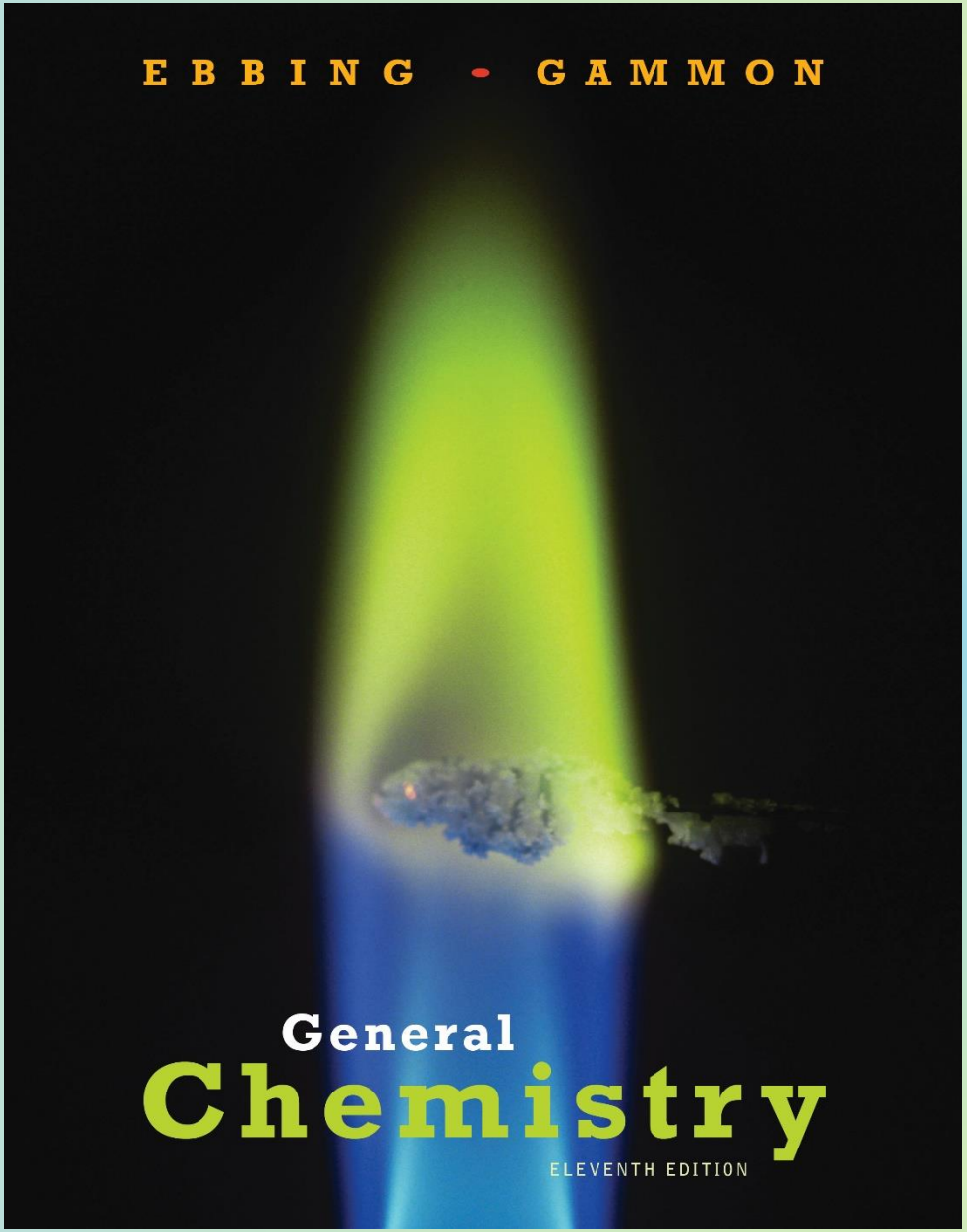
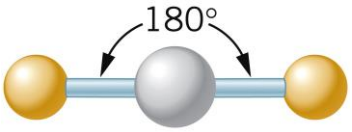
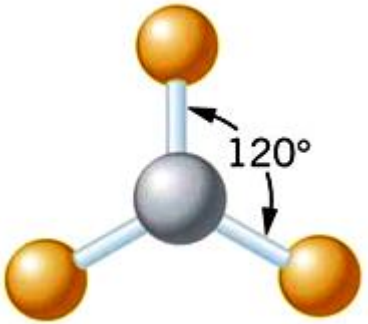
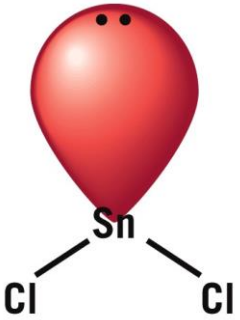
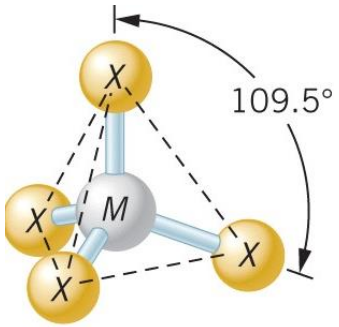
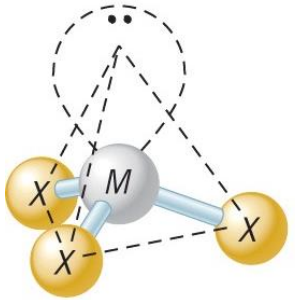
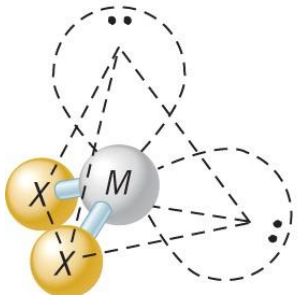
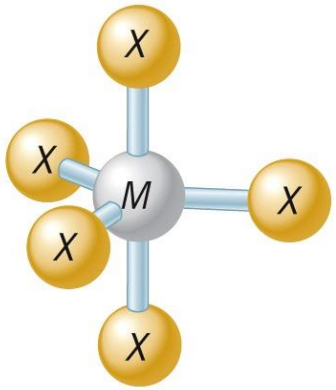
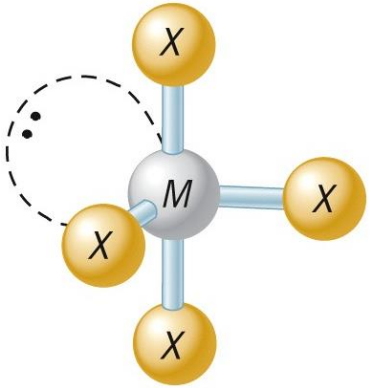


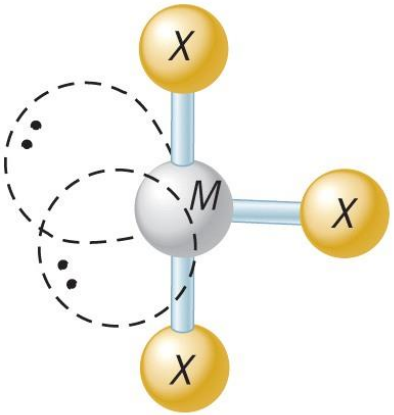
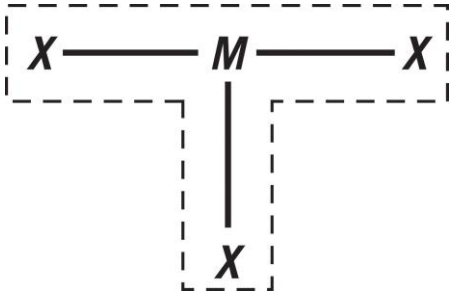
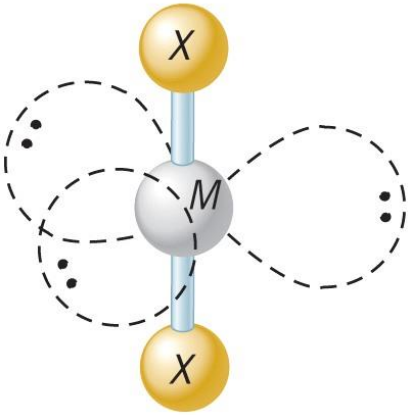
Molecular Geometry and Chemical Bonding Theory

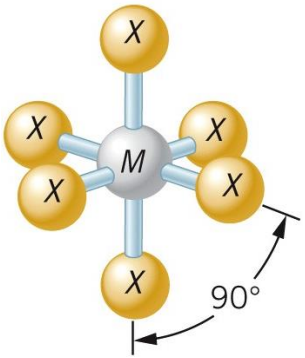
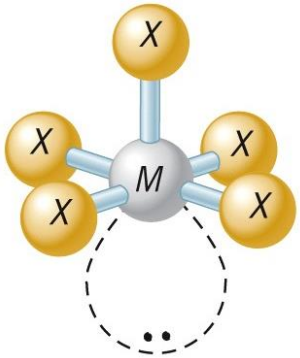
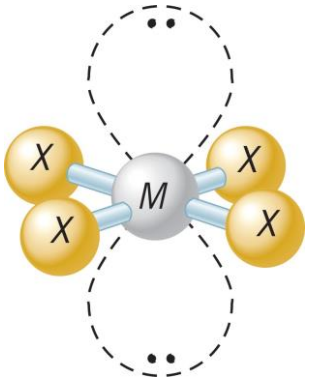
10.1 Valence-Shell Electron-Pair Repulsion (VSEPR) Model

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°

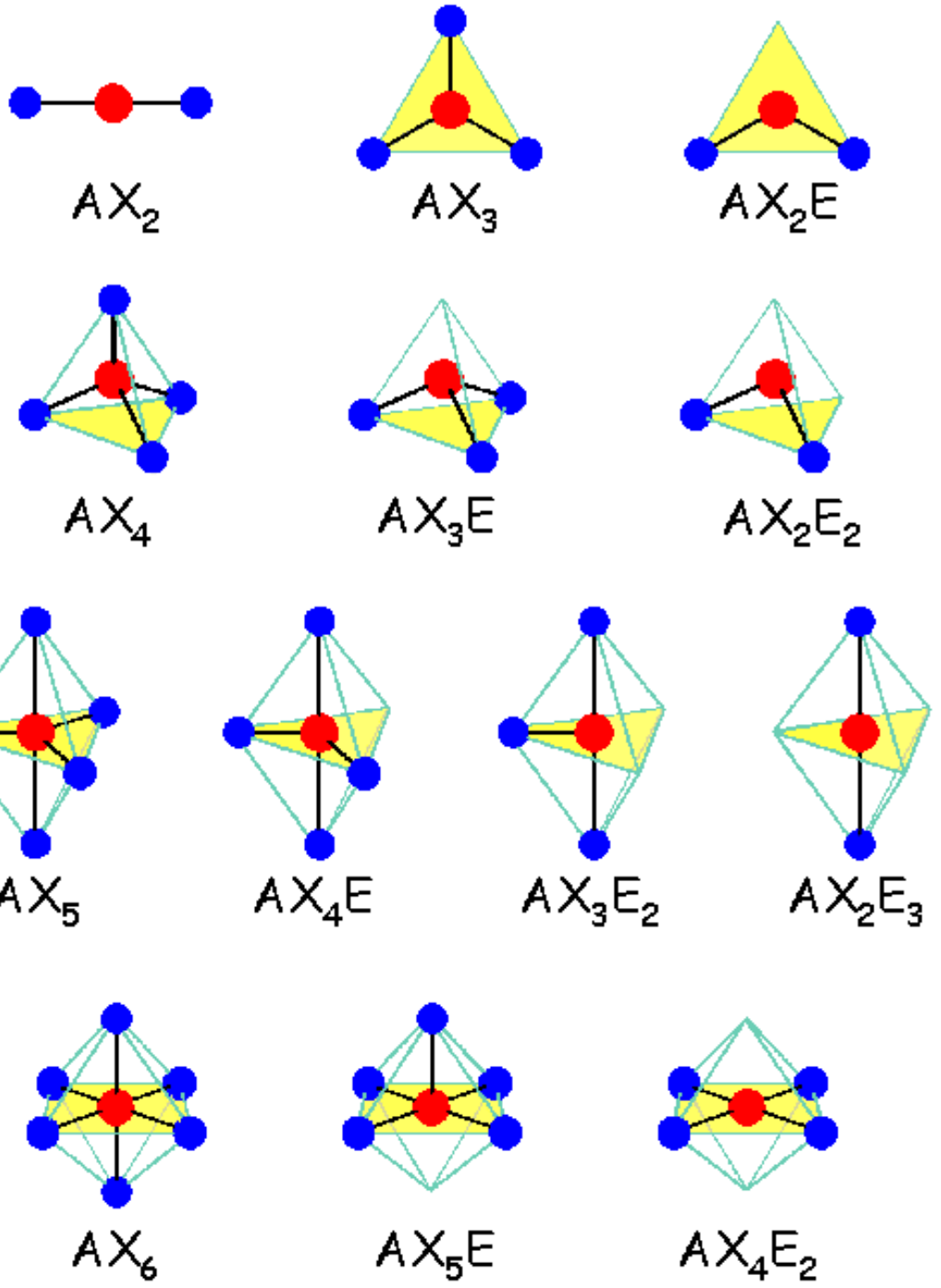
Number of Bonding Pairs	Number of Nonbonding Pairs (E)	Molecular Geometry	Molecular Shape
5	0		**AX_5** **Trigonal bipyramid** (**e.g.,** PF_5) **axial-equatorial** bond angles 90° eq-eq 120° ax-ax 180°
4	1		**AX_4E** **Distorted Tetrahedron or Seesaw** (**e.g.,** SF_4) ax-eq bond angles < 90° ax-ax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

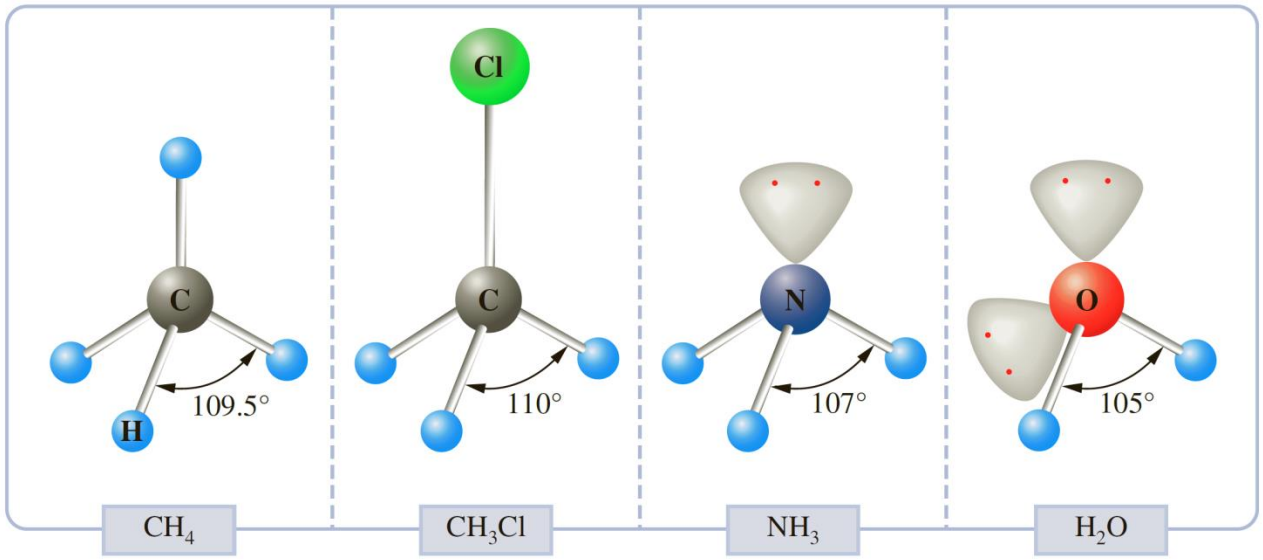
Summary of Molecular Geometries

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

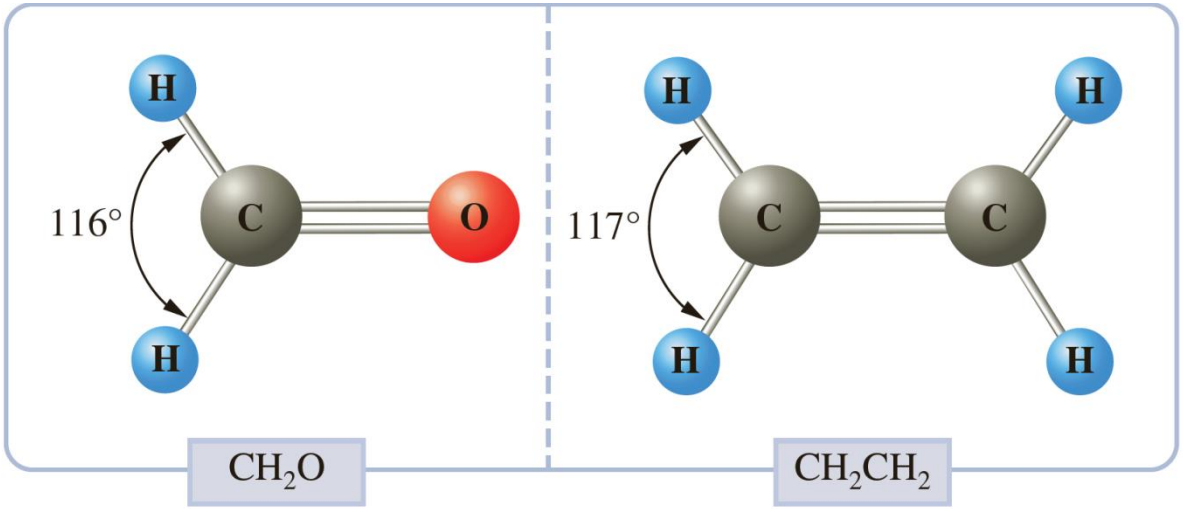


➢ Bond Angles and the Effect of Lone Pairs

✓ *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.*

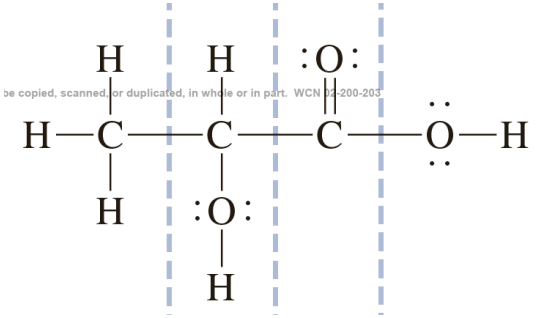


(Q) Predict the geometry of the following molecules or ions, using the VSEPR method:

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

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

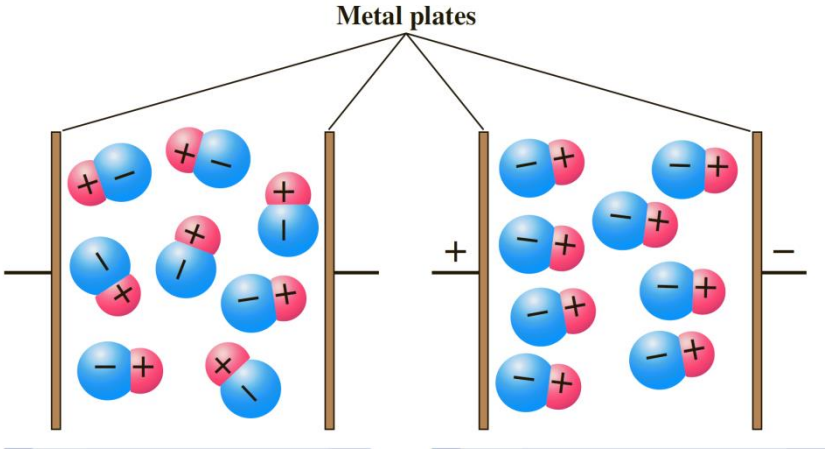
➢ Applying the VSEPR Model to Larger Molecules



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*

$$\mu = q \times d$$

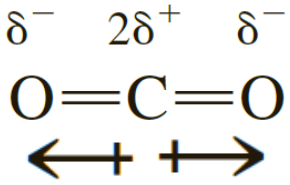
q = positive charge

–*q*= negative charge

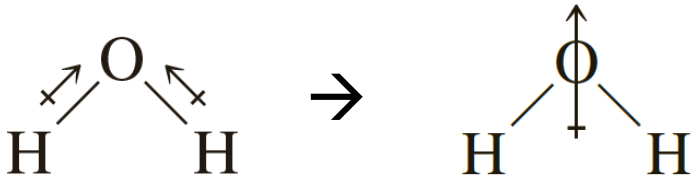
d = distance

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

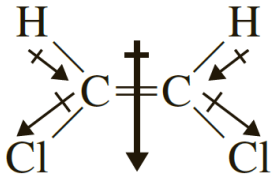
10.45 Which of the following molecules would be expected to have zero dipole moment on the basis of their geometry?

a CS_2 b TeF_2 c $SeCl_4$ d XeF_4

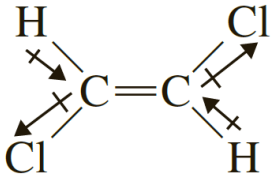
10.46 Which of the following molecules would be expected to have a dipole moment of zero because of symmetry?

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

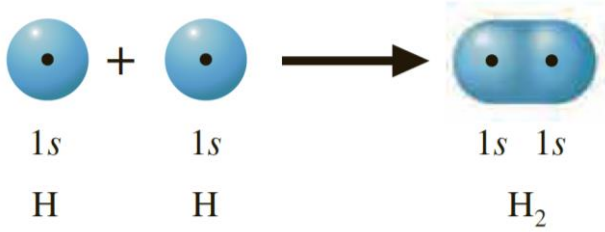
➢ Basic Theory

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



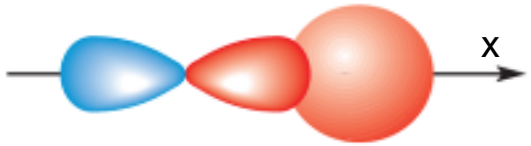
$He + He \rightarrow He_2$ (does not occur)

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

X

✓ The strength of bonding depends on orbital overlap.

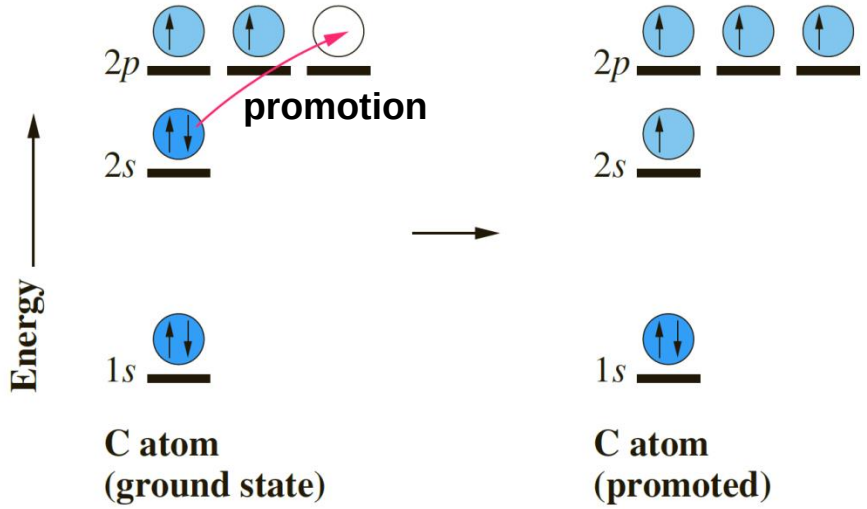
✓ *To obtain maximum overlap,* orbitals other than *s* bond only in given directions.

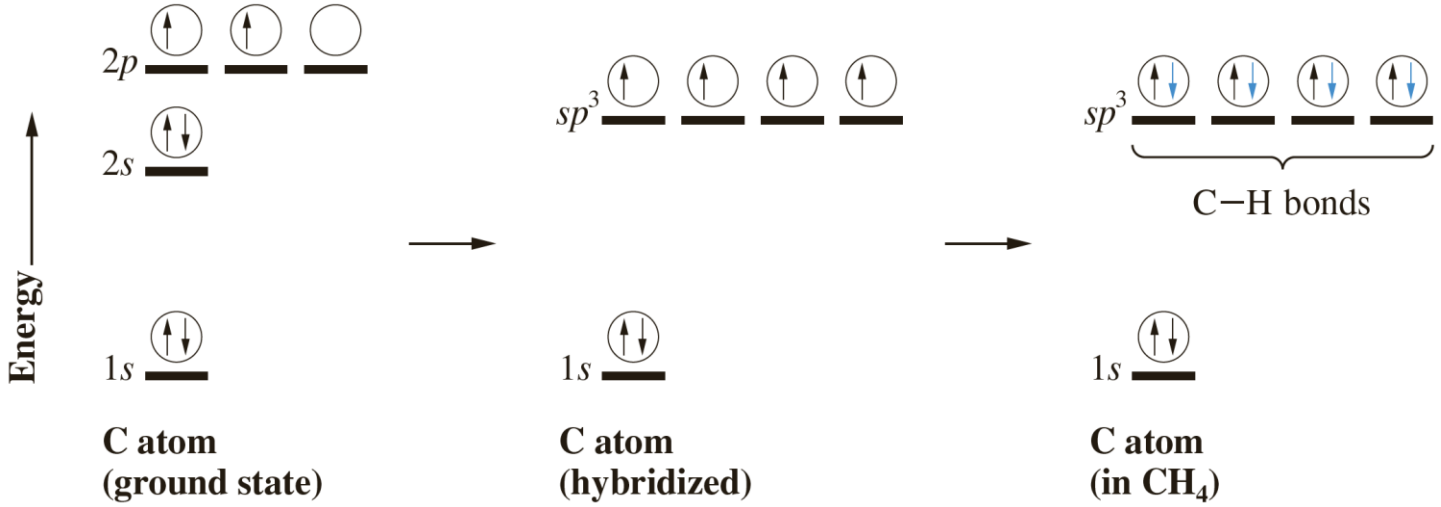


➢ Bonding in HCl

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



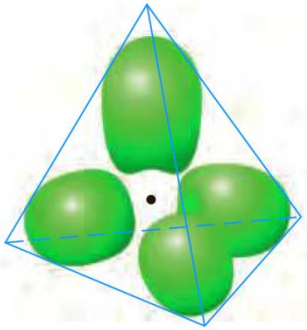


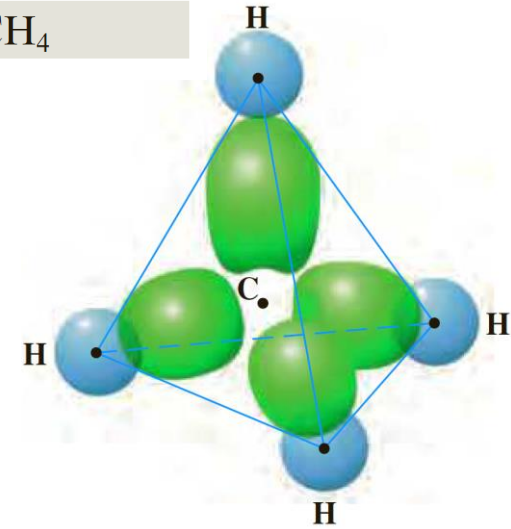
- *The number of hybrid orbitals formed always equals the number of atomic orbitals used.*

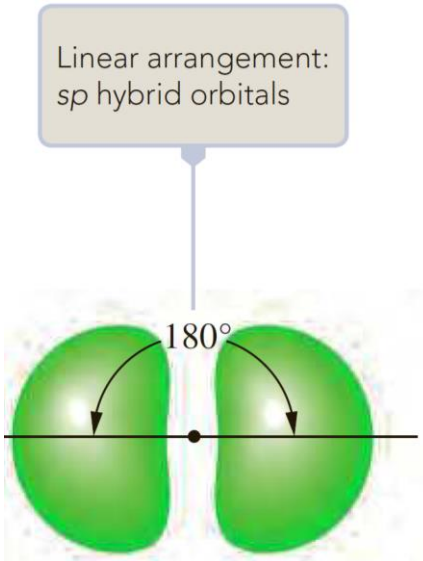
Table 10.2 Kinds of Hybrid Orbitals

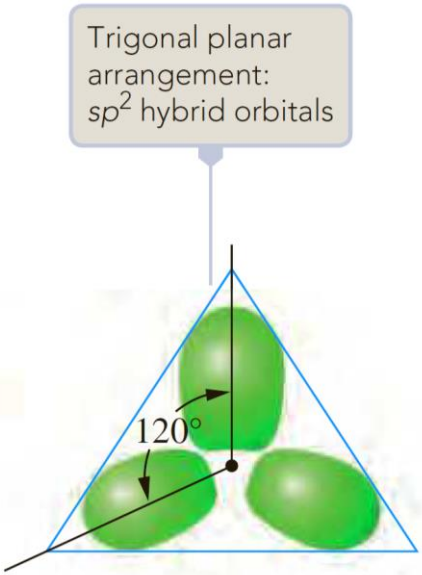
Hybrid Orbitals	Geometric Arrangement	Number of Orbitals	Example
sp	Linear	2	Be in BeF_2
sp^2	Trigonal planar	3	B in BF_3
sp^3	Tetrahedral	4	C in CH_4

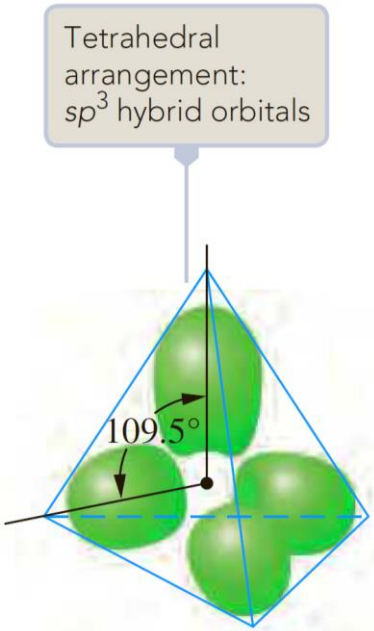
How to figure out the hybridization via Lewis structures.



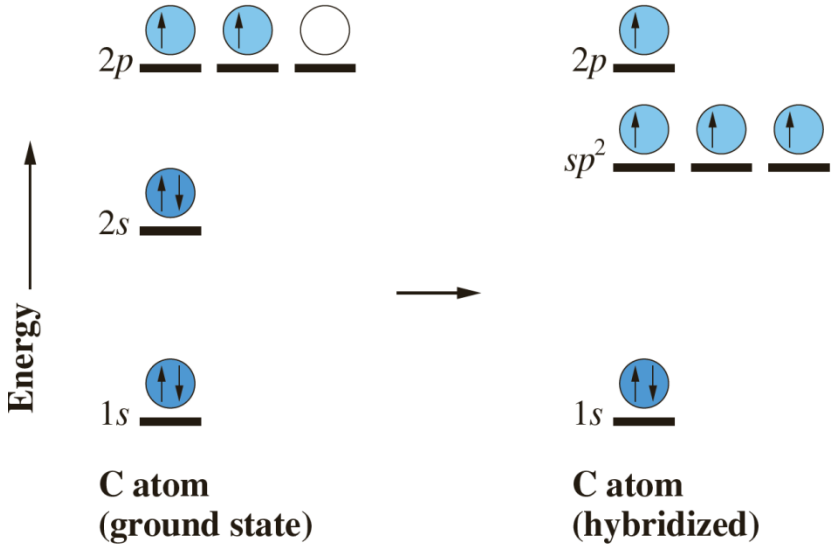


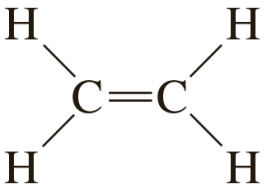




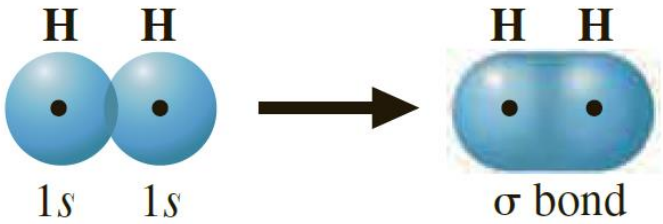


10.4 Description of Multiple Bonding

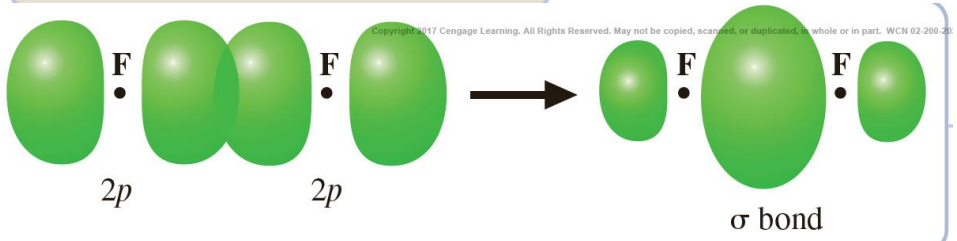




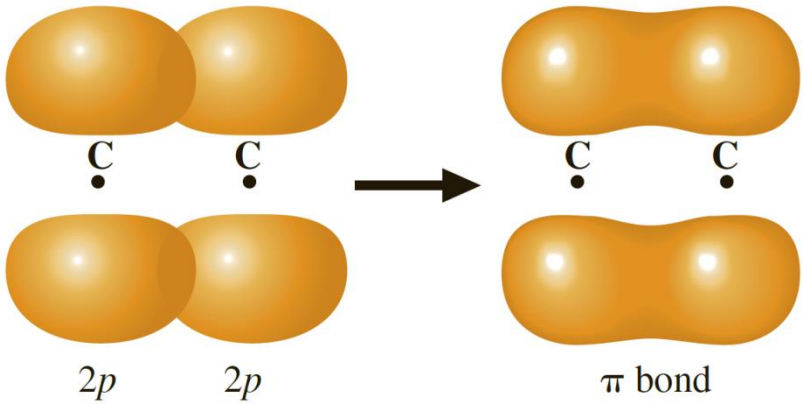
The formation of a σ bond by the overlap of two *s* orbitals.



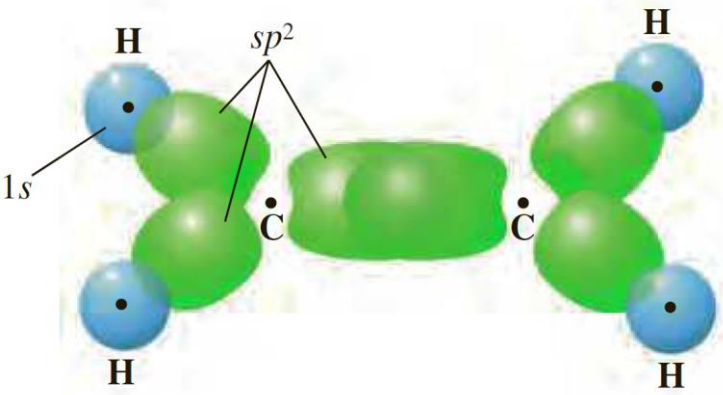
A σ bond can also be formed by the overlap of two *p* orbitals along their axes.



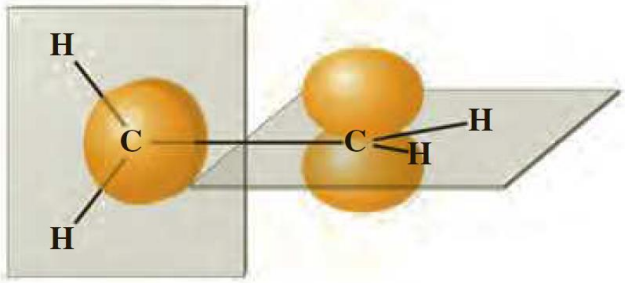
When two *p* orbitals overlap sideways, a π bond is formed.



Bonding in ethylene $H_2C=CH_2$

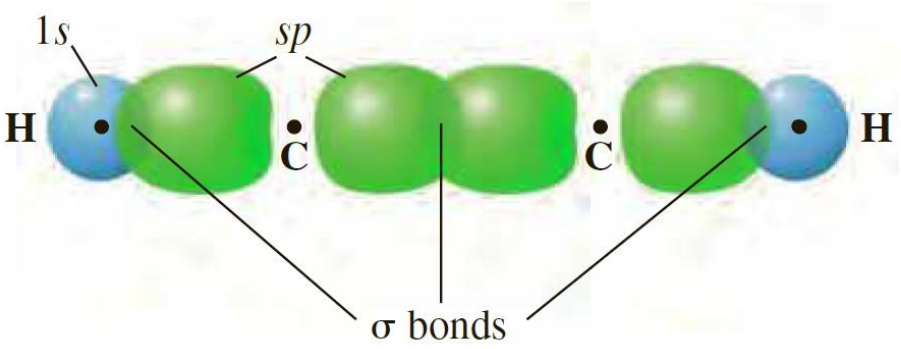


The σ-bond framework in ethylene, formed by the overlap of sp^2 hybrid orbitals on C atoms and 1*s* orbitals on H atoms.

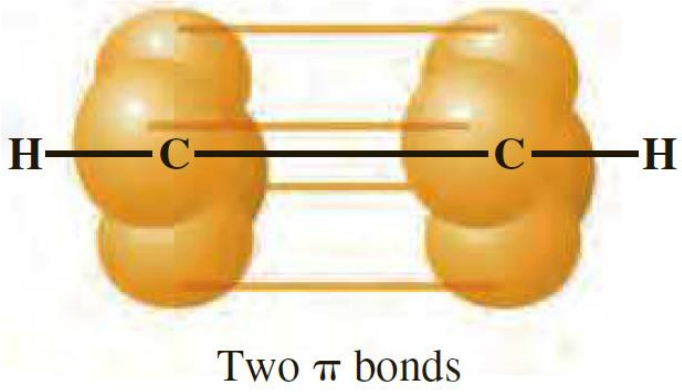


The formation of the π bond in ethylene. When the 2*p* orbitals are perpendicular to one another, there is no overlap and no bond formation. when the two —CH_2 groups rotate so that the 2*p* orbitals are parallel, a π bond forms.

Bonding in acetylene

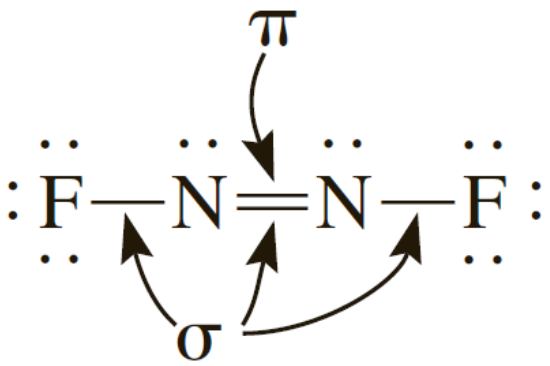


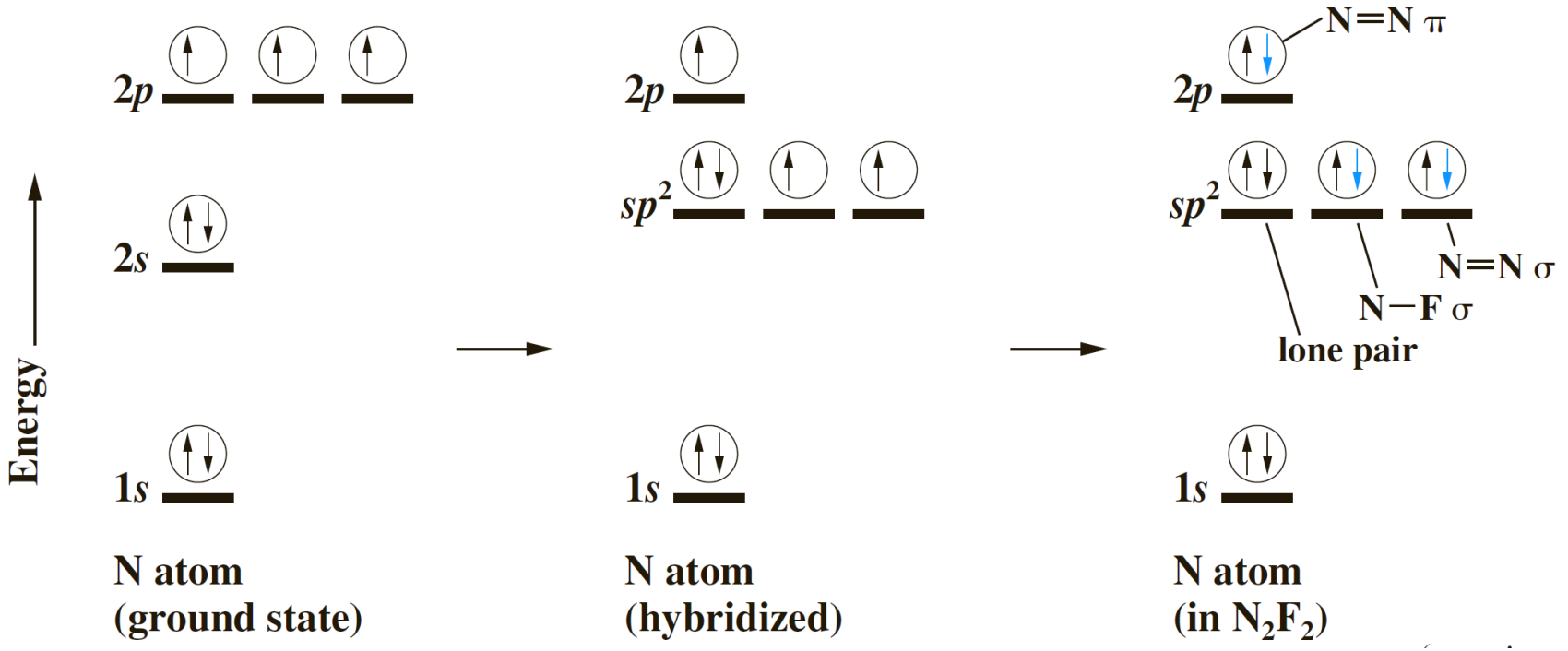
The σ-bond framework.



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.



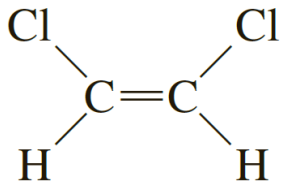


10.53 **a** Carbonyl fluoride, COF_2, is an extremely poisonous gas used in organofluorine synthesis. Give the valence bond description of the carbonyl fluoride molecule. (Both fluorine atoms are attached to the carbon atom.) **b** Nitrogen, N_2, makes up about 80% of the earth's atmosphere. Give the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

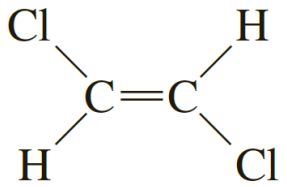
10.54 HN=NH

10.55 HCN

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

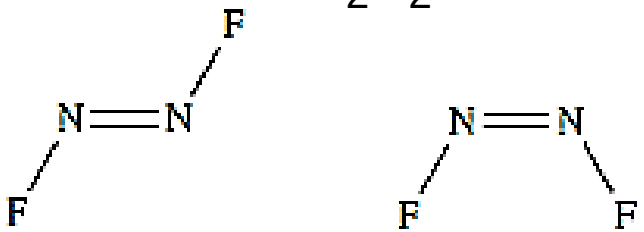


cis-1,2-Dichloroethene



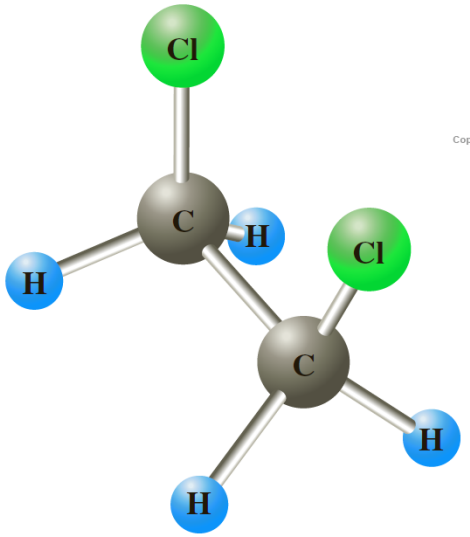
trans-1,2-Dichloroethene

✓ *cis* and *trans* isomers of N_2F_2

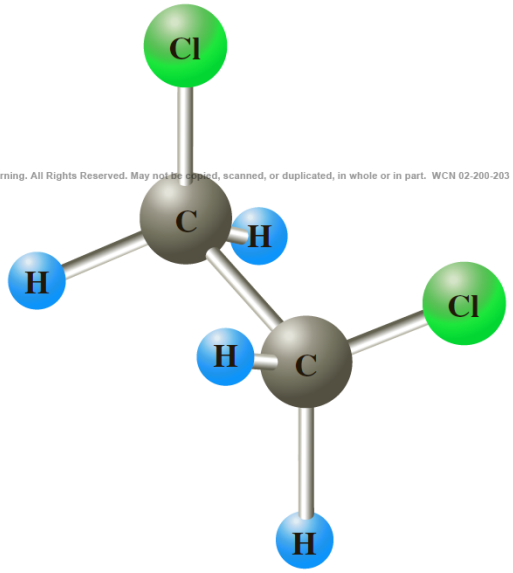


trans *cis*

✓ 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.

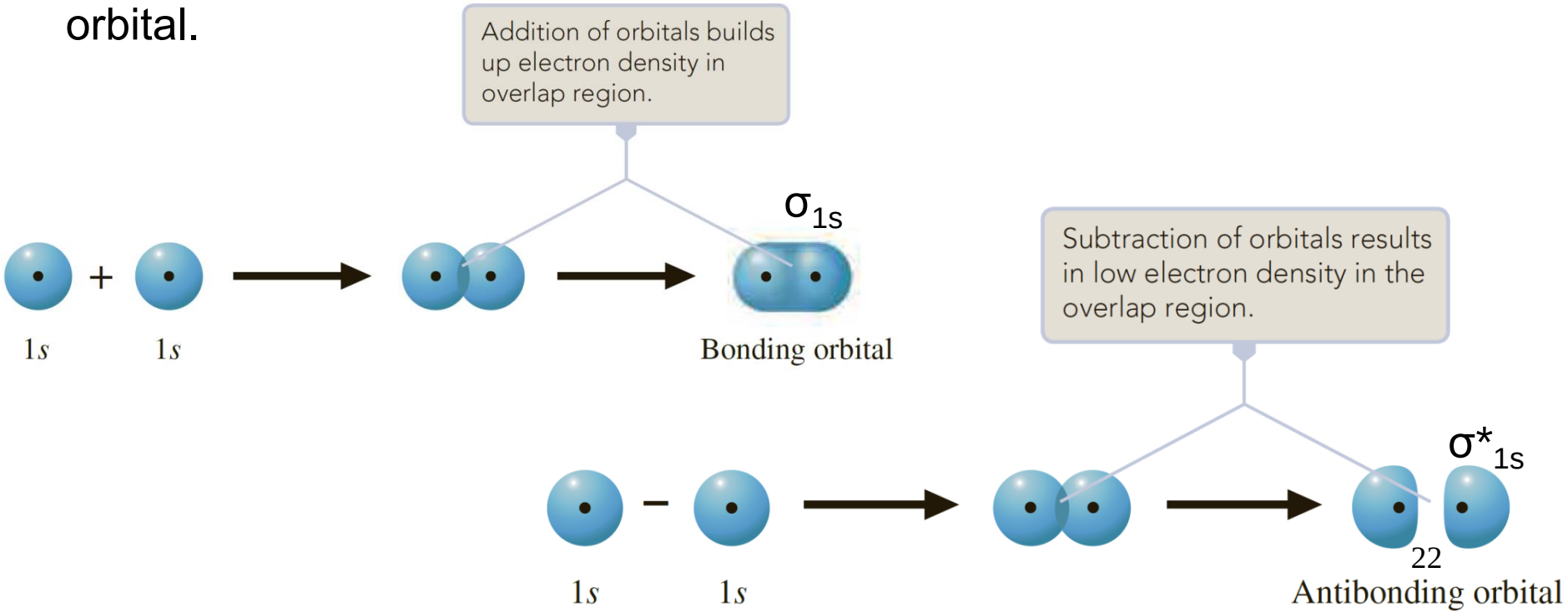


b Note that the molecule pictured at the left can be twisted easily to give the molecule pictured here.

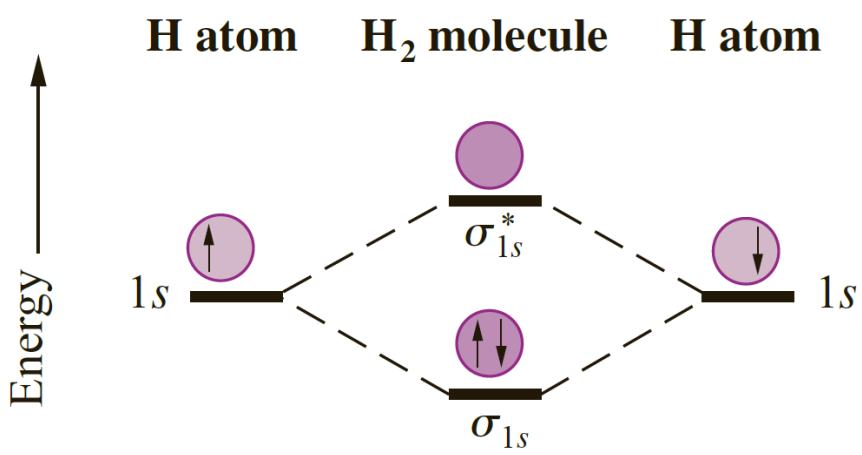
10.5 Principles of Molecular Orbital Theory

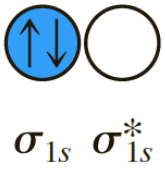
Bonding and Antibonding Orbitals

- ✓ *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.



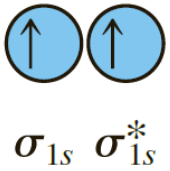
Relative energies of the 1s orbital of the H atom and the σ_{1s} and σ^*_{1s} molecular orbitals of H_2. Arrows denote occupation of the *s*1*s* orbital by electrons in the ground state of H_2.





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

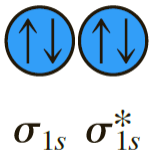
Excited state of H_2:

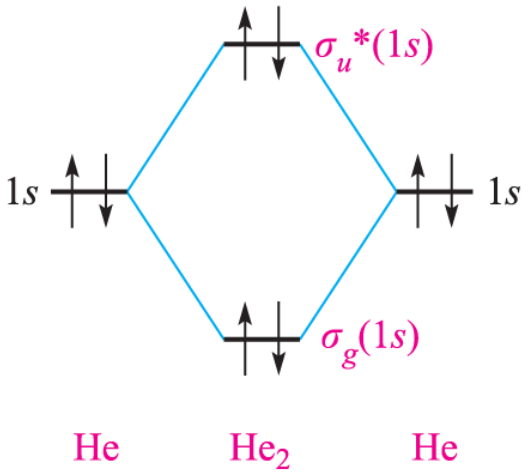


The corresponding electron configuration is: $(\sigma_{1s})^1\,(\sigma^*_{1s})^1$

✓ Why He_2 is not a stable molecule?

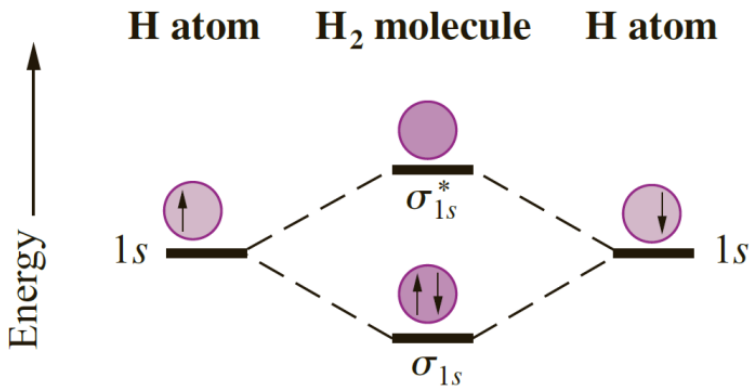
The corresponding electron configuration is: $(\sigma_{1s})^2\,(\sigma^*_{1s})^2$





➢ Bond Order

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



- ✓ For H_2, which has two bonding electrons,

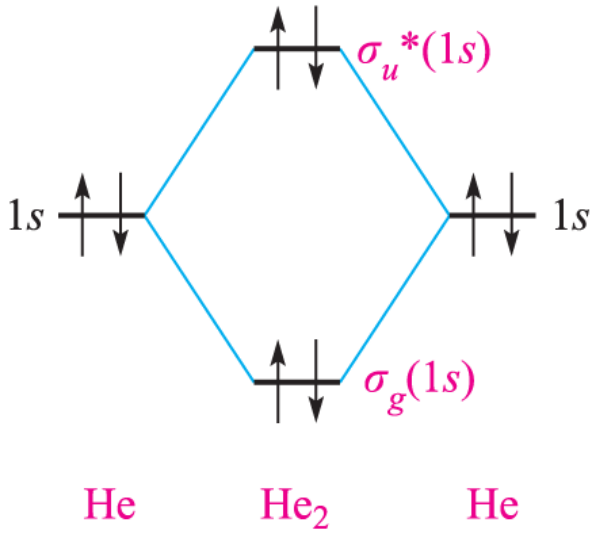
$$\text{Bond order} = \tfrac{1}{2}(2 - 0) = 1$$

  - ✓ 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

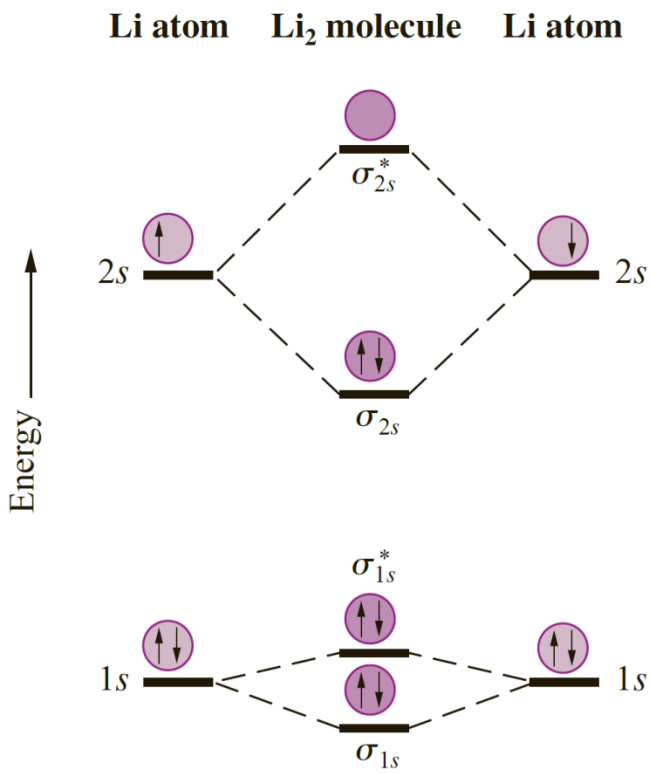
$$\text{Bond order} = \tfrac{1}{2}(2 - 2) = 0$$

- ✓ 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.*