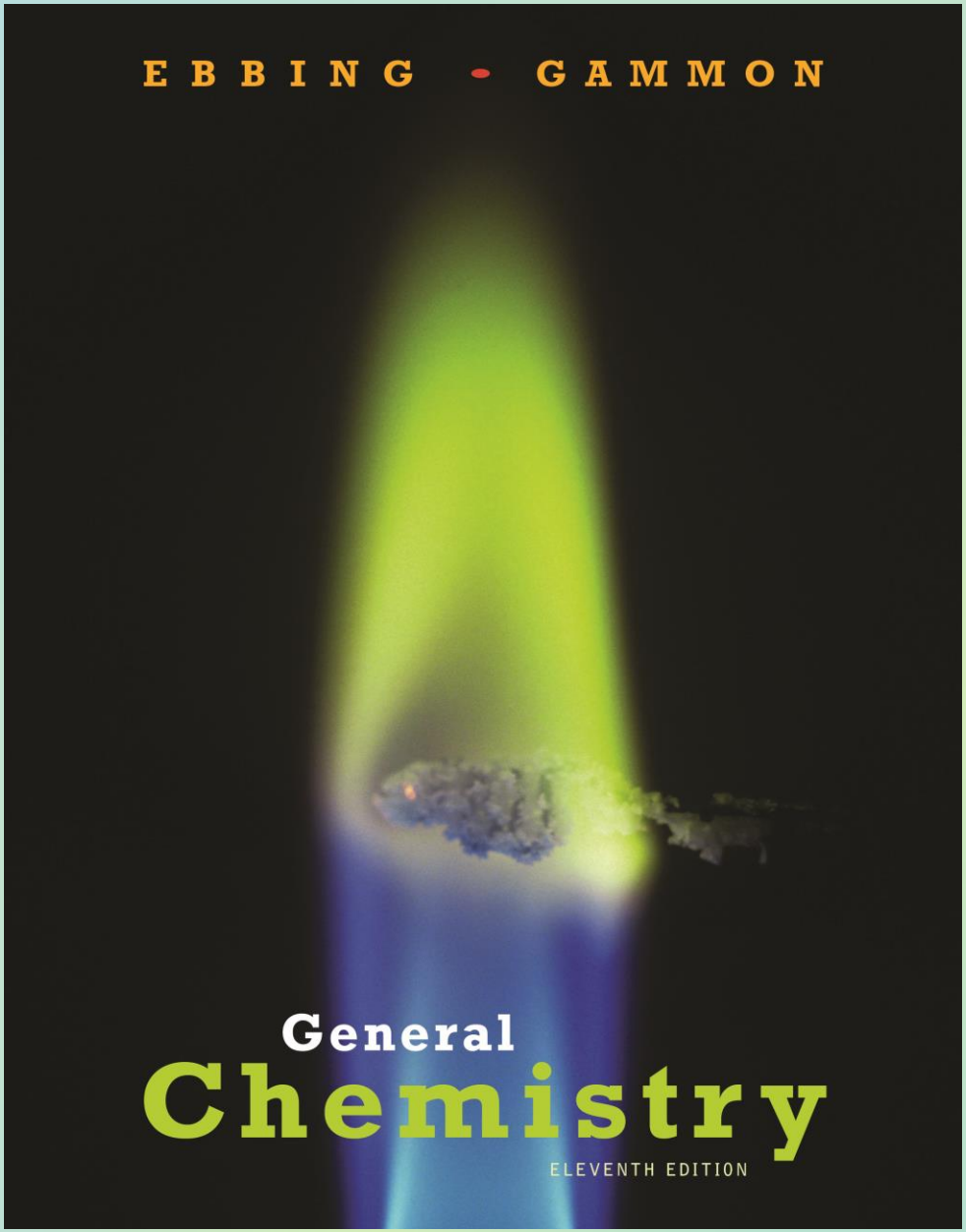
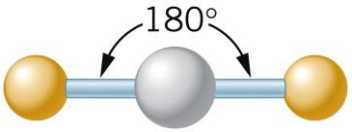
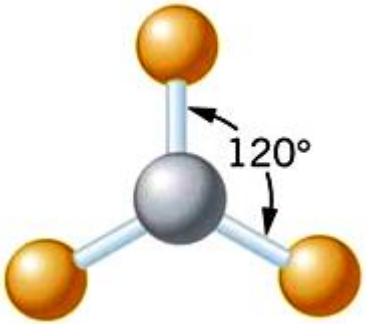
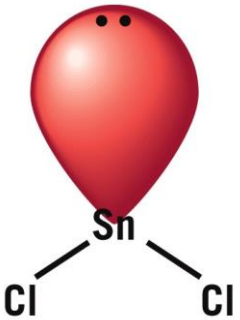
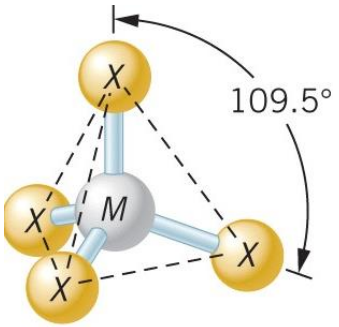
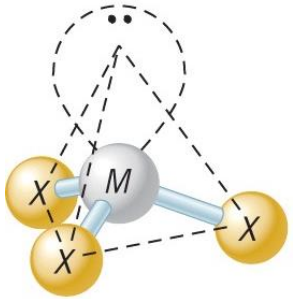
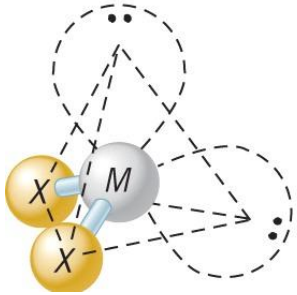
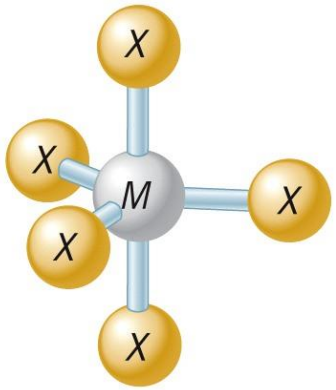
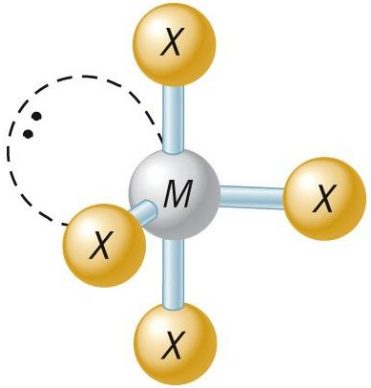


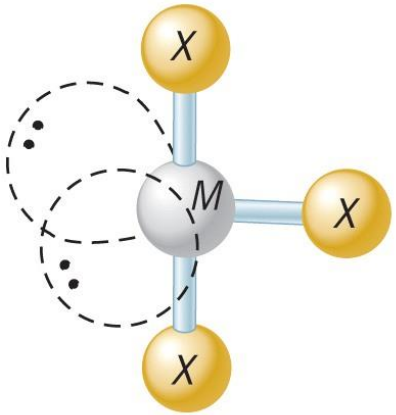
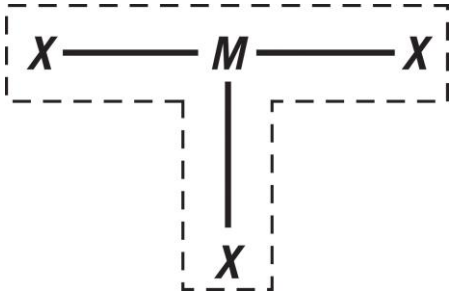
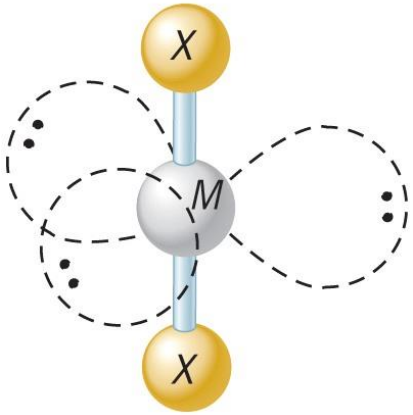
Molecular Geometry and Chemical Bonding Theory

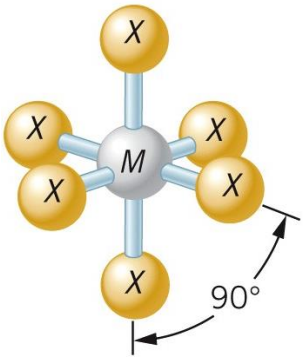
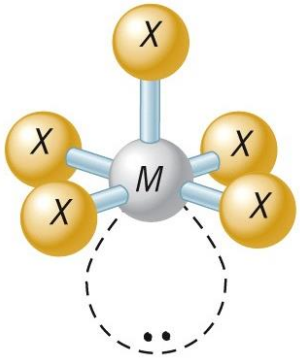
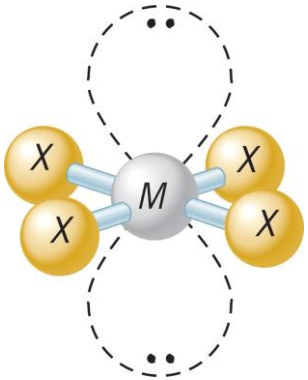
10.1 Valence-Shell Electron-Pair Repulsion (VSEPR) Model

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°

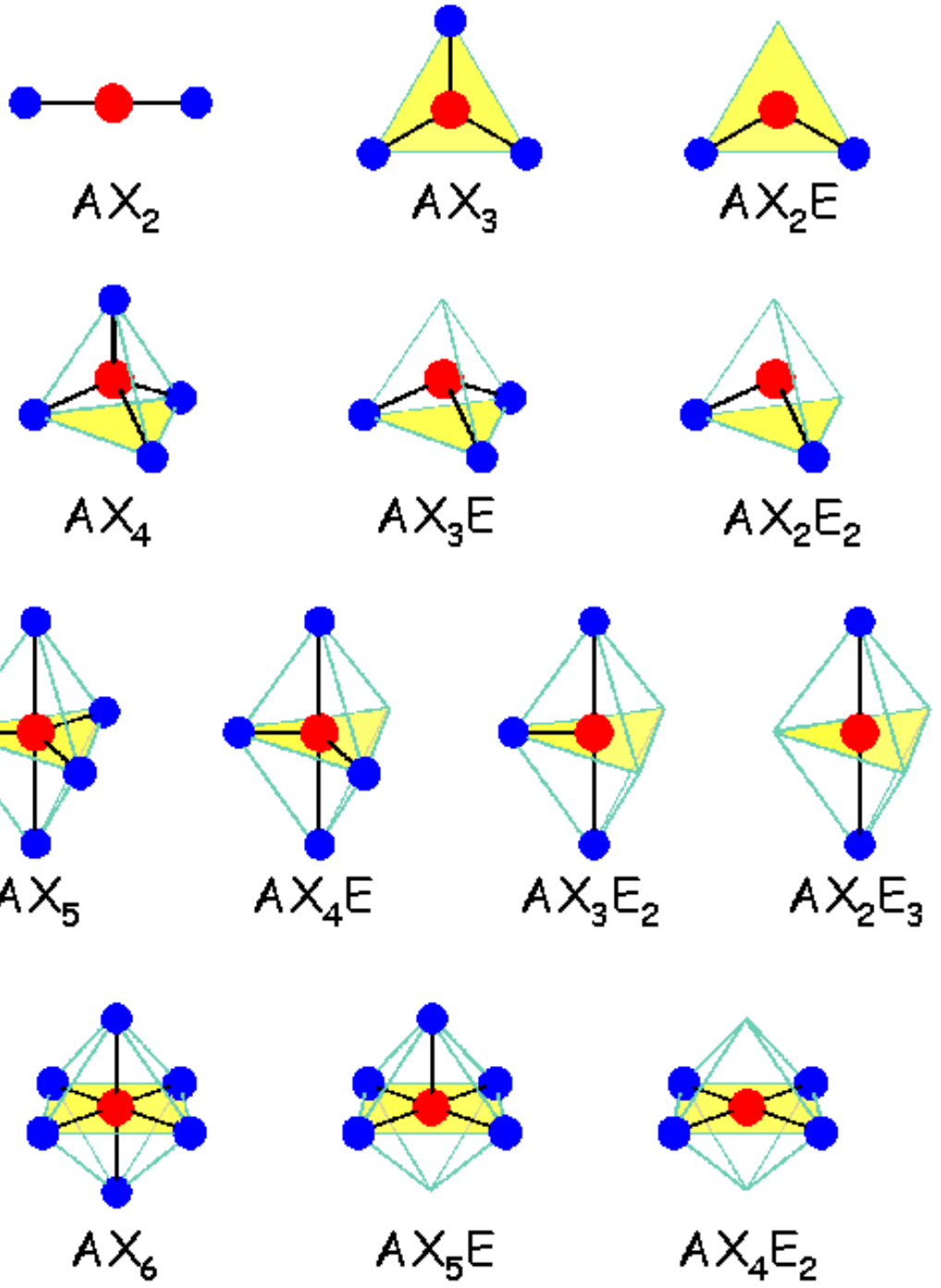
Number of Bonding Pairs	Number of Nonbonding Pairs (E)	Molecular Geometry	Molecular Shape
5	0		**AX_5** **Trigonal bipyramid** (**e.g.,** PF_5) **axial-equatorial** bond angles 90° eq-eq 120° ax-ax 180°
4	1		**AX_4E** **Distorted Tetrahedron or Seesaw** (**e.g.,** SF_4) ax-eq bond angles < 90° ax-ax 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		**Octahedral** (**e.g.,** SF_6) Bond angles 180°,90°
5	1		**Square Pyramidal** (**e.g.,** BrF_5) Bond angles 90°
4	2		**Square planar** (**e.g.,** XeF_4) Bond angles 90°, 180°

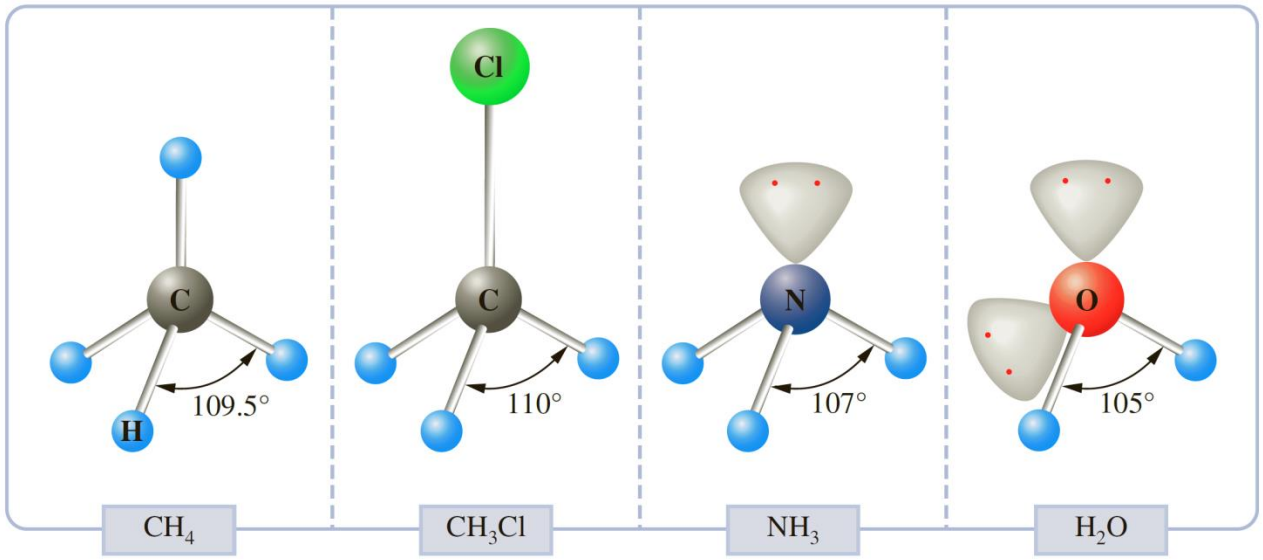
Summary of Molecular Geometries

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

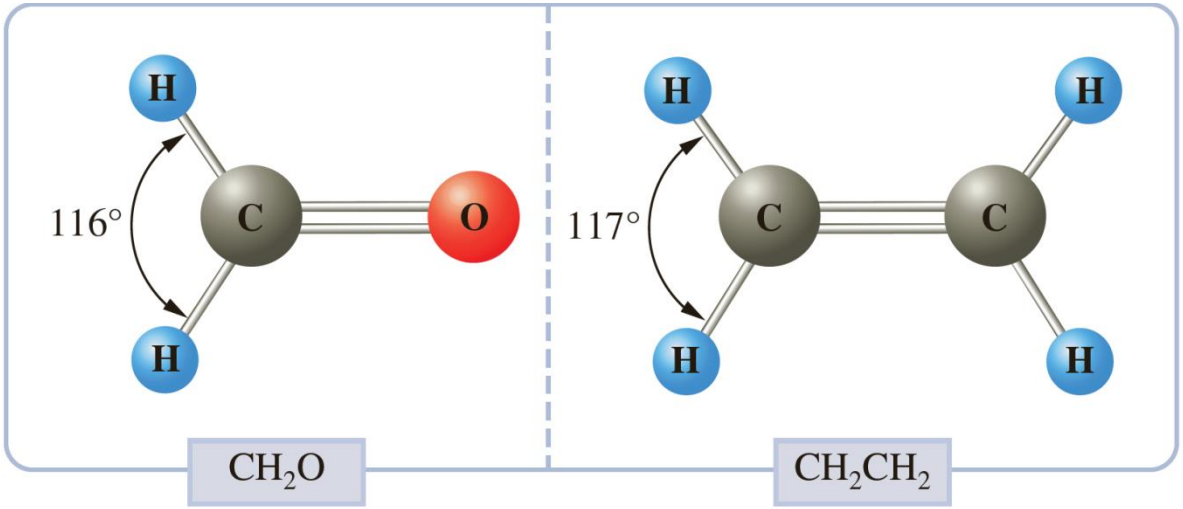


➢ Bond Angles and the Effect of Lone Pairs

✓ *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.*

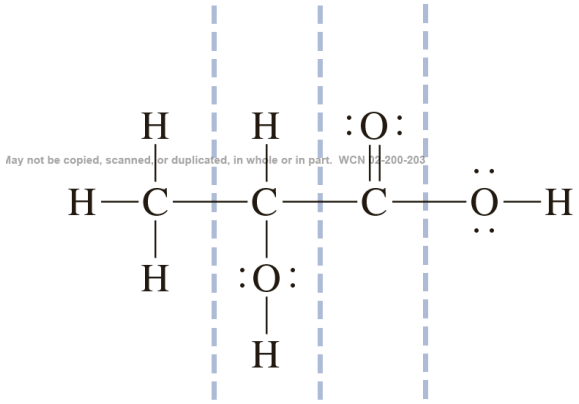


(Q) Predict the geometry of the following molecules or ions, using the VSEPR method:

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

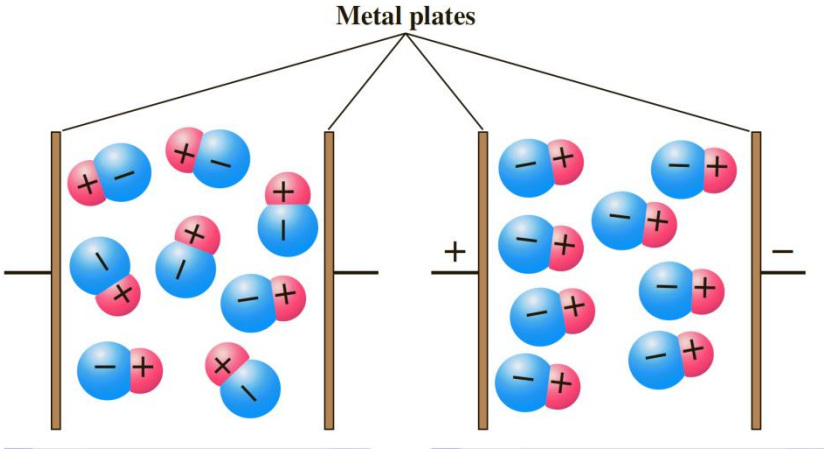
f. $TeCl_4$ **g. ICl_3**

➢ Applying the VSEPR Model to Larger Molecules



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*

$$\mu = q \times d$$

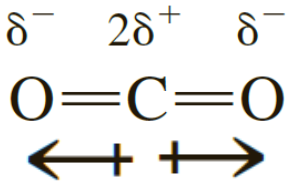
q = positive charge

–*q*= negative charge

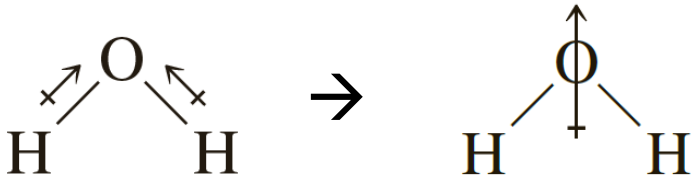
d = distance

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

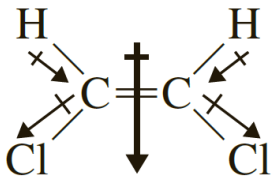
10.45 Which of the following molecules would be expected to have zero dipole moment on the basis of their geometry?

a CS_2 b TeF_2 c $SeCl_4$ d XeF_4

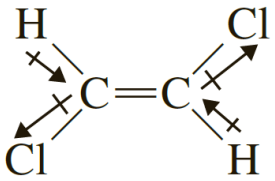
10.46 Which of the following molecules would be expected to have a dipole moment of zero because of symmetry?

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

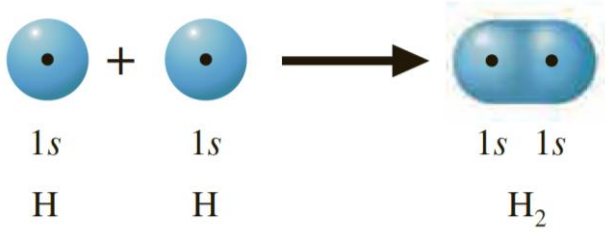
➢ Basic Theory

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



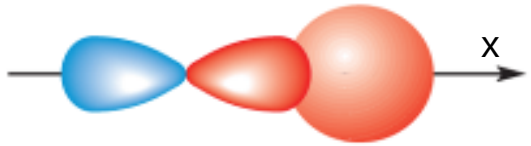
$He + He \rightarrow He_2$ (does not occur)

$1s^2 \quad 1s^2 \rightarrow$ 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

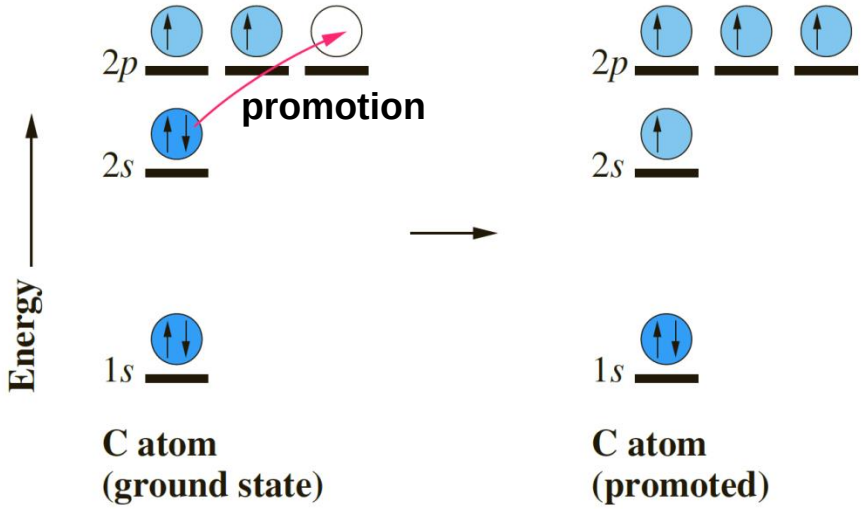
H: $1s^1$ Cl: $1s^2 2s^2 2p^6 3s^2 3p^5$

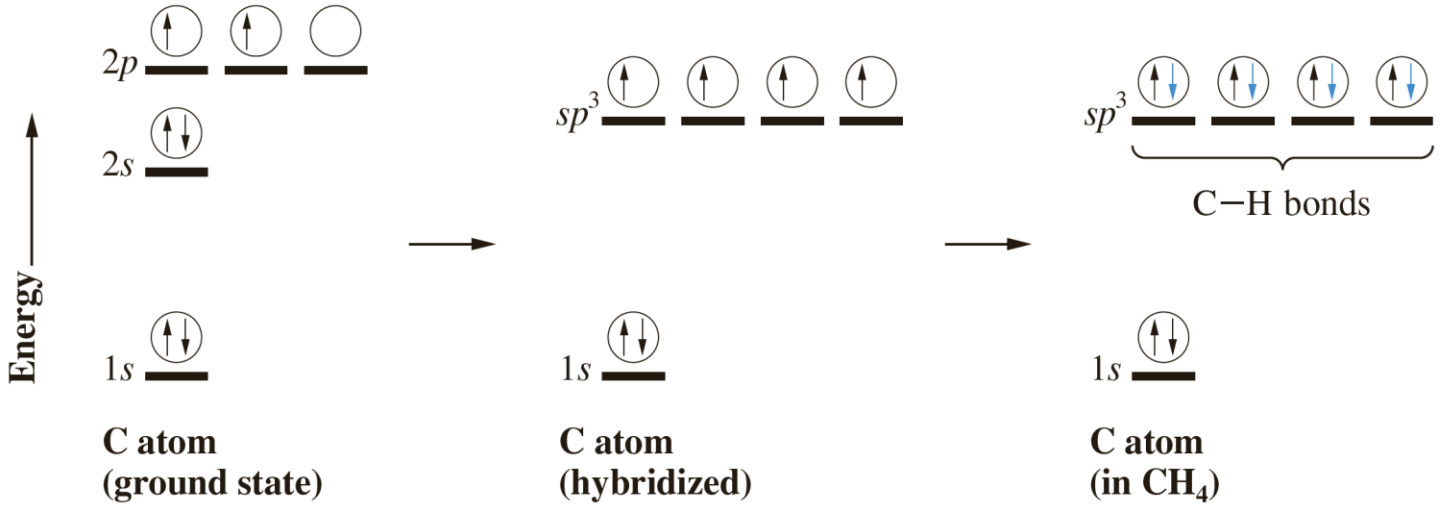
➢ Hybrid Orbitals

✓ 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



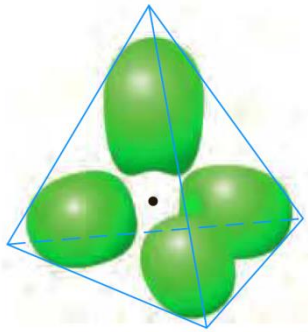


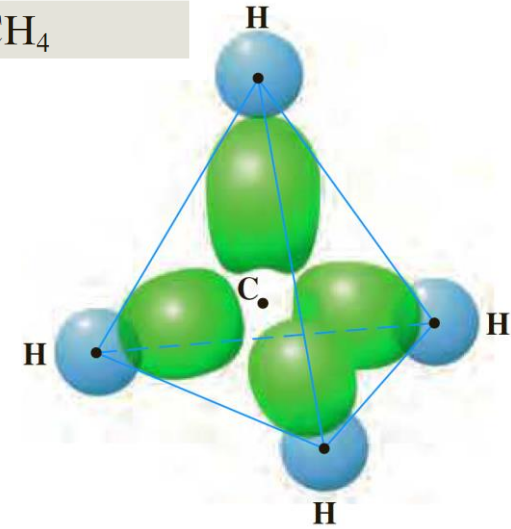
✓ *The number of hybrid orbitals formed always equals the number of atomic orbitals used.*

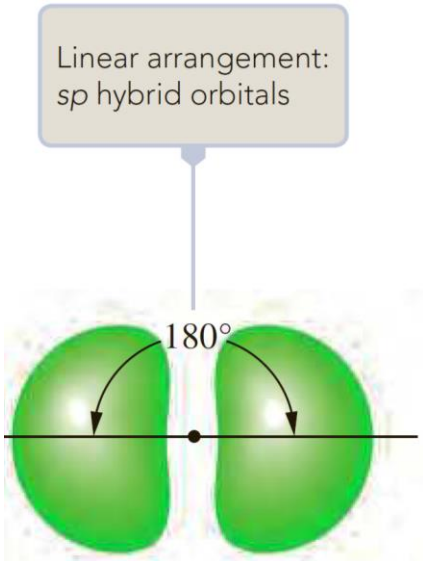
Table 10.2 Kinds of Hybrid Orbitals

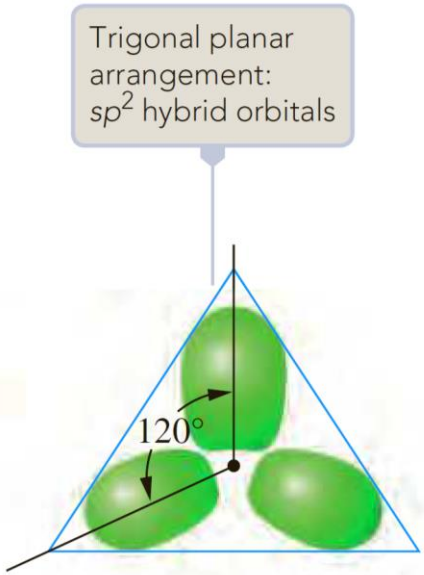
Hybrid Orbitals	Geometric Arrangement	Number of Orbitals	Example
sp	Linear	2	Be in BeF_2
sp^2	Trigonal planar	3	B in BF_3
sp^3	Tetrahedral	4	C in CH_4

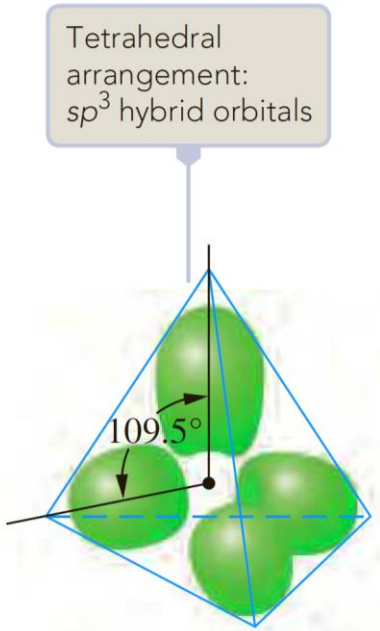
How to figure out the hybridization via Lewis structures.



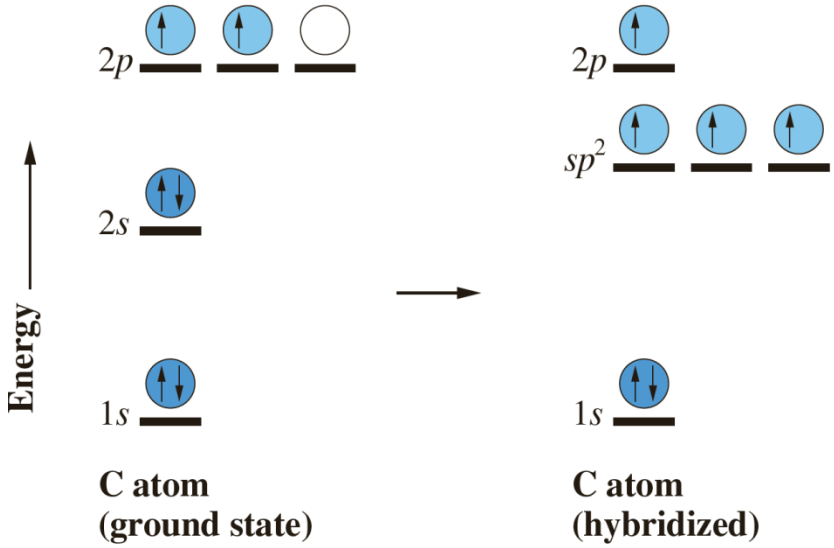


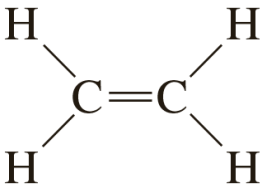




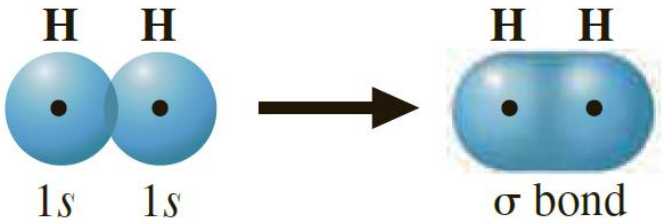


10.4 Description of Multiple Bonding

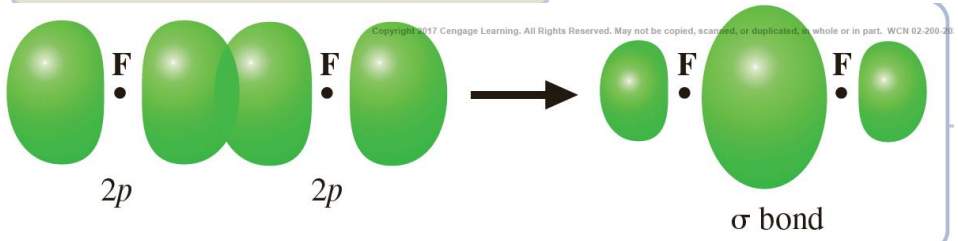




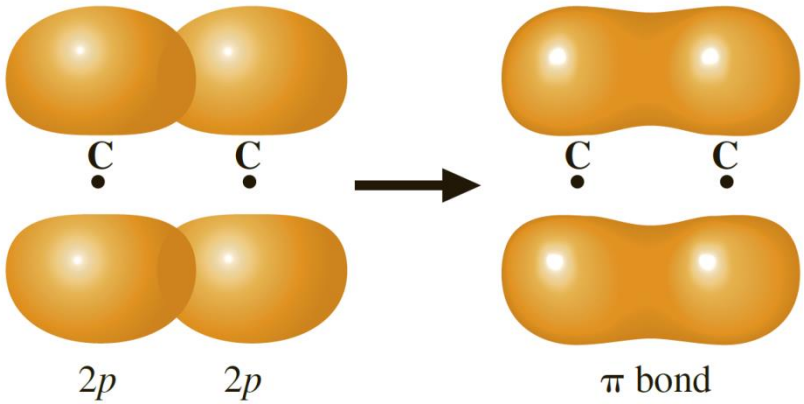
The formation of a σ bond by the overlap of two *s* orbitals.



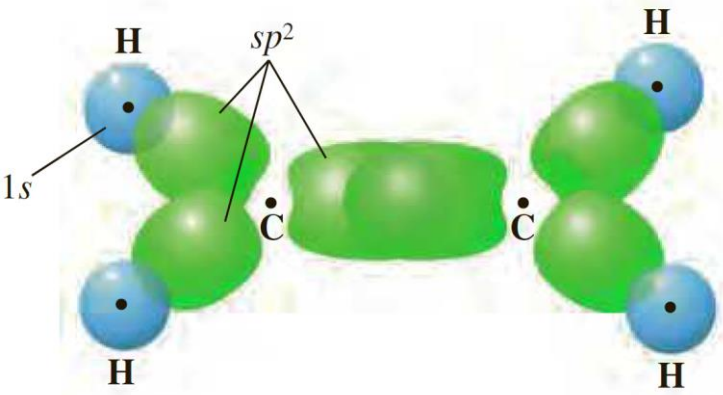
A σ bond can also be formed by the overlap of two *p* orbitals along their axes.



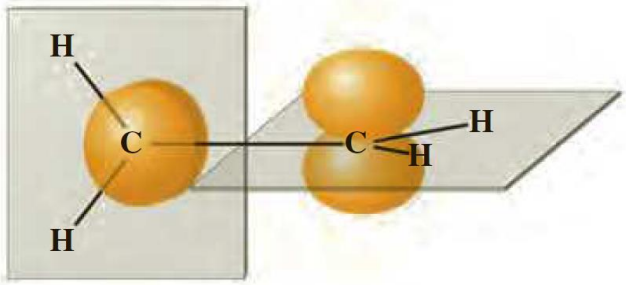
When two *p* orbitals overlap sideways, a π bond is formed.



Bonding in ethylene $H_2C=CH_2$

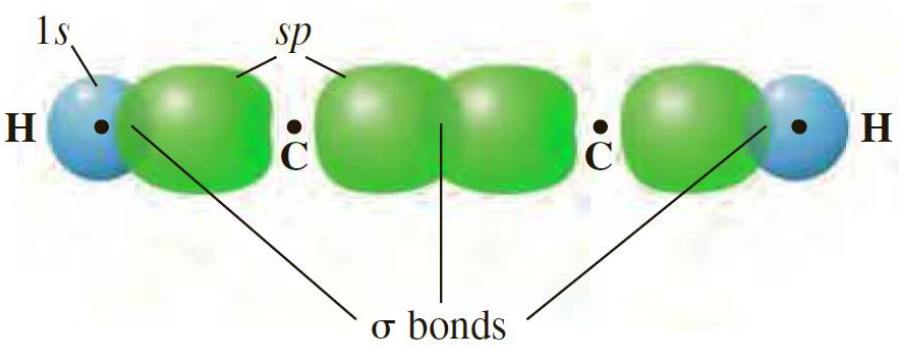


The σ-bond framework in ethylene, formed by the overlap of sp^2 hybrid orbitals on C atoms and 1*s* orbitals on H atoms.

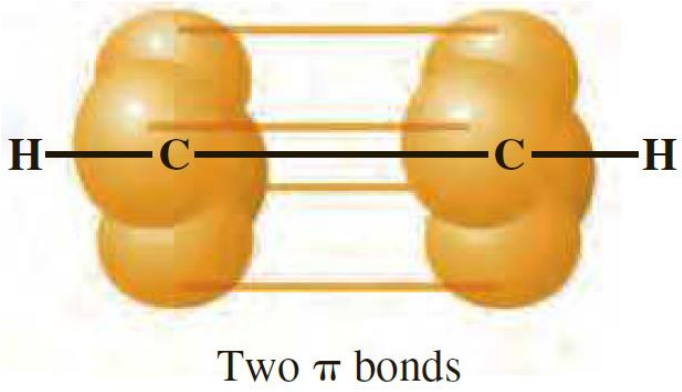


The formation of the π bond in ethylene. When the 2*p* orbitals are perpendicular to one another, there is no overlap and no bond formation. when the two —CH_2 groups rotate so that the 2*p* orbitals are parallel, a π bond forms.

Bonding in acetylene

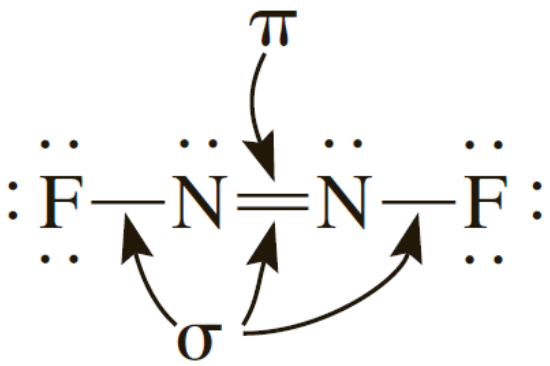


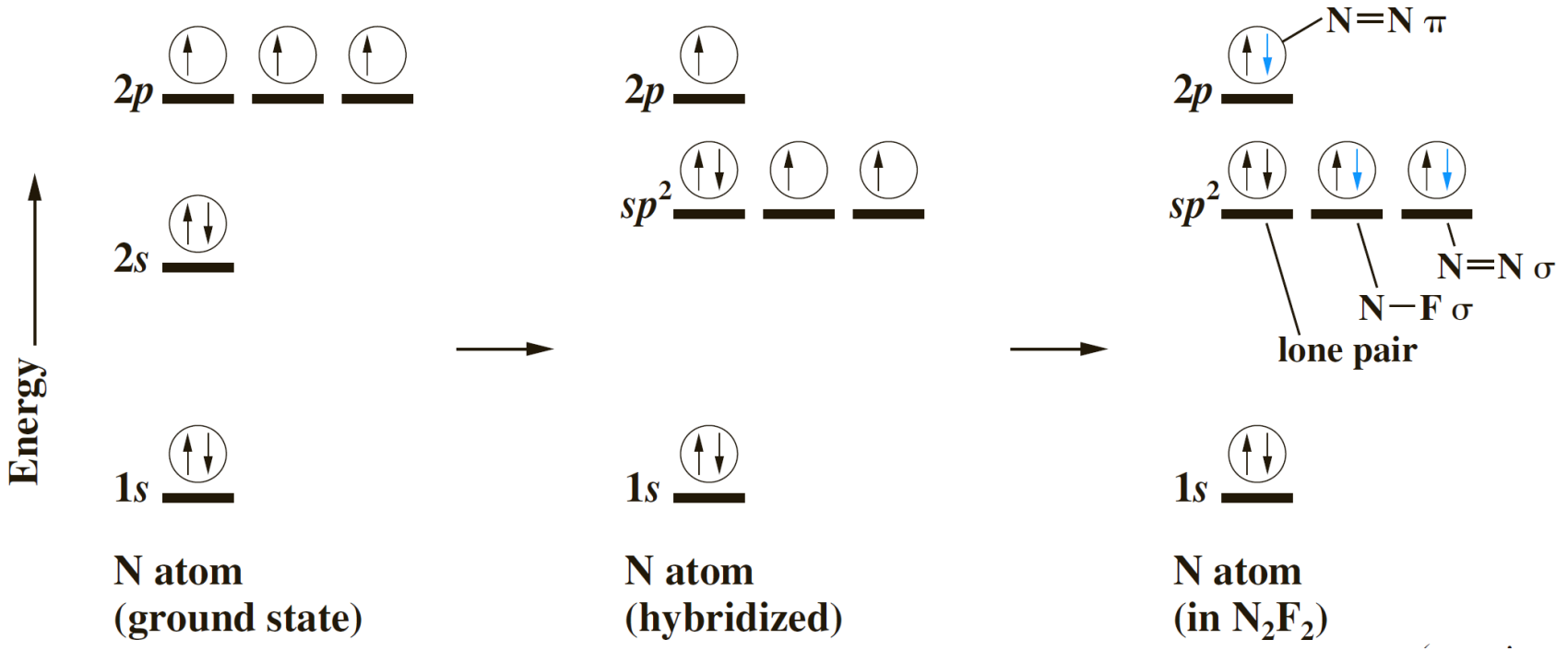
The σ-bond framework.



Two *2p* orbitals on each carbon atom begin to overlap (symbolized by lines) to form two π bonds.

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



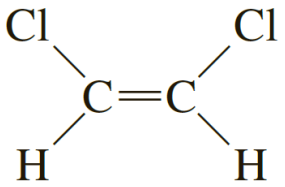


10.53 **a** Carbonyl fluoride, COF_2, is an extremely poisonous gas used in organofluorine synthesis. Give the valence bond description of the carbonyl fluoride molecule. (Both fluorine atoms are attached to the carbon atom.) **b** Nitrogen, N_2, makes up about 80% of the earth's atmosphere. Give the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

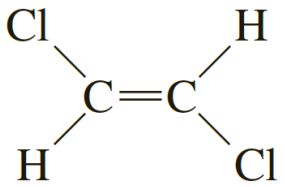
10.54 HN=NH

10.55 HCN

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



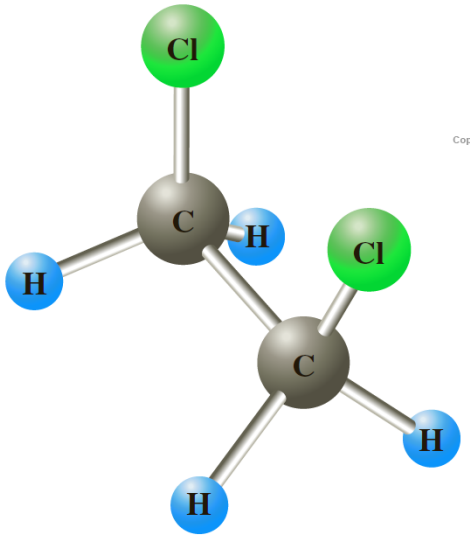
cis-1,2-Dichloroethene



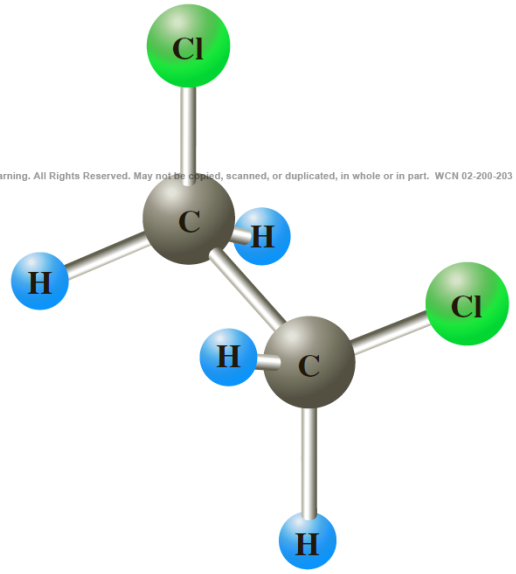
trans-1,2-Dichloroethene

✓ *cis* and *trans* isomers of N_2F_2

✓ 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.

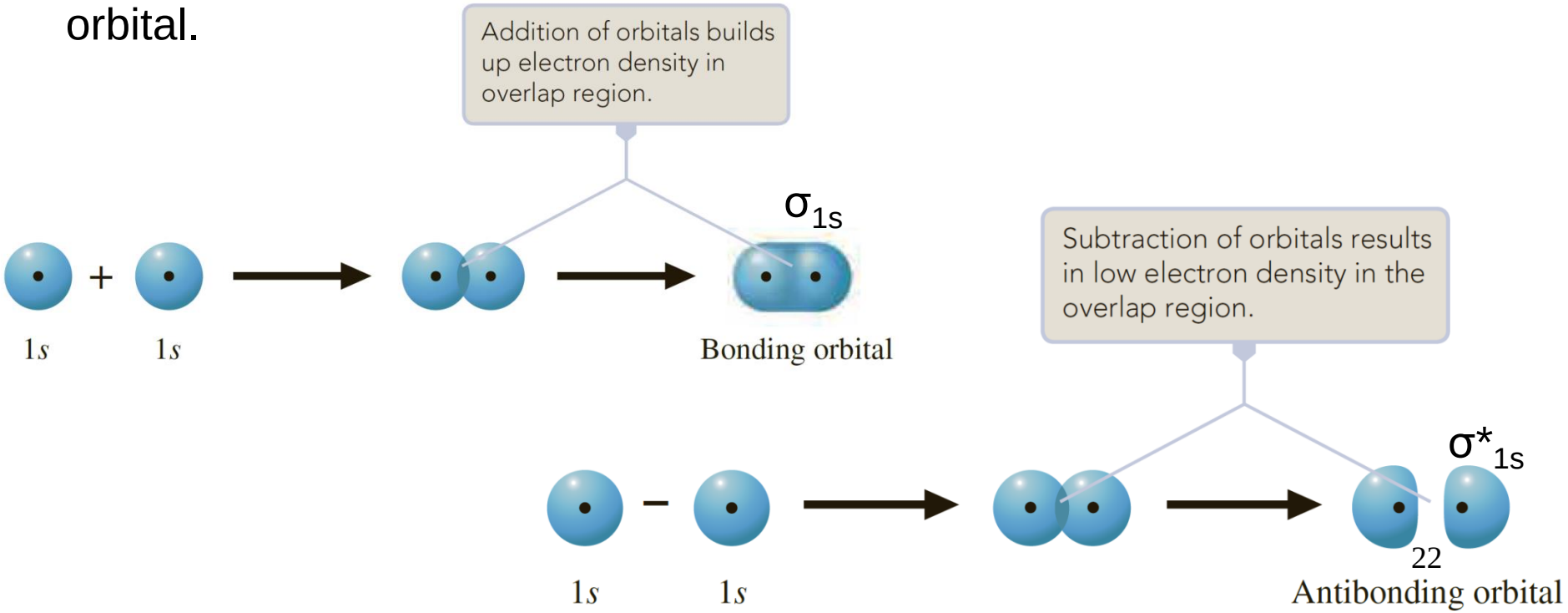


b Note that the molecule pictured at the left can be twisted easily to give the molecule pictured here.

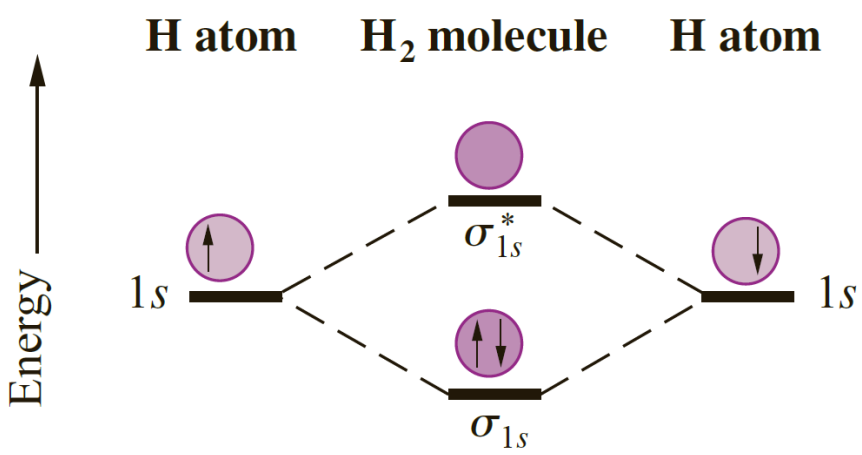
10.5 Principles of Molecular Orbital Theory

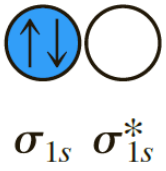
Bonding and Antibonding Orbitals

- ✓ *Molecular orbitals that are concentrated in regions between nuclei* are called **bonding orbitals.**
- ✓ *Molecular orbitals having zero values in the region between two nuclei and therefore concentrated in other regions* are called **antibonding orbitals**
- ✓ Formation of bonding and antibonding orbitals from 1s orbitals of hydrogen atoms. When the two 1*s* orbitals overlap, they can either add to give a bonding molecular orbital or subtract to give an antibonding molecular orbital.



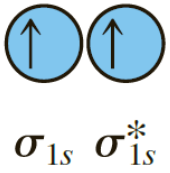
Relative energies of the 1s orbital of the H atom and the σ_{1s} and σ^*_{1s} molecular orbitals of H_2. Arrows denote occupation of the *s*1*s* orbital by electrons in the ground state of H_2.





The corresponding electron configuration is: $(\sigma_{1s})^2$

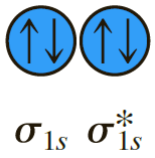
Excited state of H_2:

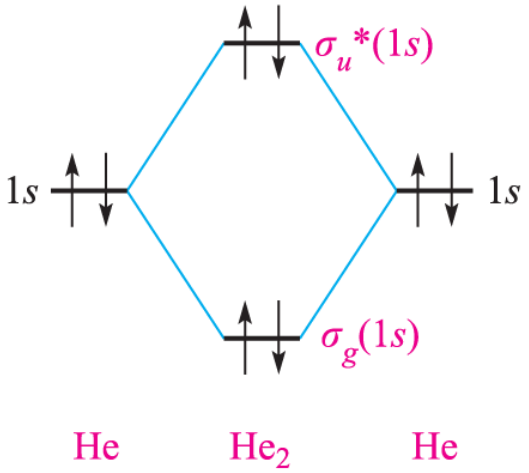


The corresponding electron configuration is: $(\sigma_{1s})^1 (\sigma^*_{1s})^1$

✓ Why He_2 is not a stable molecule?

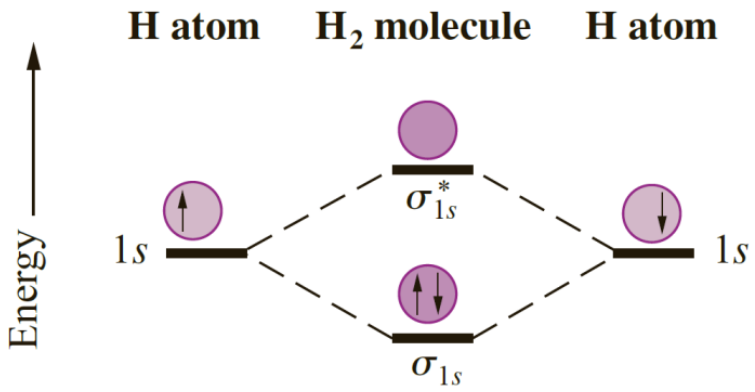
The corresponding electron configuration is: $(\sigma_{1s})^2 (\sigma^*_{1s})^2$





➢ Bond Order

$$\text{Bond order} = \tfrac{1}{2}(n_b - n_a)$$



✓ For H_2, which has two bonding electrons,

$$\text{Bond order} = \tfrac{1}{2}(2 - 0) = 1$$

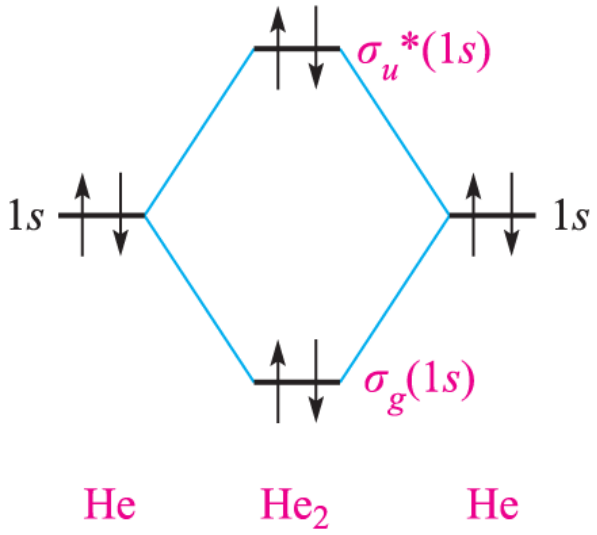
- ✓ For H_2^+ = ½ (1-0) = 1/2
- ✓ For H_2^- = ½ (2-1) = 1/2

✓ For He_2, which has two bonding and two antibonding electrons

$$\text{Bond order} = \tfrac{1}{2}(2 - 2) = 0$$

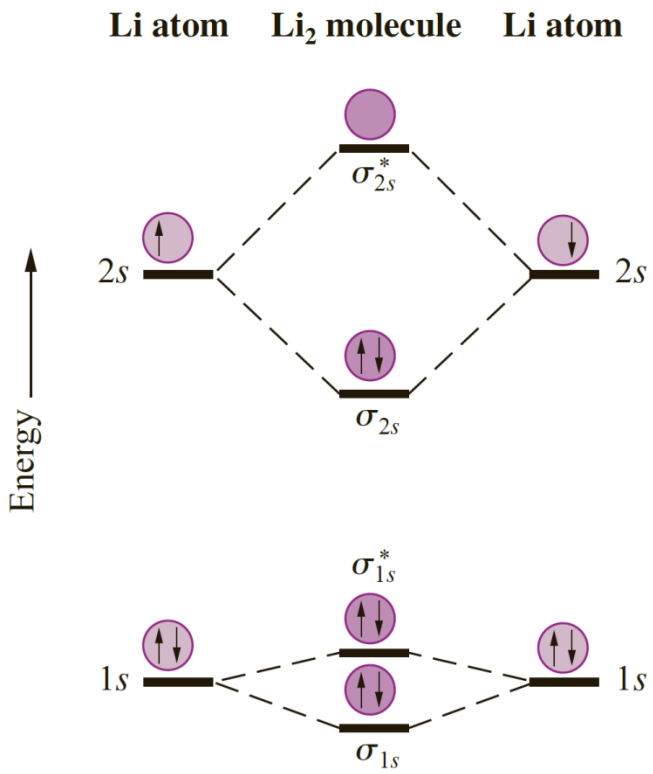
✓ For He_2^+ = ½ (2-1) = ½

✓ For He_2^{2+} = ½ (2-0) = 1



- ✓ The ground state electron configuration of Li_2:

$$Li_2 \quad (\sigma_{1s})^2(\sigma^*_{1s})^2(\sigma_{2s})^2$$



- ✓ The $(\sigma_{1s})^2(\sigma^*_{1s})^2$ part of the configuration is often abbreviated KK (which denotes the K shells, or inner shells, of the two atoms).→ $Li_2 \quad KK(\sigma_{2s})^2$
- ✓ In calculating bond order, we can ignore KK (it includes two bonding and two antibonding electrons).
- ✓ We can write: B.O of Li_2 = ½ (2-0) = 1
- ✓ Or B.O of Li_2 = ½ (4-2) = 1
- ✓ The ground state electron configuration of Be_2:

$Be_2 \quad KK(\sigma_{2s})^2(\sigma^*_{2s})^2$

- ✓ We can write: B.O of Be_2 = ½ (2-2) = 0
- ✓ Or B.O of Li_2 = ½ (4-4) = 0

- ✓ For Be_2^+ = ½ (2-1) = ½
- ✓ For Be_2^{2+} = ½ (2-0) = 1

➢ Factors That Determine Orbital Interaction

✓ The strength of the interaction between two atomic orbitals to form molecular orbitals is determined by two factors:

(1) the energy difference between the interacting orbitals and
(2) the magnitude of their overlap.

✓ *For the interaction to be strong, the energies of the two orbitals must be approximately equal and the overlap must be large.*