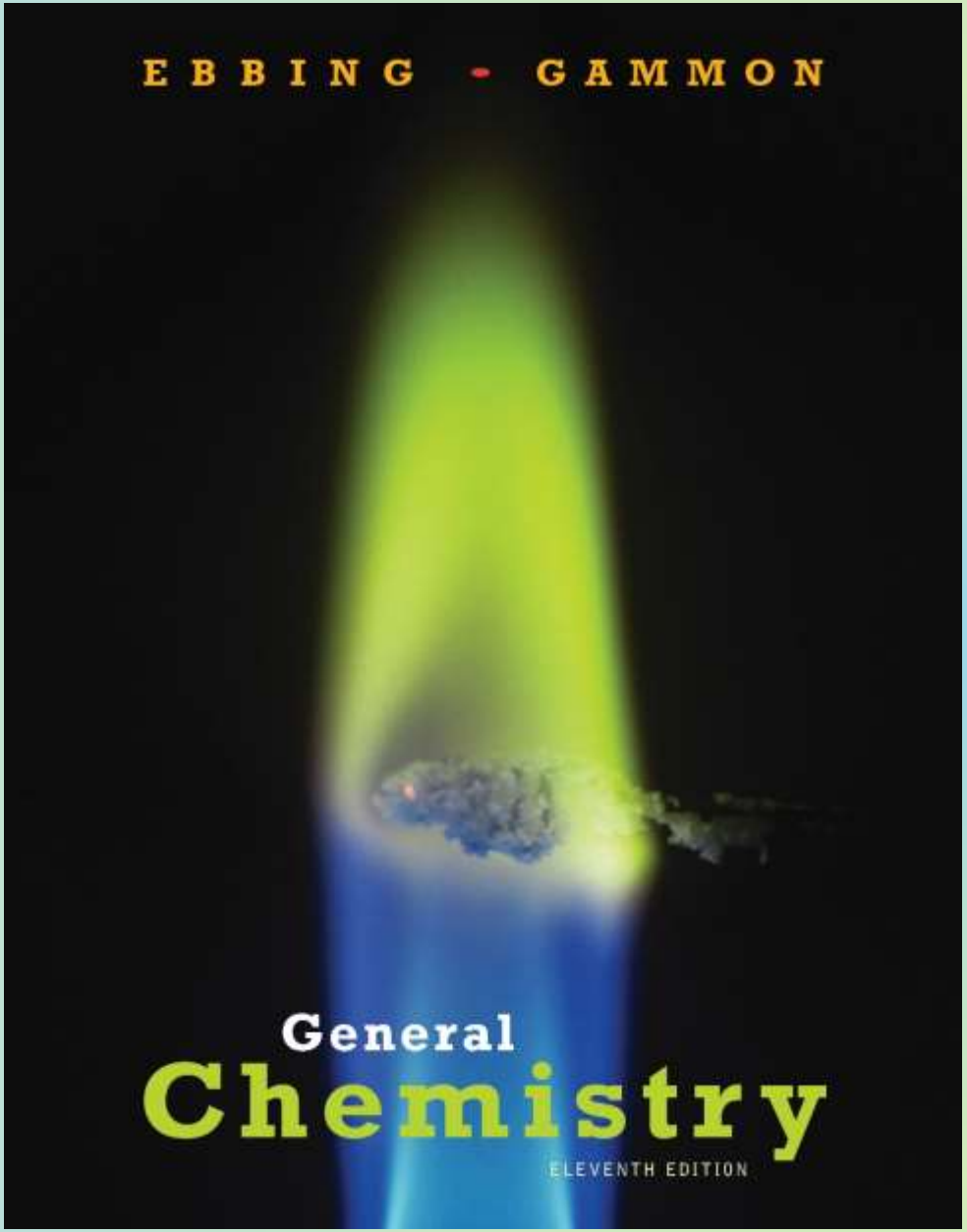
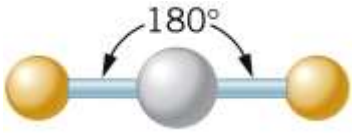
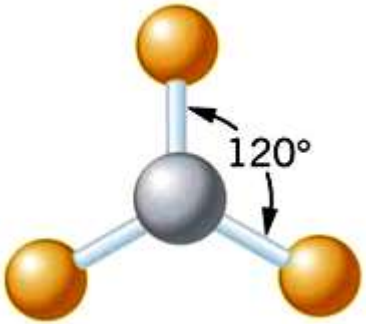
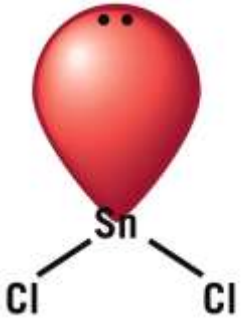
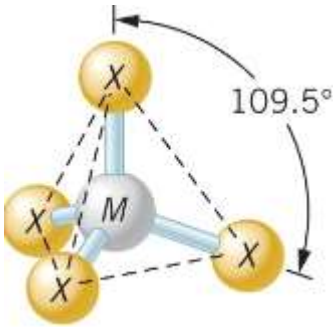
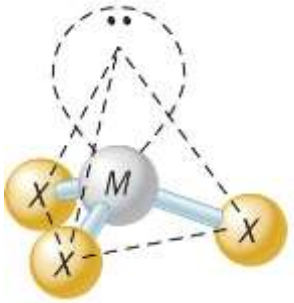
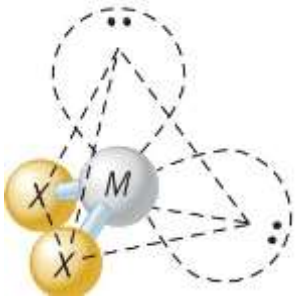
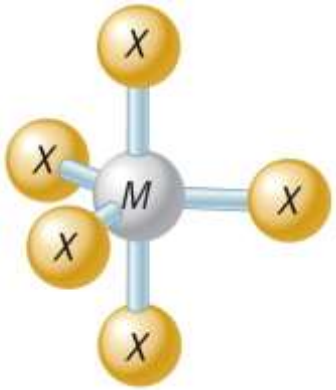
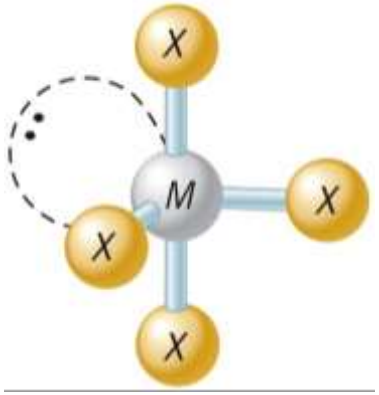


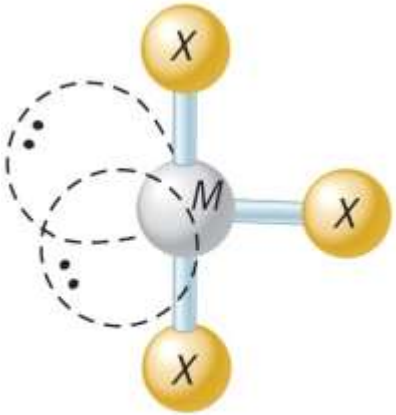
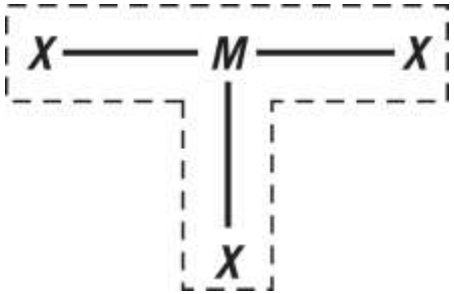
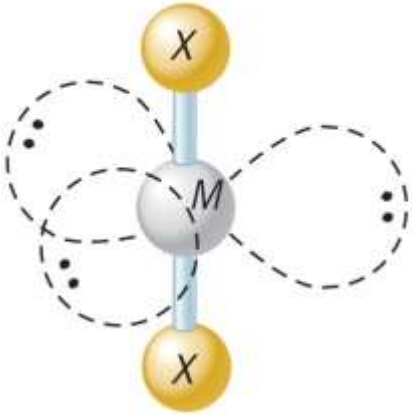

# Molecular Geometry and Chemical Bonding Theory

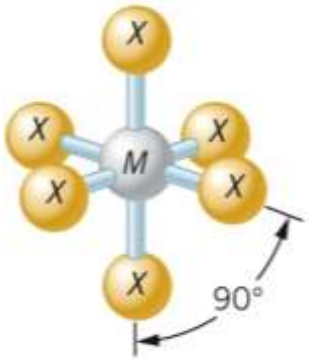
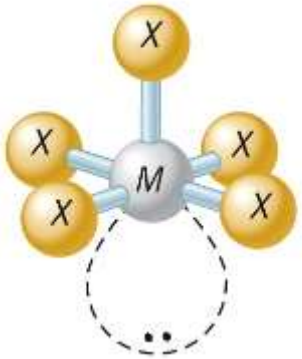
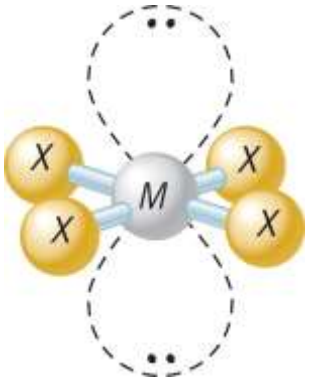
# 10.1 Valence-Shell Electron-Pair Repulsion (VSEPR) Model

| Number of Bonding Pairs | Number of Non-bonding Pairs (E) | Molecular Geometry | Molecular Shape |
|---|---|---|---|
| 2 | 0 |   | **$AX_2$ Linear** |
| 3 | 0 |   | **$AX_3$ Trigonal Planar** (**e.g.,** $BCl_3$) All bond angles 120° |
| 2 | 1 |   | **$AX_2E$ Bent** (**e.g.,** $SO_2$) Bond <120° |

| Number of Bonding Pairs | Number of Nonbonding Pairs (E) | Molecular Geometry | Molecular Shape |
|---|---|---|---|
| 4 | 0 |   | **$AX_4$ Tetrahedral** (**e.g.,** $CH_4$) All bond angles 109.5° |
| 3 | 1 |   | **$AX_3E$ Trigonal pyramidal** (**e.g.,** $NH_3$) Bond angle **less than** 109.5° |
| 2 | 2 |   | **$AX_2E_2$ bent** (**e.g.,** $H_2O$) Bond angle less than109.5° |

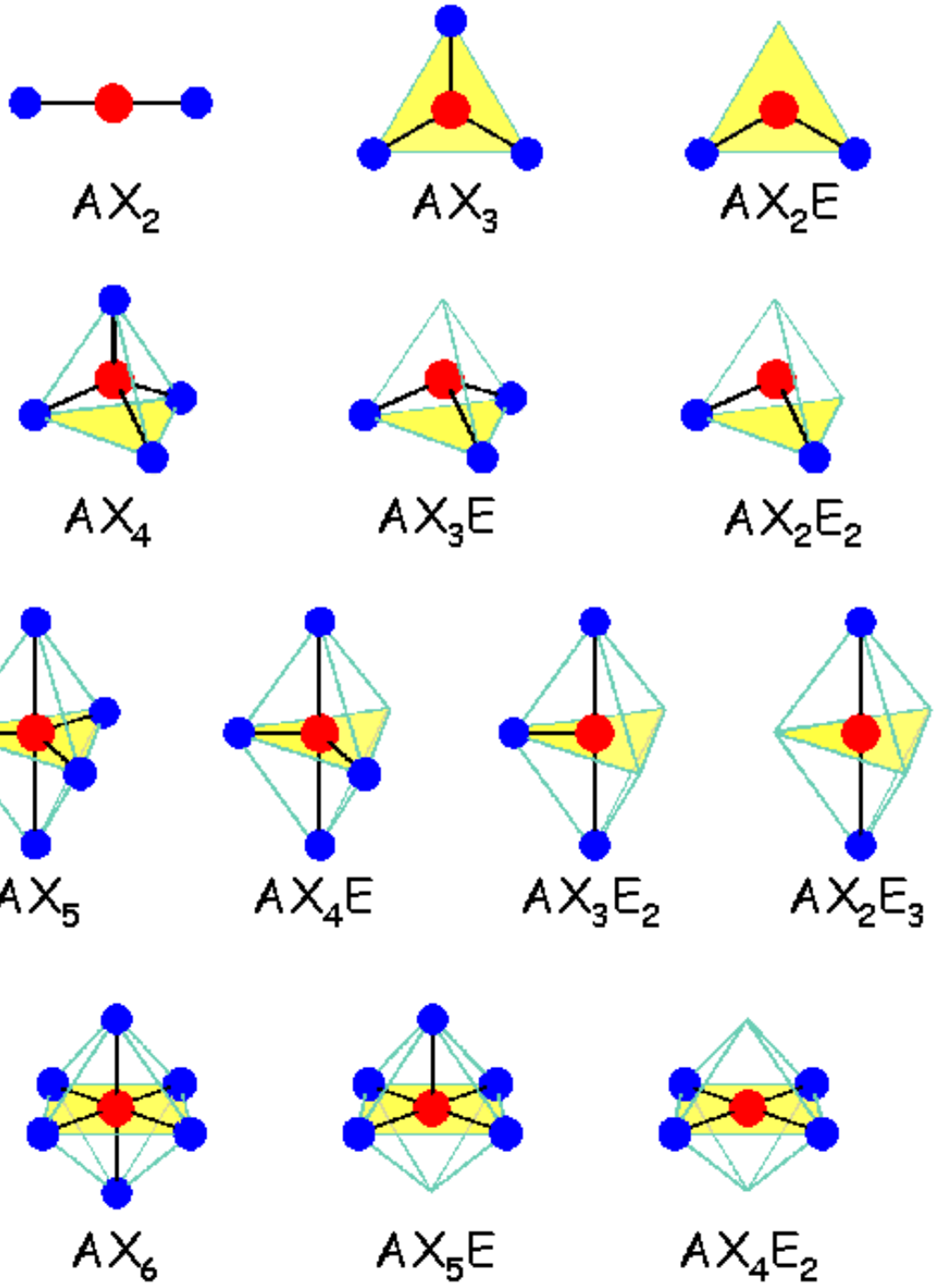
| Number of Bonding Pairs | Number of Nonbonding Pairs (E) | Molecular Geometry | Molecular Shape |
|---|---|---|---|
| 5 | 0 |  | **$AX_5$**<br>**Trigonal bipyramid**<br>(**e.g.,** $PF_5$)<br>**axial-equatorial** bond angles 90°<br>eq-eq 120°<br>ax-ax 180° |
| 4 | 1 |  | **$AX_4E$**<br>**Distorted Tetrahedron or Seesaw**<br>(**e.g.,** $SF_4$)<br>ax-eq bond angles < 90°<br>ax-ax 180° |

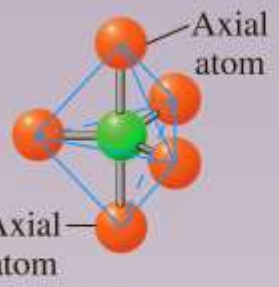
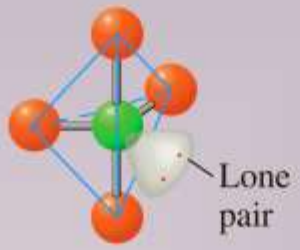
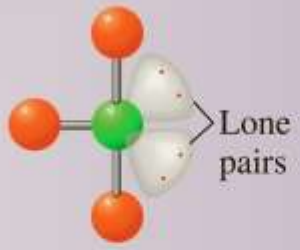
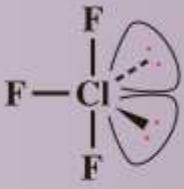
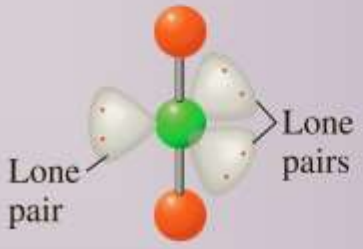
| Number of Bonding Pairs | Number of Nonbonding Pairs (E) | Molecular Geometry | Molecular Shape |
|---|---|---|---|
| 3 | 2 |  | **$AX_3E_2$ T-shape** (**e.g.,** $ClF_3$) Bond angles 90°  |
| 2 | 3 |  | **$AX_2E_3$ Linear** (**e.g.,** $I_3^-$) Bond angles 180° |

| Number of Bonding Pairs | Number of Nonbonding Pairs (E) | Molecular Geometry | Molecular Shape |
|---|---|---|---|
| 6 | 0 |  | **$AX_6$ Octahedral** (**e.g.,** $SF_6$) Bond angles 180°,90° |
| 5 | 1 |  | **$AX_5E$ Square Pyramidal** (**e.g.,** $BrF_5$) Bond angles 90° |
| 4 | 2 |  | **$AX_4E_2$ Square planar** (**e.g.,** $XeF_4$) Bond angles 90°, 180° |

# Summary of Molecular Geometries

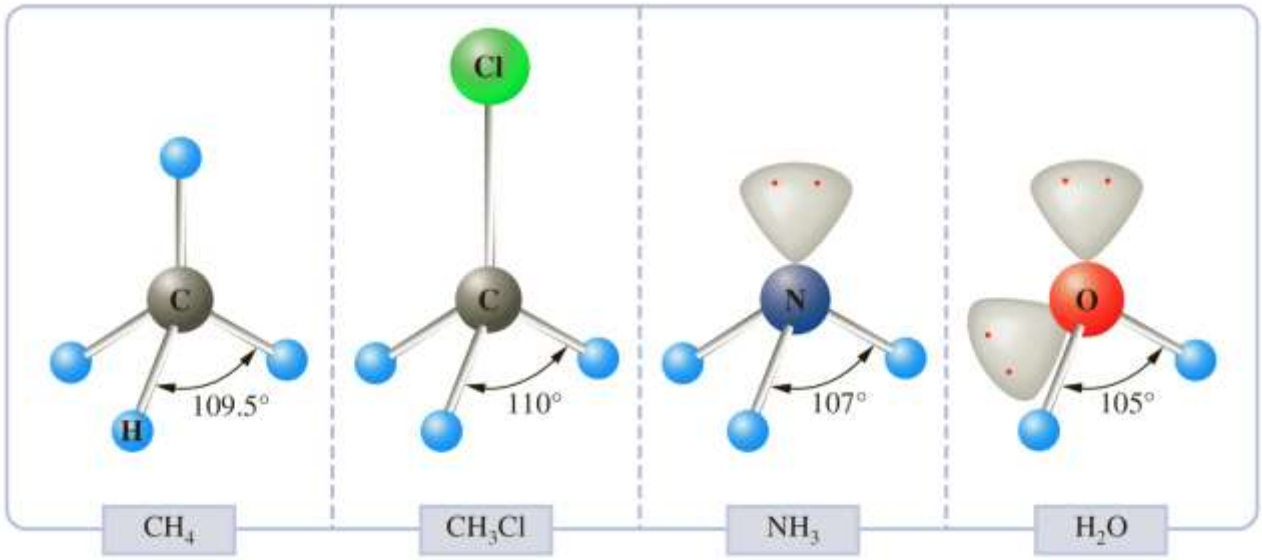
- ✓ **VSEPR is based on minimizing electron repulsion in the molecule**
- ✓ The direction in space of the bonding pairs gives the molecular geometry



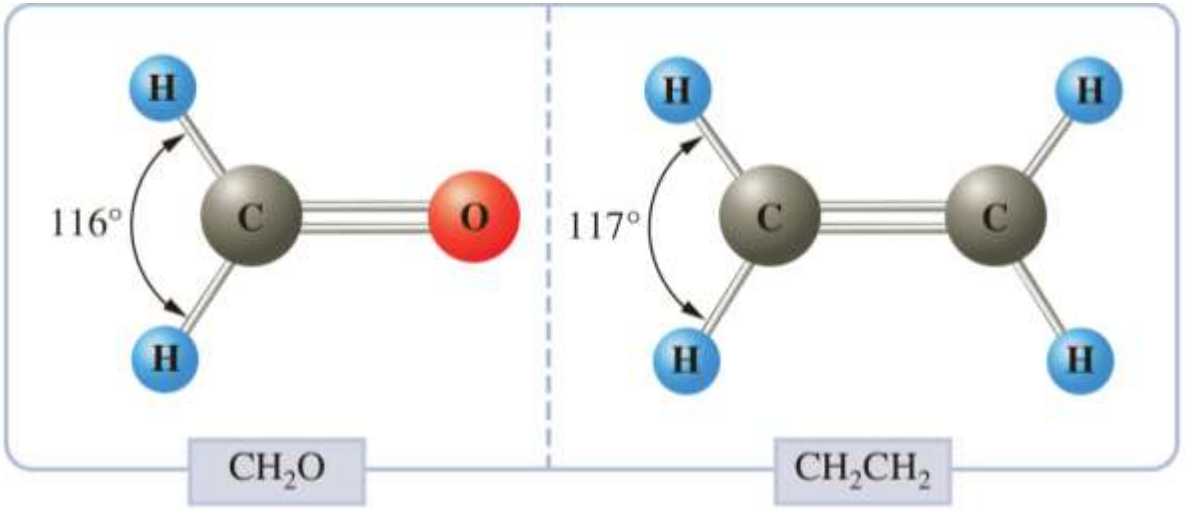
| Electron Pairs | | | Arrangement of Pairs | Molecular Geometry | | Example | |
|---|---|---|---|---|---|---|---|
| Total | Bonding | Lone | | | | | |
| 5 | 5 | 0 | Trigonal bipyramidal | Trigonal bipyramidal $AX_5$ |   | $PCl_5$ |   |
| | 4 | 1 | | Seesaw (or distorted tetrahedron) $AX_4$ |   | $SF_4$ |   |
| | 3 | 2 | | T-shaped $AX_3$ |   | $ClF_3$ |   |
| | 2 | 3 | | Linear $AX_2$ |   | $XeF_2$ |   |

# ➢ Bond Angles and the Effect of Lone Pairs

✓ *A lone pair require more space than a bonding pair.*




✓ *Multiple bonds require more space than single bonds because of the greater number of electrons.*

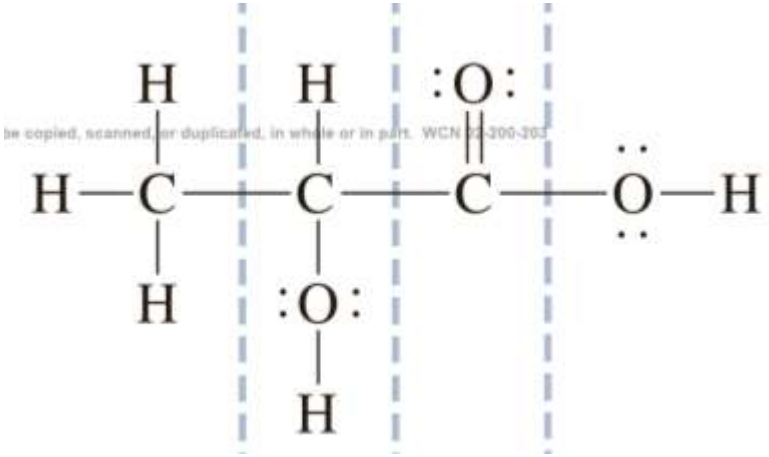


(Q) Predict the geometry of the following molecules or ions, using the VSEPR method:

**a. $BeCl_2$ b. $NO_2^-$ c. $SiCl_4$ d. $ClO_3^-$ e. $OF_2$**

**f. $TeCl_4$ g. $ICl_3$**

## ➢ Applying the VSEPR Model to Larger Molecules

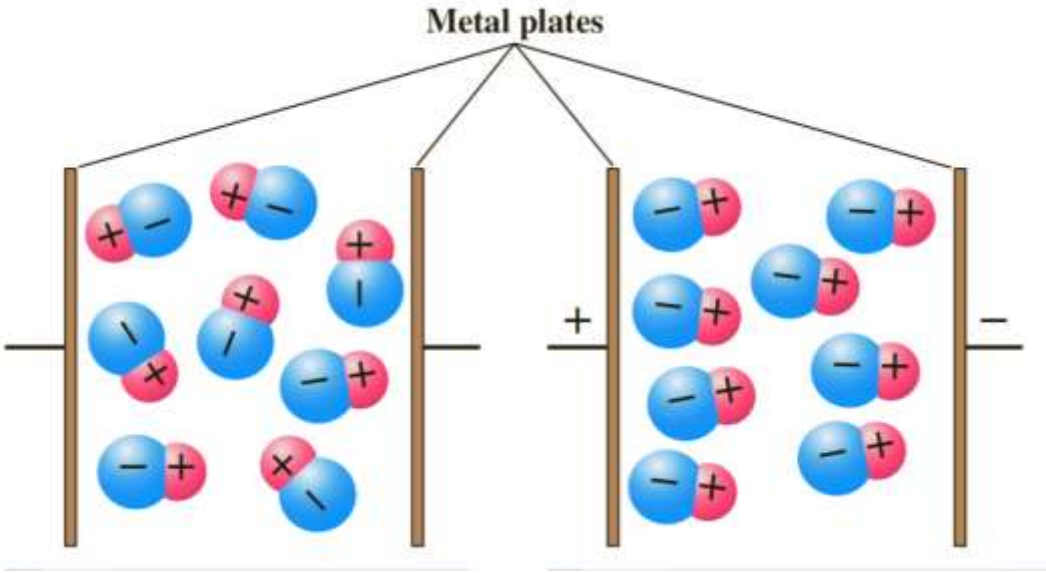




| 1 IA | | | | | | | | | | | | 13 IIIA | 14 IVA | 15 VA | 16 VIA | 17 VIIA | 18 VIIIA |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 H Hydrogen 1.008 | 2 IIA | | | | | | | | | | | | | | | | 2 He Helium 4.002602 |
| 3 Li Lithium 6.94 | 4 Be Beryllium 9.0121831 | | | | | | | | | | | 5 B Boron 10.81 | 6 C Carbon 12.011 | 7 N Nitrogen 14.007 | 8 O Oxygen 15.999 | 9 F Fluorine 18.998403163 | 10 Ne Neon 20.1797 |
| 11 Na Sodium 22.98976928 | 12 Mg Magnesium 24.305 | 3 IIIB | 4 IVB | 5 VB | 6 VIB | 7 VIIB | 8 VIIIB | 9 VIIIB | 10 VIIIB | 11 IB | 12 IIB | 13 Al Aluminium 26.9815385 | 14 Si Silicon 28.085 | 15 P Phosphorus 30.973761998 | 16 S Sulfur 32.06 | 17 Cl Chlorine 35.45 | 18 Ar Argon 39.948 |
| 19 K Potassium 39.0983 | 20 Ca Calcium 40.078 | 21 Sc Scandium 44.955908 | 22 Ti Titanium 47.867 | 23 V Vanadium 50.9415 | 24 Cr Chromium 51.9961 | 25 Mn Manganese 54.938044 | 26 Fe Iron 55.845 | 27 Co Cobalt 58.933194 | 28 Ni Nickel 58.6934 | 29 Cu Copper 63.546 | 30 Zn Zinc 65.38 | 31 Ga Gallium 69.723 | 32 Ge Germanium 72.630 | 33 As Arsenic 74.921595 | 34 Se Selenium 78.971 | 35 Br Bromine 79.904 | 36 Kr Krypton 83.798 |
| 37 Rb Rubidium 85.4678 | 38 Sr Strontium 87.62 | 39 Y Yttrium 88.90584 | 40 Zr Zirconium 91.224 | 41 Nb Niobium 92.90637 | 42 Mo Molybdenum 95.95 | 43 Tc Technetium (98) | 44 Ru Ruthenium 101.07 | 45 Rh Rhodium 102.90550 | 46 Pd Palladium 106.42 | 47 Ag Silver 107.8682 | 48 Cd Cadmium 112.414 | 49 In Indium 114.818 | 50 Sn Tin 118.710 | 51 Sb Antimony 121.760 | 52 Te Tellurium 127.60 | 53 I Iodine 126.90447 | 54 Xe Xenon 131.293 |

# 10.2 Dipole Moment and Molecular Geometry

✓ Alignment of polar molecules by an electric field




✓ **dipole moment** is *a quantitative measure of the degree of charge separation in* ***a molecule*** *and is therefore an indicator of the polarity of the molecule*

$$\mu = q \times d$$

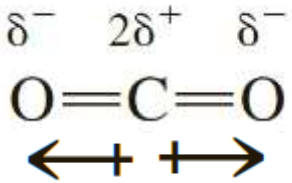
$q$ = positive charge

$-q$ = negative charge

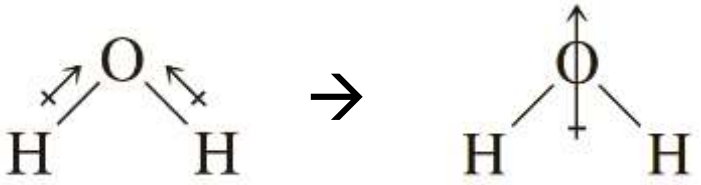
$d$ = distance

**10.43** $AsF_3$ has a dipole moment of 2.59 D. Which of the following geometries are possible: trigonal planar, trigonal pyramidal, or T-shaped?

- ✓ dipole moment of HCl is 1.08 D.
- ✓ SI units: coulomb x meter (C·m)
- ✓ 1 D = 3.34 x $10^{-30}$ C·m




bond dipole




- ✓ (linear, trigonal planar, and tetrahedral) give molecules of zero dipole moment; that is, the molecules are ***nonpolar***

**Table 10.1** Relationship Between Molecular Geometry and Dipole Moment

| Formula | Molecular Geometry | Dipole Moment* |
|---|---|---|
| AX | Linear | Can be nonzero |
| $AX_2$ | Linear | Zero |
| | Bent | Can be nonzero |
| $AX_3$ | Trigonal planar | Zero |
| | Trigonal pyramidal | Can be nonzero |
| | T-shaped | Can be nonzero |
| $AX_4$ | Tetrahedral | Zero |
| | Square planar | Zero |
| | Seesaw | Can be nonzero |
| $AX_5$ | Trigonal bipyramidal | Zero |
| | Square pyramidal | Can be nonzero |
| $AX_6$ | Octahedral | Zero |

Exercise 10.4 Which of the following would be expected to have a dipole moment of zero? Explain

a. $SOCl_2$ b. $SiF_4$ c. $OF_2$

(Q) Explain why the dipole moment of $NF_3$ = 0.2 D, while that of $NH_3$ =1.47 D

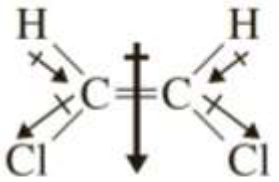
**10.45** Which of the following molecules would be expected to have zero dipole moment on the basis of their geometry?

a $CS_2$ b $TeF_2$ c $SeCl_4$ d $XeF_4$

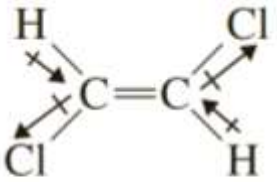
**10.46** Which of the following molecules would be expected to have a dipole moment of zero because of symmetry?

a $BeBr_2$ b $H_2Se$ c $AsF_3$ d $SeF_6$

- **Effect of Polarity on Molecular Properties**




*cis*-1,2-Dichloroethene




*trans*-1,2-Dichloroethene

| | | |
|---|---|---|
| Dipole moment: | 1.9 D | 0 D |
| B.P (°C) | 60.2 | 48.5 |

# 10.3 Valence Bond Theory

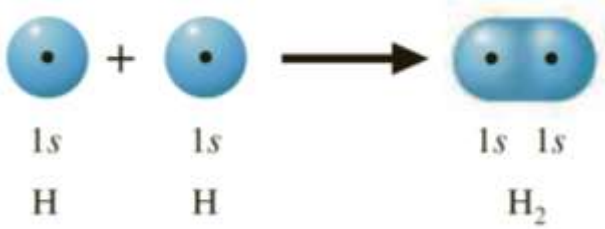
## ➢ Basic Theory

A bond forms between two atoms when the following conditions are met:

1. The orbitals containing the electrons *overlap*.
2. The sum of the electrons in both orbitals is no more than two.

$H + H \rightarrow H_2$

$1s^1 \quad 1s^1 \rightarrow$ Total 2e in the newly formed $H_2$ orbital




$He + He \rightarrow He_2$ (does not occur)

$1s^2 \quad 1s^2 \rightarrow$ Total 4e (XXXXX)

X

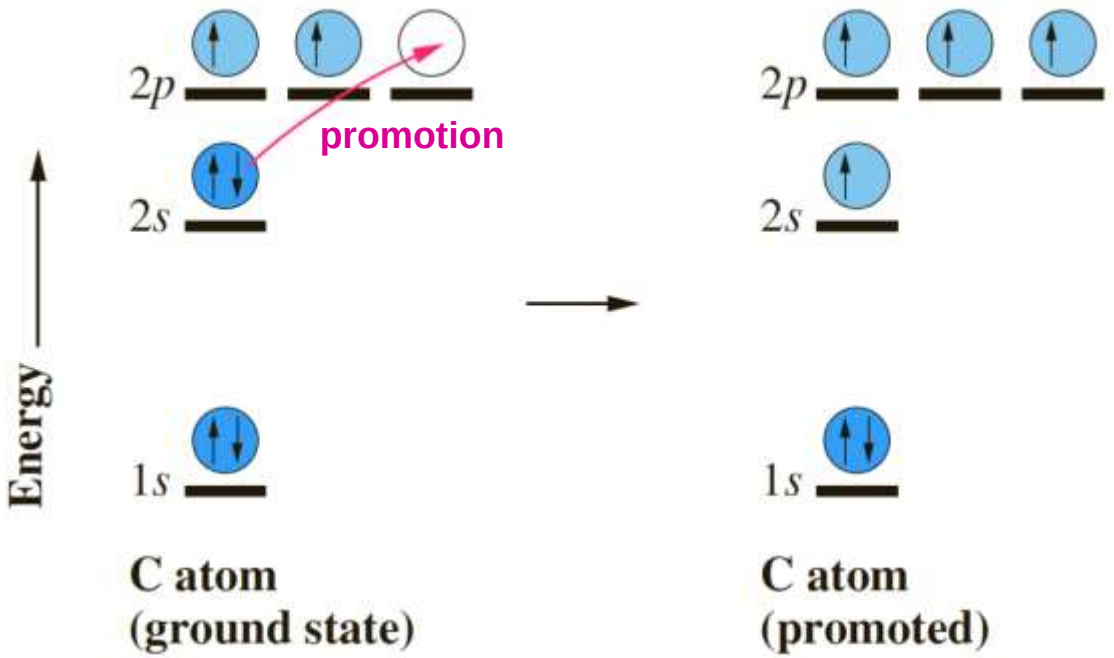
✓ The strength of bonding depends on orbital overlap.

✓ *To obtain maximum overlap,* orbitals other than *s* bond only in given directions.


## ➢ Bonding in HCl

H: $1s^1$ Cl: $1s^2 2s^2 2p^6 3s^2 3p^5$

- **Hybrid Orbitals**
- ✓ **Bonding in $CH_4$**

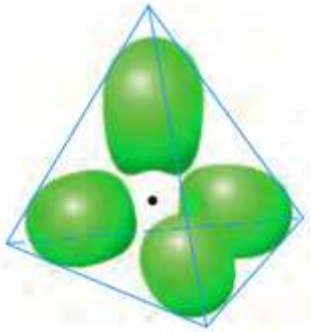



- ✓ Experiment shows that the four C-H bonds in $CH_4$ are identical. This implies that the carbon orbitals involved in bonding are also equivalent.

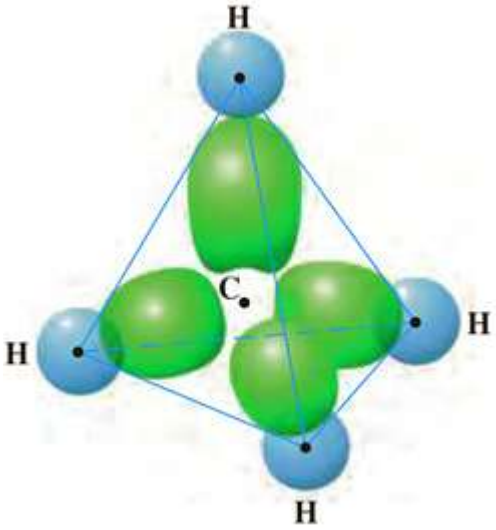
- ✓ → **Hybrid orbitals are used**


- ✓ *The number of hybrid orbitals formed always equals the number of atomic orbitals used.*

- ✓ Shape of a single $sp^3$ hybrid orbital.
- ✓ Each orbital consists of two lobes. One lobe is small, but dense, and concentrated near the nucleus.
- ✓ The other lobe is large, but diffuse.
- ✓ Bonding occurs with the large lobe, since it extends farther from the nucleus.



- ✓ Four hybrid orbitals are arranged tetrahedrally in space. (Small lobes are omitted here for clarity, and large lobes are stylized and greatly narrowed for ease in depicting the directional bonding.)




- ✓ Bonding in $CH_4$.
- ✓ Each C—H bond is formed by the overlap of:
- ✓ 1s orbital from a hydrogen atom **+** one $sp^3$ hybrid orbital of the carbon atom.

- ✓ **Number of hybrid orbitals formed = number of atomic orbitals used.**

$s + p \rightarrow 2 \times sp$

$s + 2p \rightarrow 3 \times sp^2$

$s + 3p \rightarrow 4 \times sp^3$

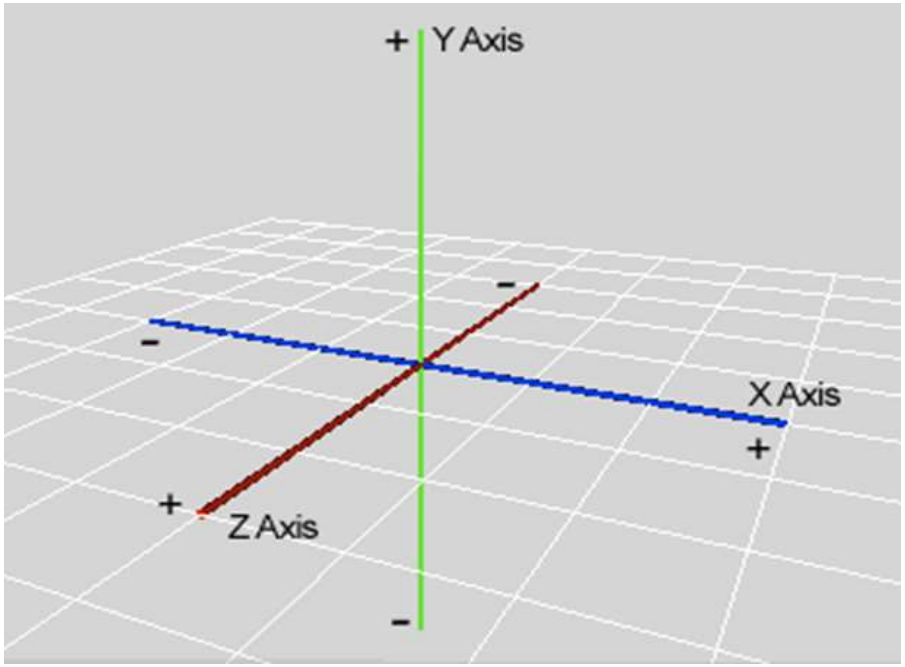
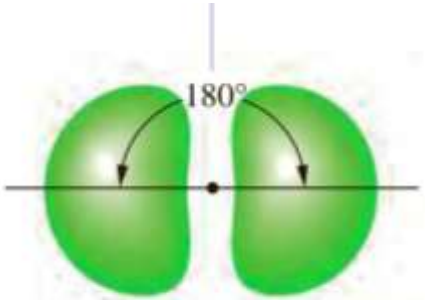
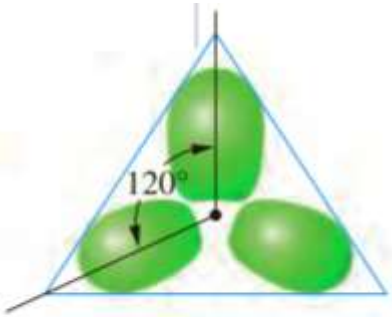
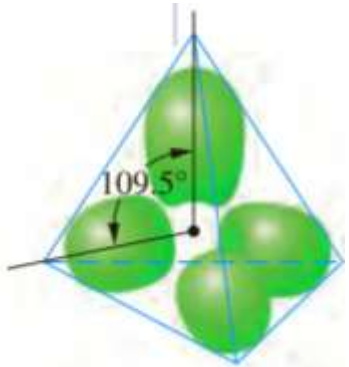



**Table 10.2** Kinds of Hybrid Orbitals

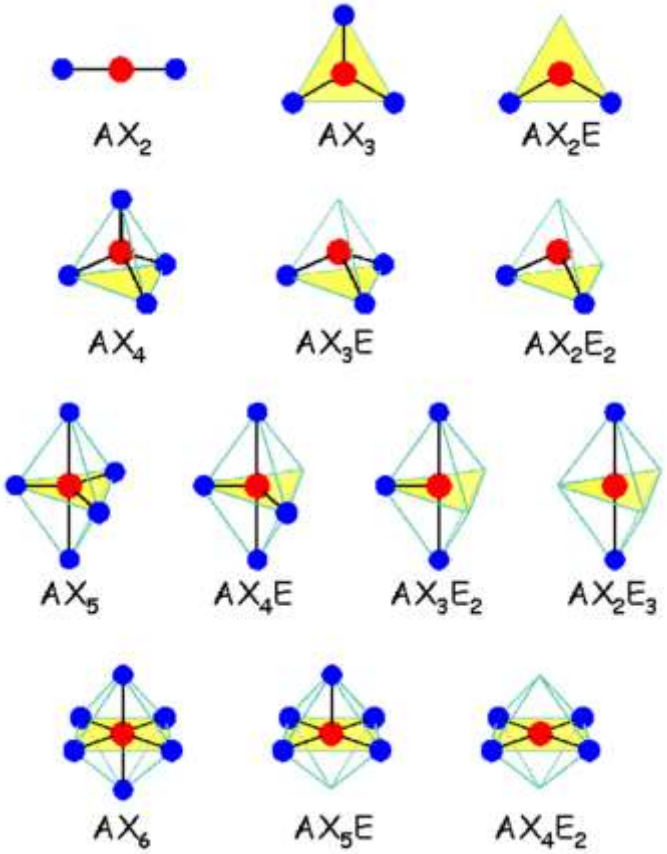
| Hybrid Orbitals | Geometric Arrangement | Number of Orbitals | Example |
|---|---|---|---|
| *sp* | Linear | 2 | Be in $BeF_2$ |
| $sp^2$ | Trigonal planar | 3 | B in $BF_3$ |
| $sp^3$ | Tetrahedral | 4 | C in $CH_4$ |



# How to figure out the hybridization via Lewis structures !

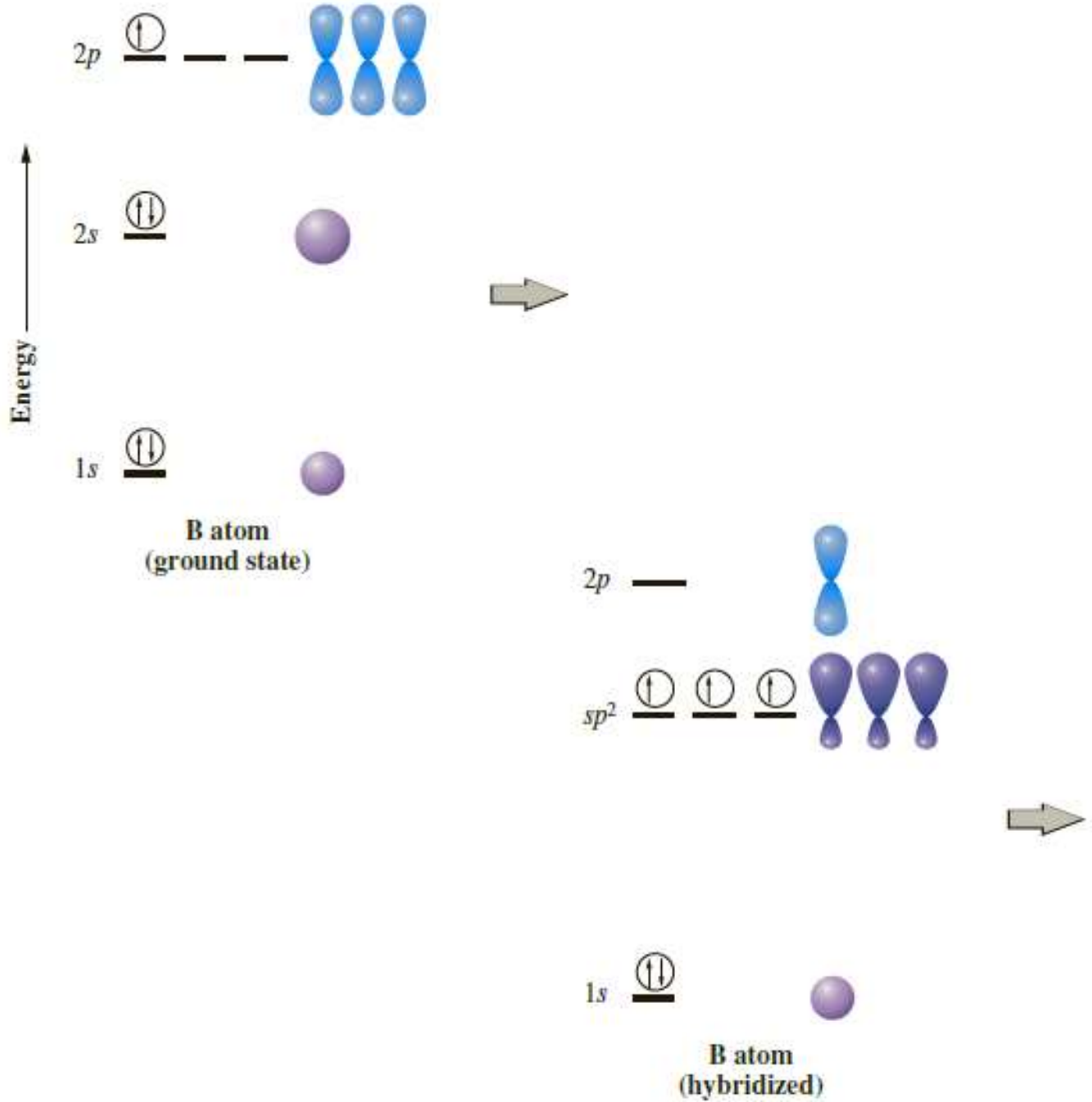



- **More Than Eight Electrons About a Central Atom**

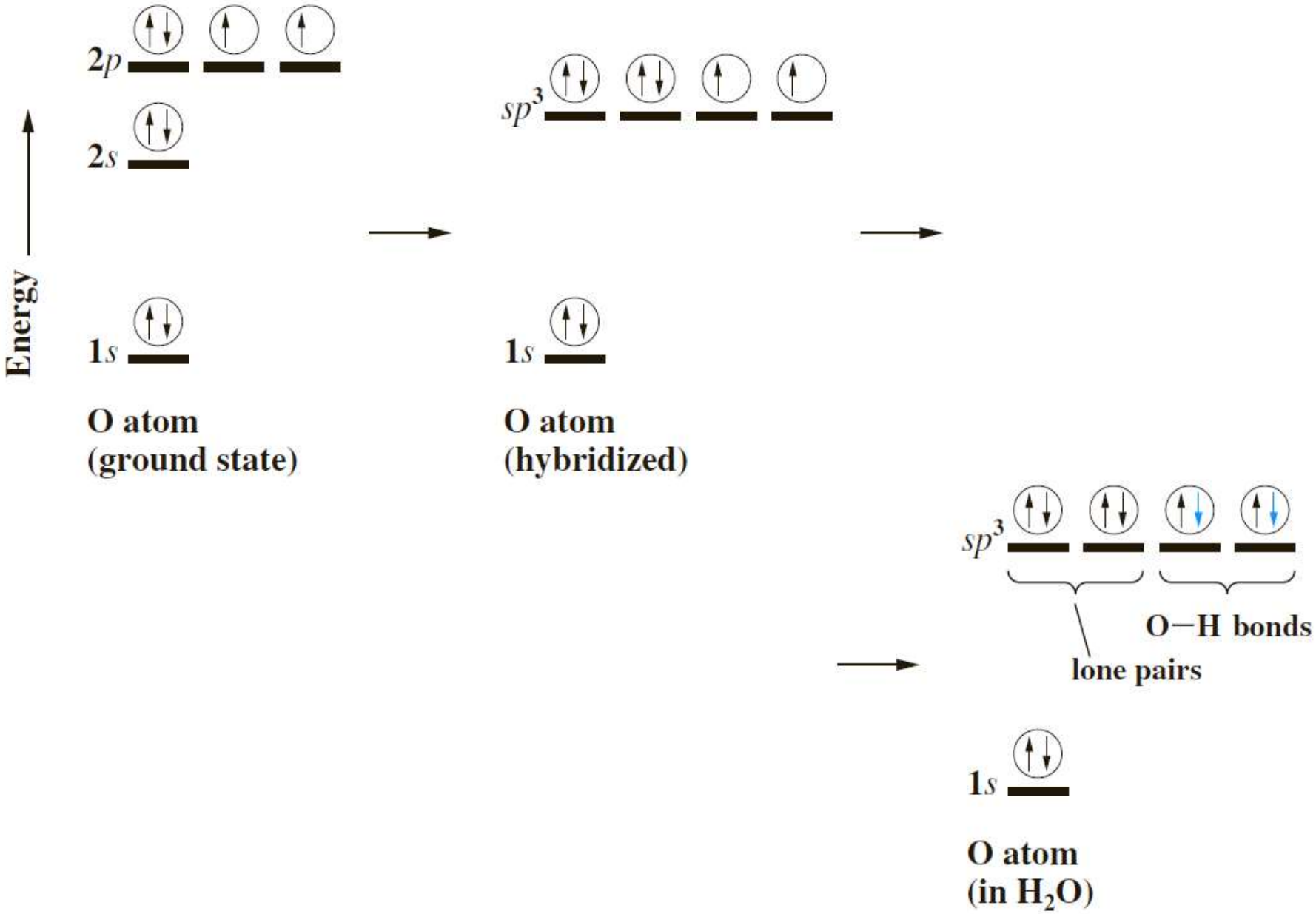
$PF_5$ → $sp^3d$

$SF_6$ → $sp^3d^2$

- Hybridization in $BF_3$



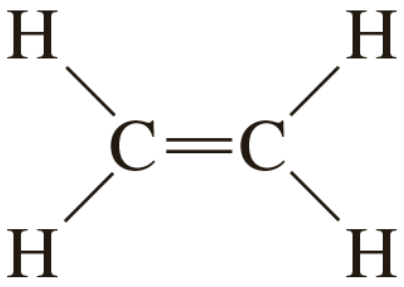
- Hybridization in $H_2O$

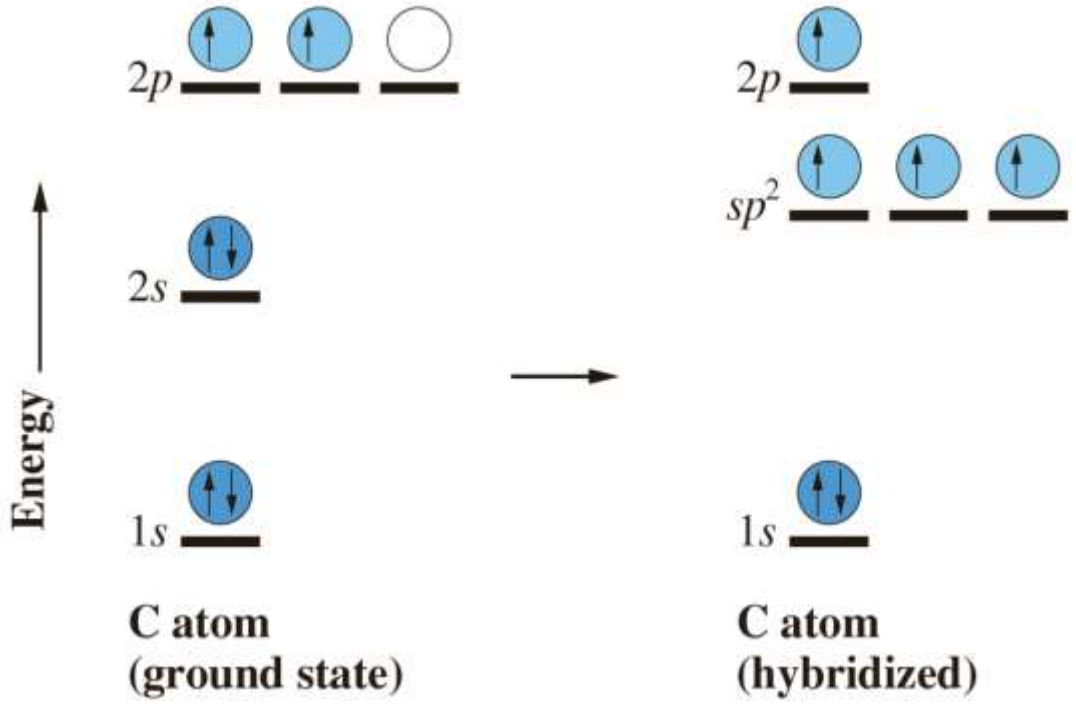


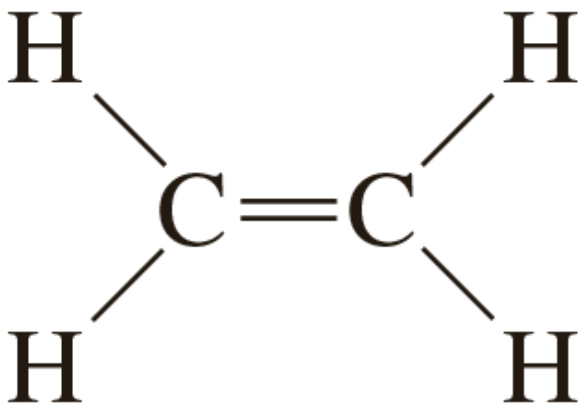
# 10.4 Description of Multiple Bonding

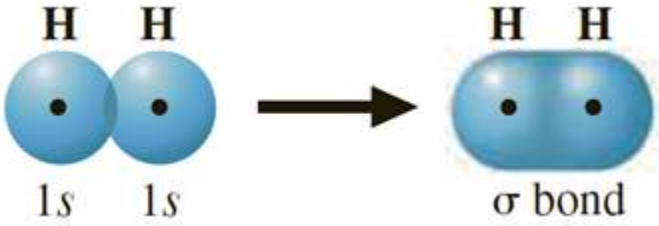
- ✓ More than one orbital from each bonding atom might overlap
- ✓ One hybrid orbital is needed for each bond (whether a single or a multiple bond) and for each lone pair

➢ **Bonding in ethylene $H_2C=CH_2$**

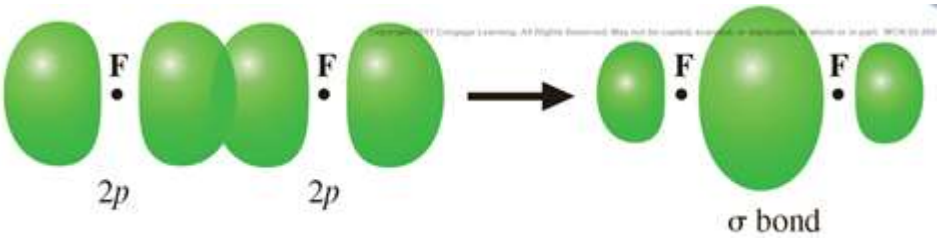


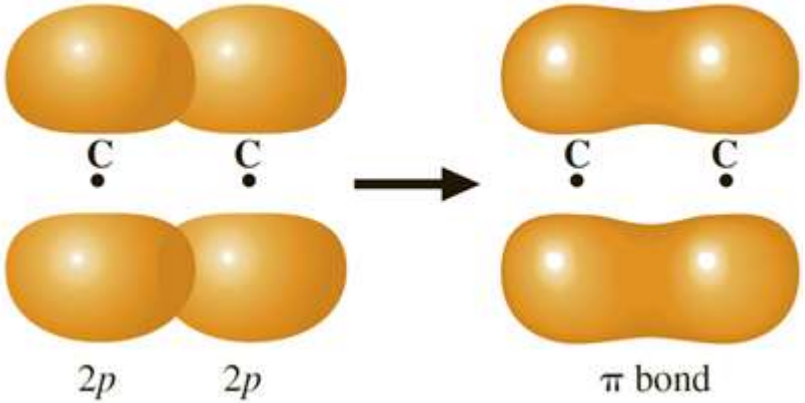

H
H
C
C
H
H




The formation of a σ bond by the overlap of two *s* orbitals.

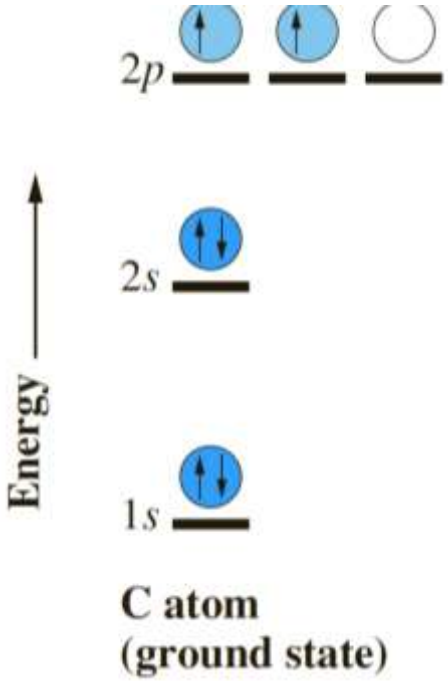



A σ bond can also be formed by the overlap of two *p* orbitals along their axes.



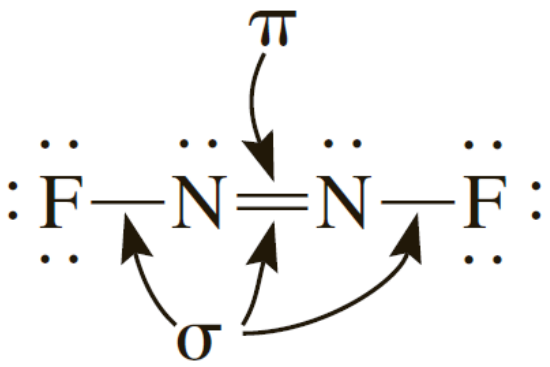

When two *p* orbitals overlap sideways, a π bond is formed.

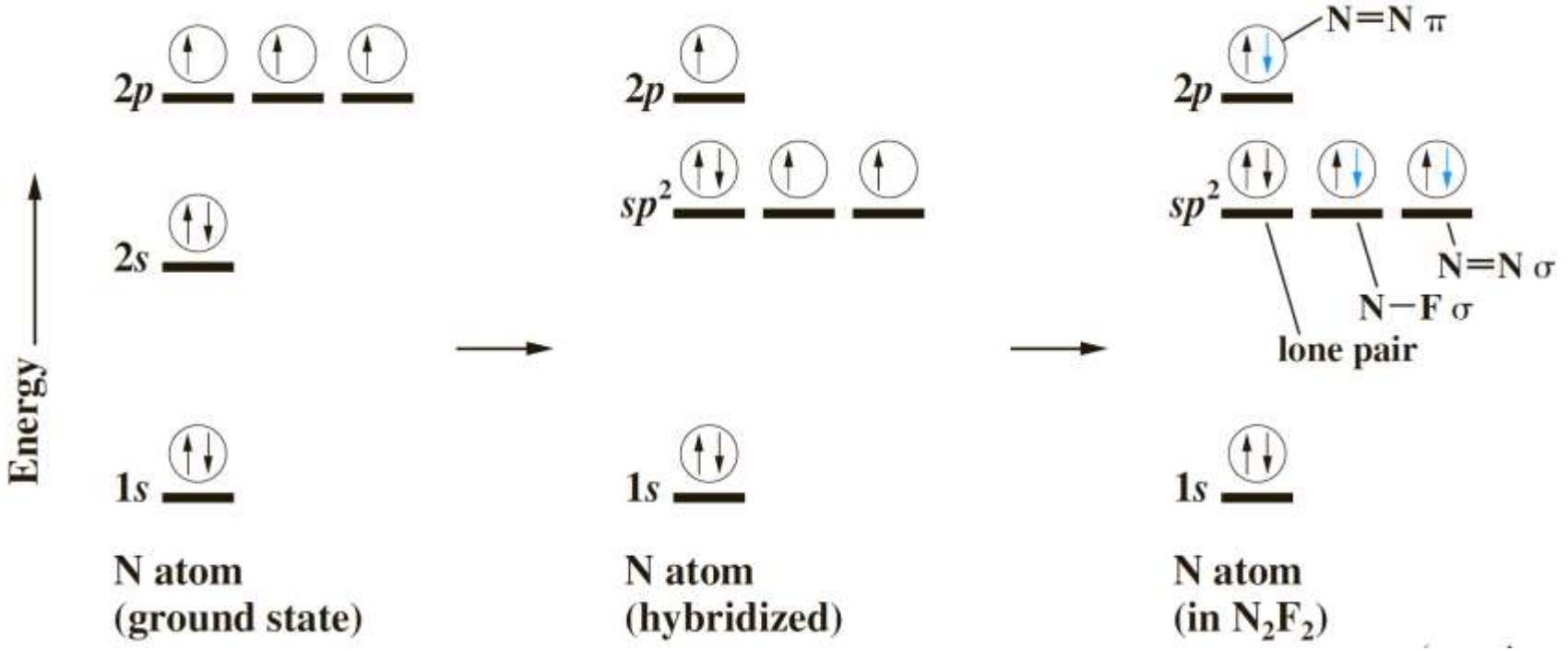
## ➢ Bonding in acetylene H—C≡C—H




H—C≡C—H

(Q) Describe the bonding on a given N atom in dinitrogen difluoride, $N_2F_2$, using valence bond theory.



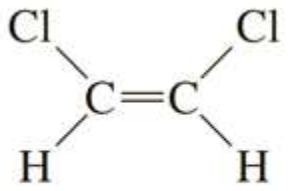



**10.53** **a** Carbonyl fluoride, $COF_2$, is an extremely poisonous gas used in organofluorine synthesis. Give the valence bond description of the carbonyl fluoride molecule. (Both fluorine atoms are attached to the carbon atom.) **b** Nitrogen, $N_2$, makes up about 80% of the earth's atmosphere. Give the valence bond description of this molecule.

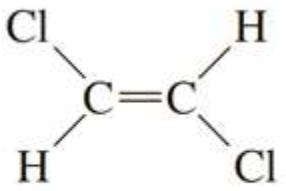
10.54 HN=NH

10.55 HCN

✓ *Isomers* are compounds of the same molecular formula but with different arrangements of the atoms.



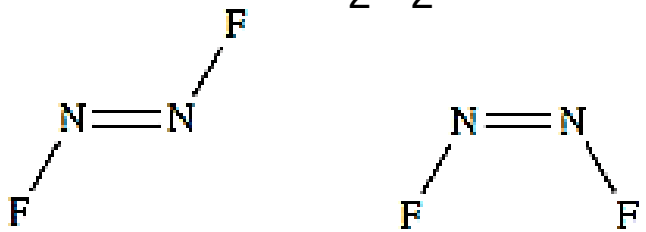

*cis*-1,2-Dichloroethene




*trans*-1,2-Dichloroethene

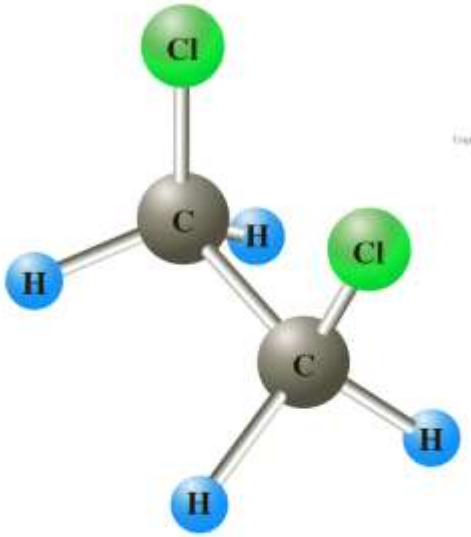
| | | |
|---|---|---|
| Dipole moment: | 1.9 D | 0 D |
| B.P (°C) | 60.2 | 48.5 |

✓ *cis* and *trans* isomers of $N_2F_2$

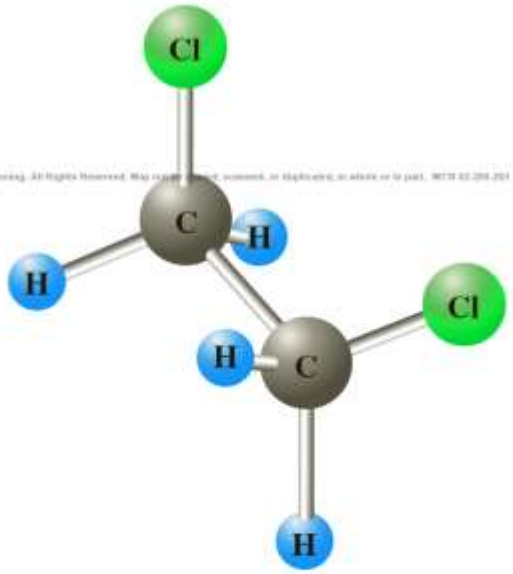



*trans* *cis*

✓ Lack of geometric isomers in 1,2-dichloroethane




a Because of rotation about the carbon–carbon bond in 1,2-dichloroethane, geometric isomers are not possible.




b Note that the molecule pictured at the left can be twisted easily to give the molecule pictured here.