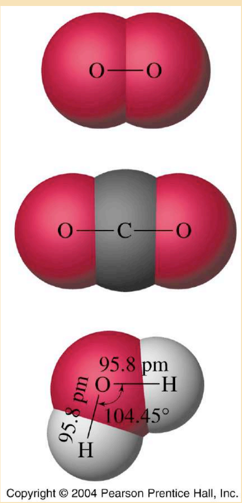
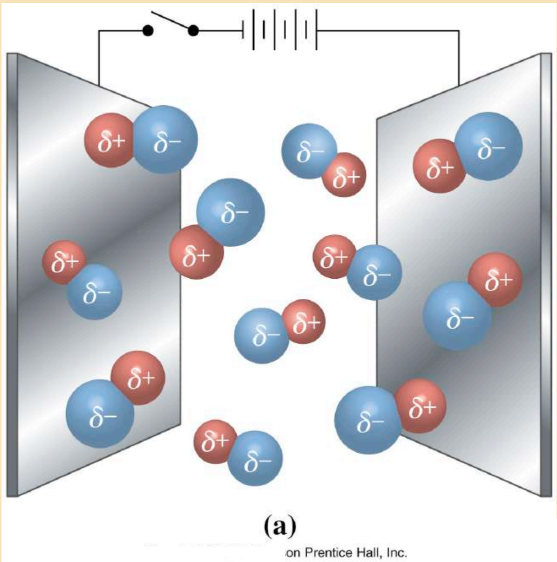
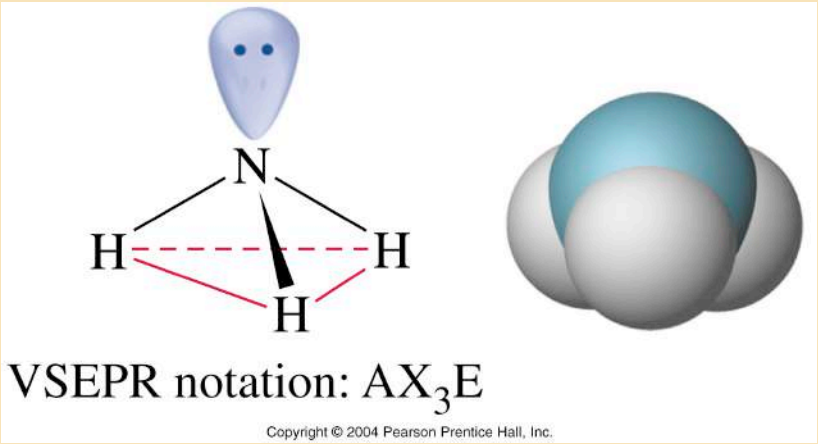
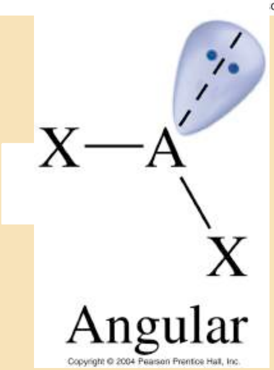
Chapter Ten

Bonding Theory and Molecular Structure







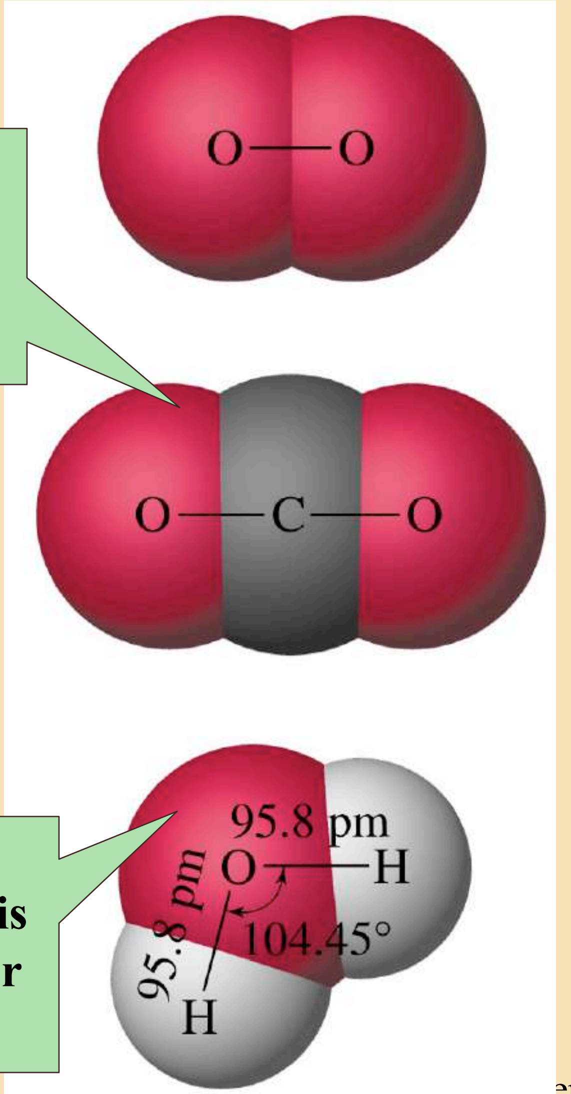


Molecular Geometry

- ***Molecular geometry*** is simply the ***shape*** of a molecule.
- Molecular geometry is described by the geometric figure formed when the atomic nuclei are joined by (imaginary) straight lines.
- Molecular geometry is found ***using*** the Lewis structure, but the Lewis structure itself does NOT necessarily represent the molecule's shape.

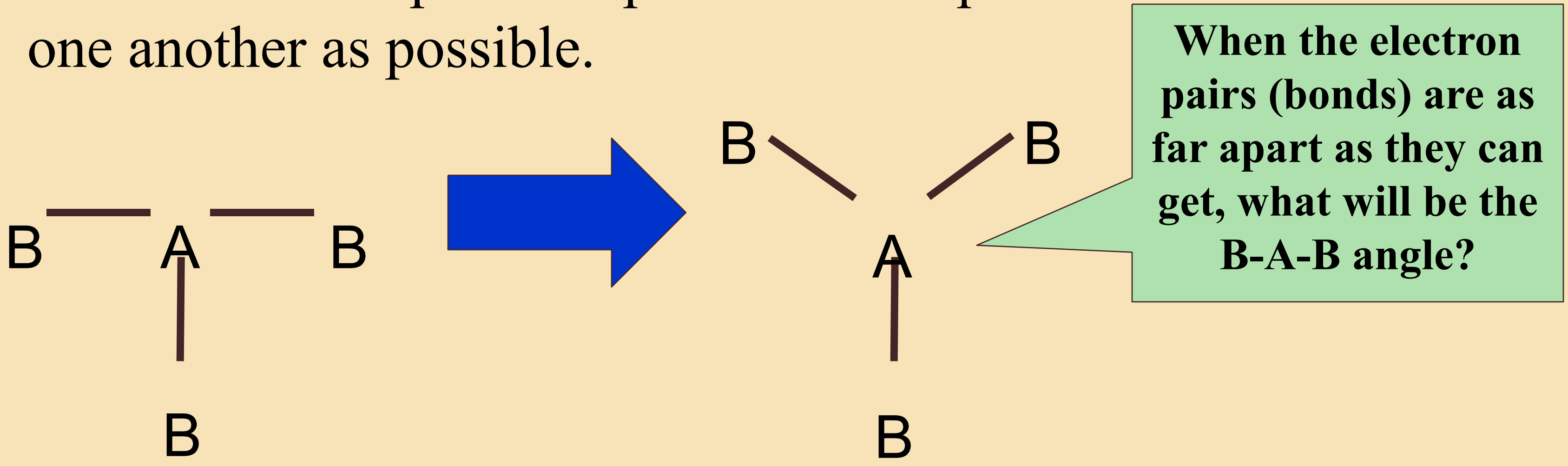
A carbon dioxide molecule is *linear.*

A water molecule is *angular* or *bent.*



VSEPR

- ***Valence-Shell Electron-Pair Repulsion (VSEPR)*** is a simple method for determining geometry.
- Basis: pairs of valence electrons in bonded atoms repel one another.
- These mutual repulsions push electron pairs as far from one another as possible.

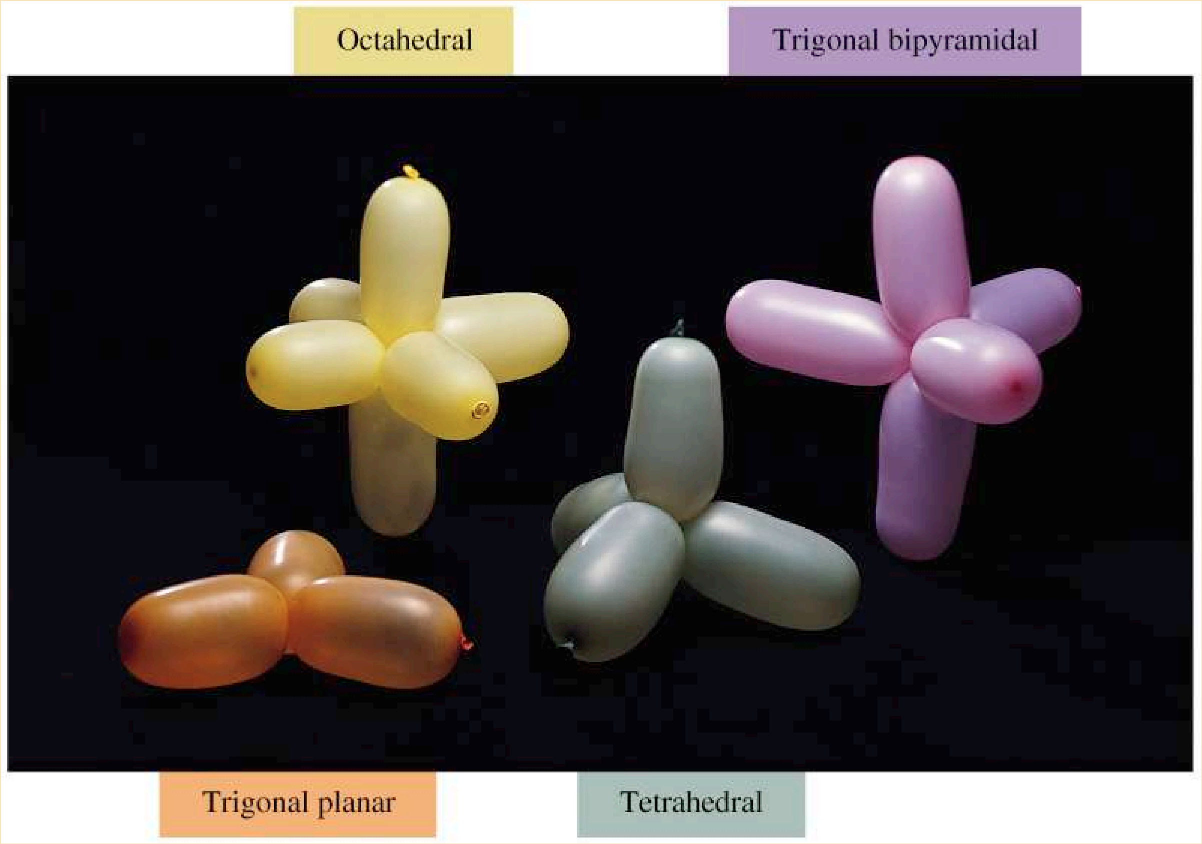


Electron-Group Geometries

- An ***electron group*** is a collection of valence electrons, localized in a region around a central atom.
- One electron group:
  - an unshared pair of valence electrons or
  - a bond (single, double, *or* triple)
- The repulsions among electron groups lead to an orientation of the groups that is called the **electron-group geometry**.
- These geometries are based on the ***number*** of electron groups:

Electron groups	Electron-group geometry
2	Linear
3	Trigonal planar
4	Tetrahedral
5	Trigonal bipyramidal
6	Octahedral

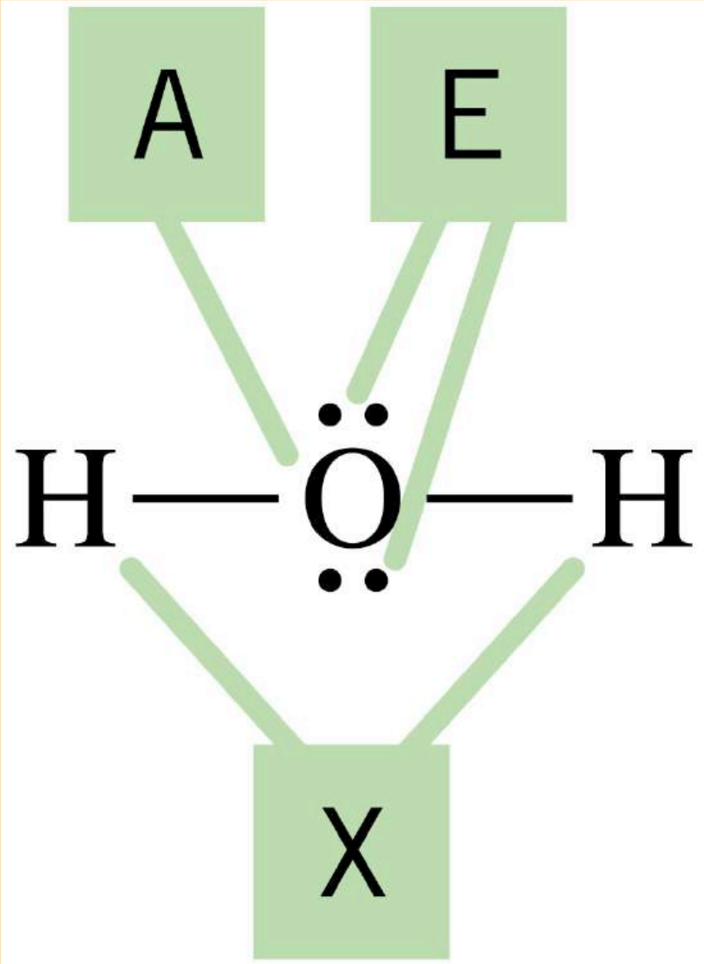
A Balloon Analogy



- Electron groups repel one another in the same way that balloons push one another apart.
- When four balloons, tied at the middle, push themselves apart as much as possible, they make a *tetrahedral* shape.

VSEPR Notation

- In the VSEPR notation used to describe molecular geometries, the central atom in a structure is denoted as **A**, terminal atoms as **X**, and the lone pairs of electrons as **E**.
- The H_2O molecule would therefore carry the designation AX_2E_2.



VSEPR Notation

- For structures with no lone pairs on the central atom (**AX_n**), the molecular geometry is the same as the electron-group geometry.
- When there are lone pairs, the molecular geometry is ***derived from*** the electron-group geometry.
- In either case, the electron-group geometry is the ***tool*** we use to obtain the molecular geometry.

Table 10.1 (Part 1) VSEPR Notation, Electron-Group Geometry, and Molecular Geometry

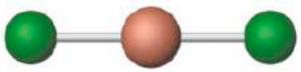
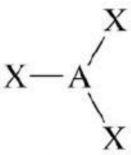
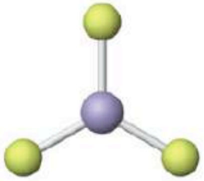
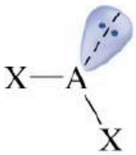
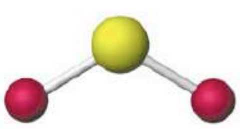
Number of Electron Groups	Electron-Group Geometry	Number of Lone Pairs	VSEPR Notation	Molecular Geometry	Ideal Bond Angles	Example	Molecular Model
2	Linear	0	AX_2	X—A—X Linear	180°	$BeCl_2$	
3	Trigonal planar	0	AX_3	 Trigonal planar	120°	BF_3	
3	Trigonal planar	1	AX_2E	 Angular	120°	SO_2	

Table 10.1 (Part 2) VSEPR Notation, Electron-Group Geometry, and Molecular Geometry

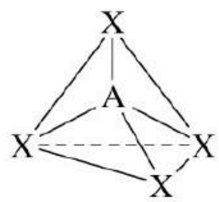
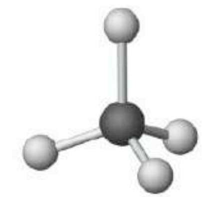
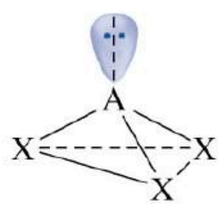
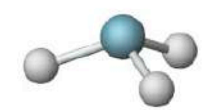
Number of Electron Groups	Electron-Group Geometry	Number of Lone Pairs	VSEPR Notation	Molecular Geometry	Ideal Bond Angles	Example	Molecular Model
4	Tetrahedral	0	AX_4	 Tetrahedral	109.5°	CH_4	
4	Tetrahedral	1	AX_3E	 Trigonal pyramidal	109.5°	NH_3	

Table 10.1 (Part 3) VSEPR Notation, Electron-Group Geometry, and Molecular Geometry

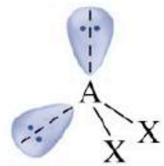
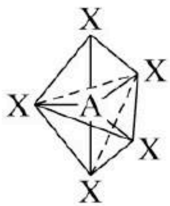
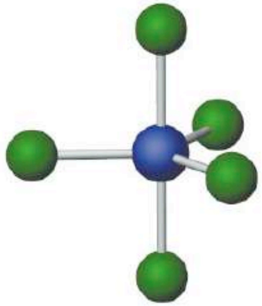
Number of Electron Groups	Electron-Group Geometry	Number of Lone Pairs	VSEPR Notation	Molecular Geometry	Ideal Bond Angles	Example	Molecular Model
4	Tetrahedral	2	AX_2E_2	 Angular	109.5°	OH_2	
5	Trigonal bipyramidal	0	AX_5	 Trigonal bipyramidal	90°, 120°, 180°	PCl_5	

Table 10.1 (Part 4) VSEPR Notation, Electron-Group Geometry, and Molecular Geometry

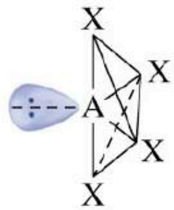
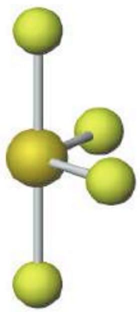
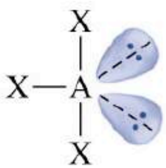
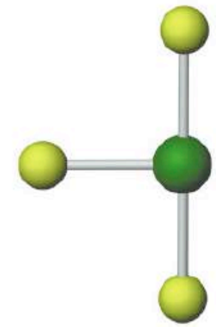
Number of Electron Groups	Electron-Group Geometry	Number of Lone Pairs	VSEPR Notation	Molecular Geometry	Ideal Bond Angles	Example	Molecular Model
5	Trigonal bipyramidal	1	AX_4E	 Seesaw	90°, 120°, 180°	SF_4	
5	Trigonal bipyramidal	2	AX_3E_2	 T-shaped	90°, 180°	ClF_3	

Table 10.1 (Part 5) VSEPR Notation, Electron-Group Geometry, and Molecular Geometry

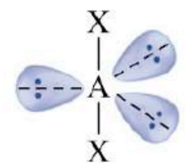
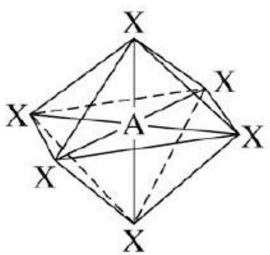
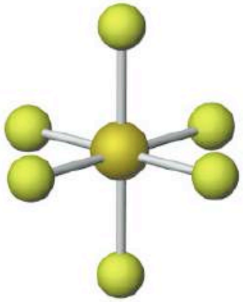
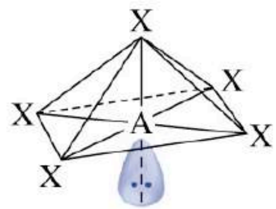
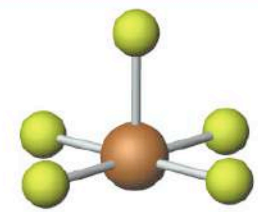
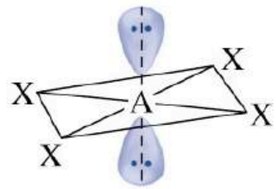
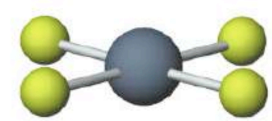
Number of Electron Groups	Electron-Group Geometry	Number of Lone Pairs	VSEPR Notation	Molecular Geometry	Ideal Bond Angles	Example	Molecular Model
5	Trigonal bipyramidal	3	AX_2E_3	 Linear	180°	XeF_2	
6	Octahedral	0	AX_6	 Octahedral	90°, 180°	SF_6	

Table 10.1 (Part 6) VSEPR Notation, Electron-Group Geometry, and Molecular Geometry

Number of Electron Groups	Electron-Group Geometry	Number of Lone Pairs	VSEPR Notation	Molecular Geometry	Ideal Bond Angles	Example	Molecular Model
6	Octahedral	1	AX_5E	 Square pyramidal	90°	BrF_5	
6	Octahedral	2	AX_4E_2	 Square planar	90°	XeF_4	

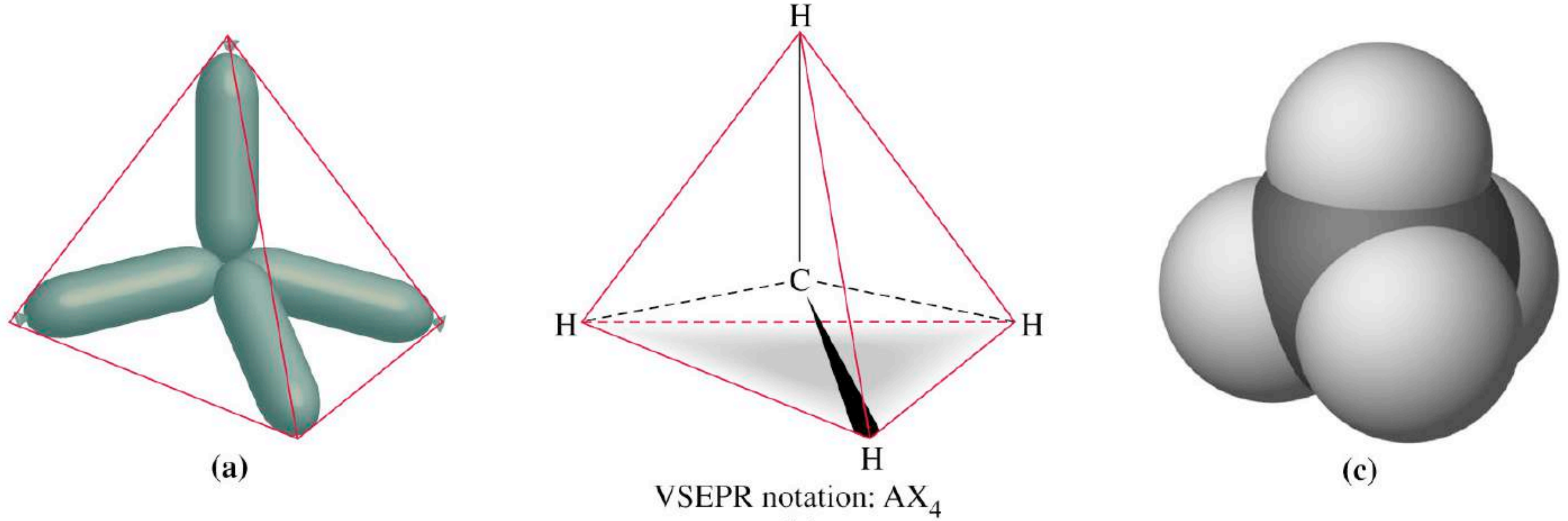
Example 10.1

Use the VSEPR method to predict the shape of the nitrate ion.

Structures with No Lone Pairs

- AX_2: both the electron-group geometry and the molecular geometry for two electron groups is *linear*.
- AX_3: these molecules have a *trigonal planar* geometry.
- AX_4: these molecules have a *tetrahedral* geometry.
- AX_5: these molecules have a *trigonal bipyramidal* geometry.
- AX_6: these molecules have an *octahedral* geometry.
- The AX_5 and AX_6 require an expanded valence shell and, therefore, the central atom is a third-period or higher element.

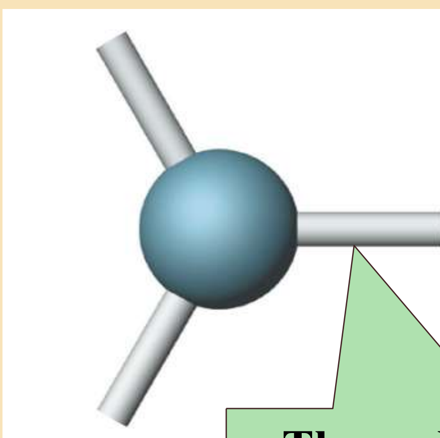
Geometry of Methane

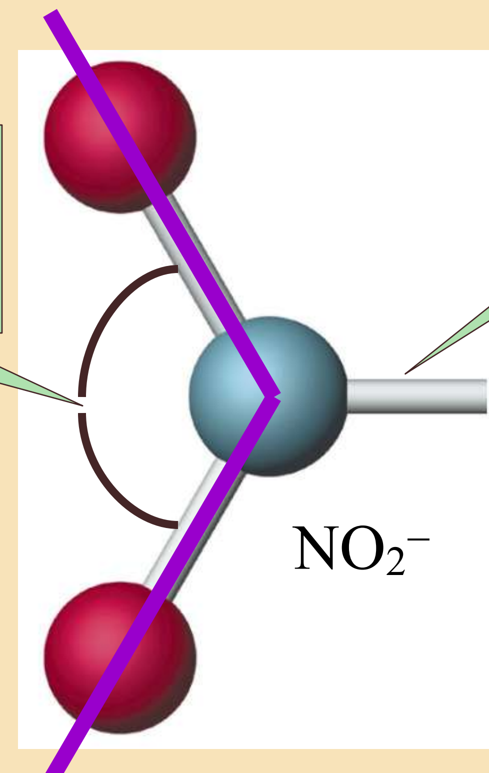


(a) (b) (c)

Structures with Lone Pairs

- Electron groups on the central atom repel one another, whether they are shared pairs or lone pairs.
- However, the geometry of the ***molecule*** is found using the bonded atoms.

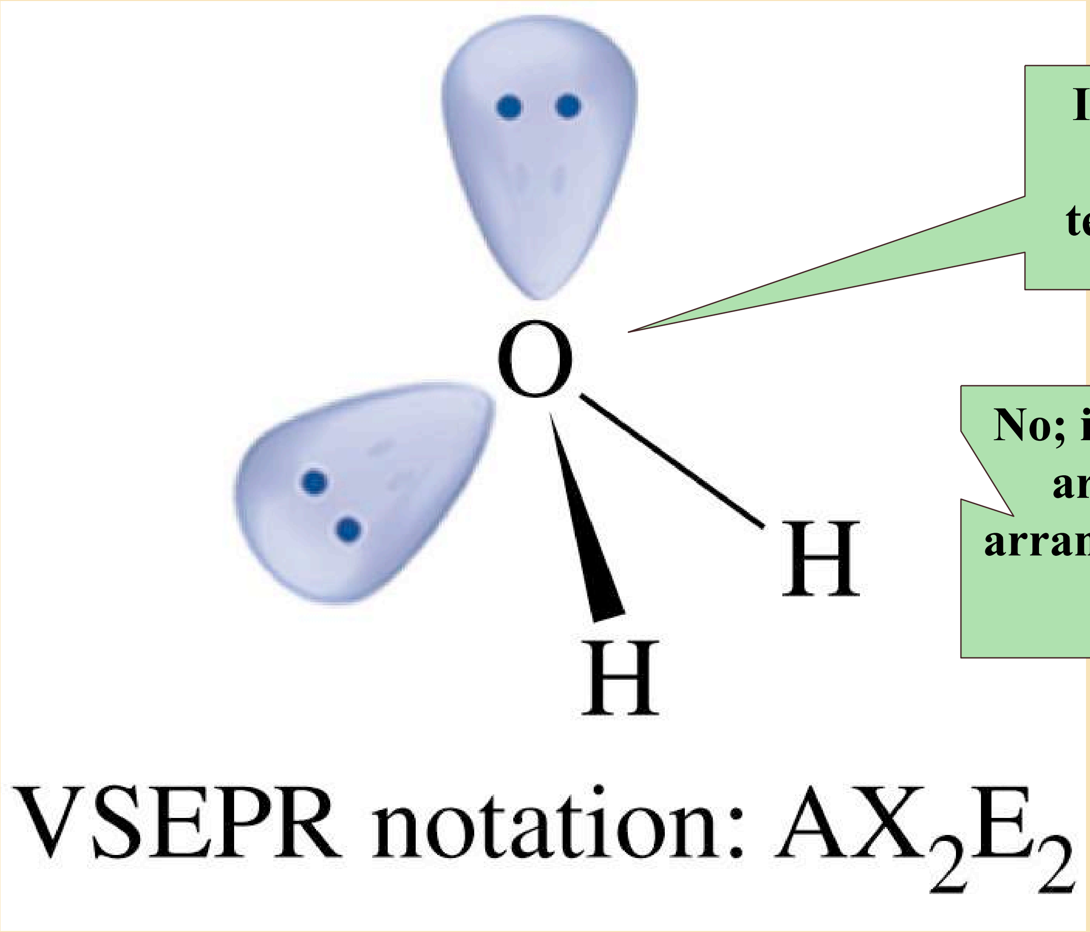




Some Structures with Lone Pairs

- AX_2E: these molecules have an electron-group ***trigonal planar*** geometry, but a ***bent*** molecular geometry.
- AX_2E_2: these molecules have an electron-group ***tetrahedral*** geometry, but a ***bent*** molecular geometry.
- AX_3E: these molecules have an electron-group ***tetrahedral*** geometry, but a ***trigonal pyramidal*** molecular geometry.
- AX_4E: these molecules have an electron-group ***trigonal bipyramidal*** geometry, but a ***seesaw*** molecular geometry.
- AX_4E_2: these molecules have an electron-group ***octahedral*** geometry, but a ***square planar*** molecular geometry.

Molecular Geometry of Water



Is the water molecule tetrahedral?

No; its electron groups are tetrahedrally arranged. The *molecule* is _______.

Example 10.2

Use the VSEPR method to predict the molecular geometry of XeF_2.

Example 10.3

Use the VSEPR method to describe, as best you can, the molecular geometry of the nitric acid molecule, HNO_3.

Polar Molecules and Dipole Moments

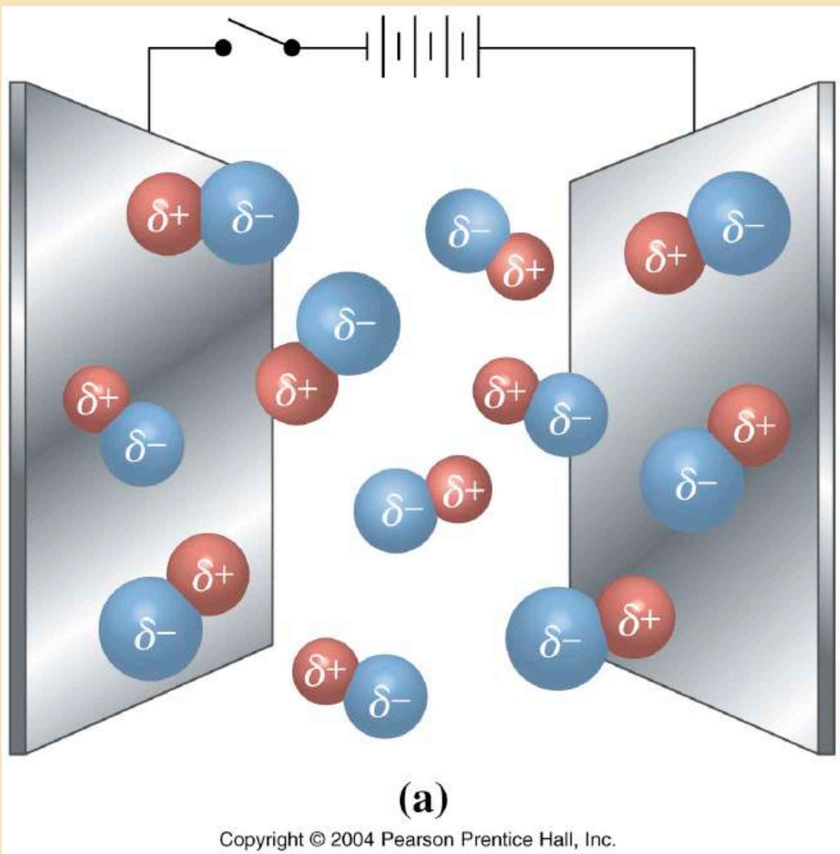
- A ***polar bond*** (Chapter 9) has separate centers of positive and negative charge.
- A ***molecule*** with separate centers of positive and negative charge is a ***polar molecule.***
- The ***dipole moment (μ)*** of a molecule is the product of the magnitude of the charge (δ) and the distance (*d*) that separates the centers of positive and negative charge.

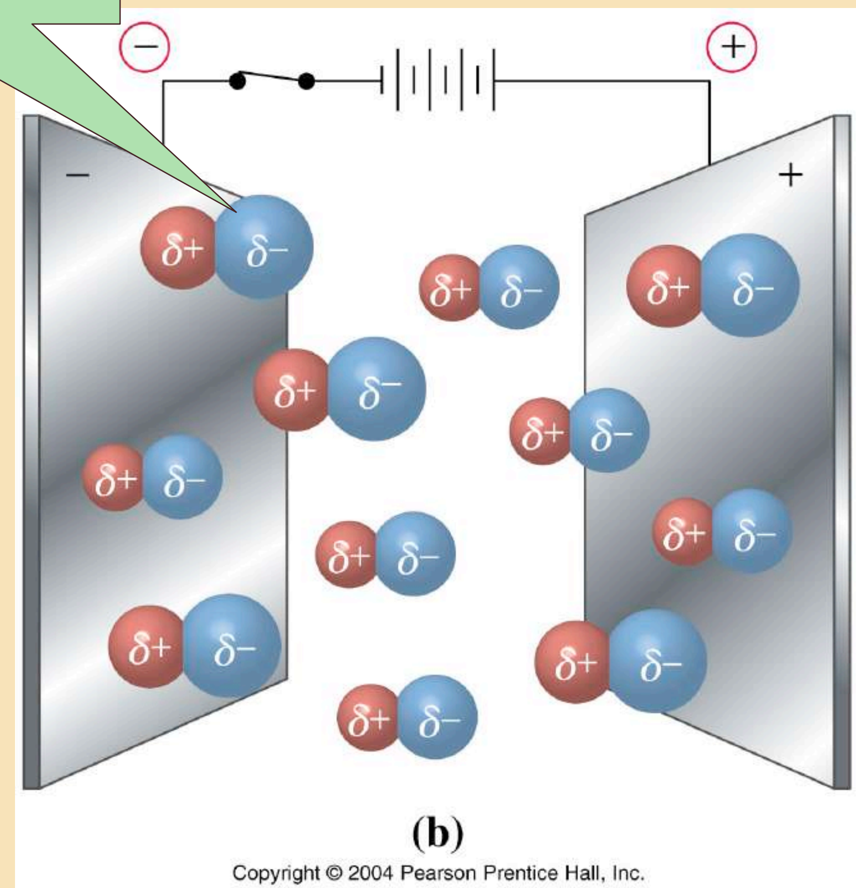
$$\mu = \delta d$$

- A unit of dipole moment is the ***debye (D)***.
- One debye (D) is equal to 3.34×10^{-30} C m.

Polar Molecules in an Electric Field

An electric field causes polar molecules to align with the field.





Example 10.4

Explain whether you expect the following molecules to be polar or nonpolar.

(a) $CHCl_3$ **(b)** CCl_4

Example 10.5 A Conceptual Example

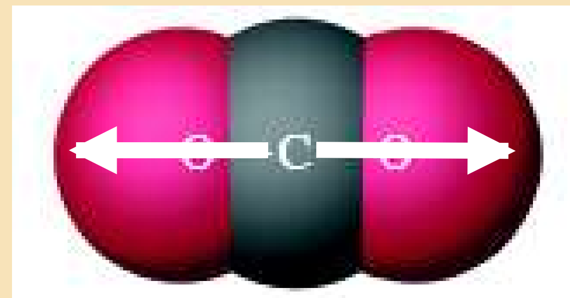
Of the two compounds NOF and NO_2F, one has μ = 1.81 D and the other has μ = 0.47 D. Which dipole moment do you predict for each compound? Explain.

Bond Dipoles and Molecular Dipoles

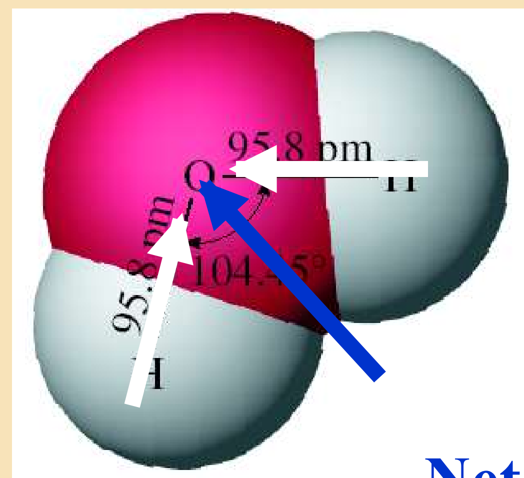
- A polar covalent bond has a ***bond dipole***; a separation of positive and negative charge centers in an individual bond.
- Bond dipoles have both a ***magnitude*** and a ***direction*** (they are ***vector*** quantities).
- Ordinarily, a polar molecule must have polar bonds, *BUT* … polar bonds are not sufficient.
- A molecule may have polar bonds and be a ***nonpolar*** molecule – *IF* the bond dipoles cancel.

Bond Dipoles and Molecular Dipoles

- CO_2 has polar bonds, but is a linear molecule; the bond dipoles cancel and it has no net dipole moment (μ = 0 D).
- The water molecule has polar bonds also, but is an ***angular*** molecule.
- The bond dipoles do ***not*** cancel (μ = 1.84 D), so water is a ***polar*** molecule.



No net dipole



Net dipole

Molecular Shapes and Dipole Moments

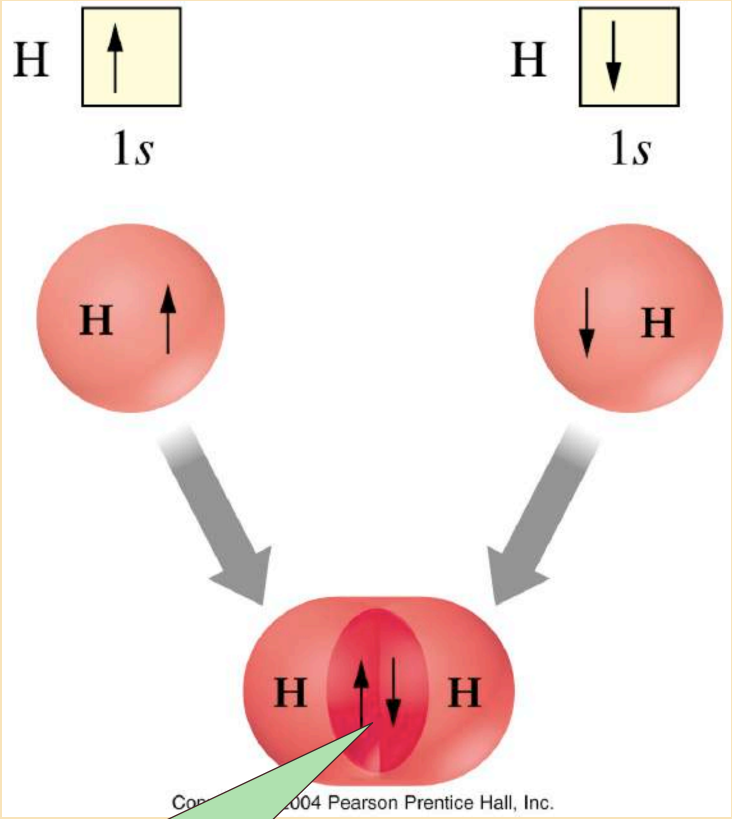
To predict molecular polarity:

1. Use electronegativity values to predict bond dipoles.
2. Use the VSEPR method to predict the molecular shape.
3. From the molecular shape, determine whether bond dipoles cancel to give a nonpolar molecule, or combine to produce a resultant dipole moment for the molecule.

Note: Lone-pair electrons can also make a contribution to dipole moments.

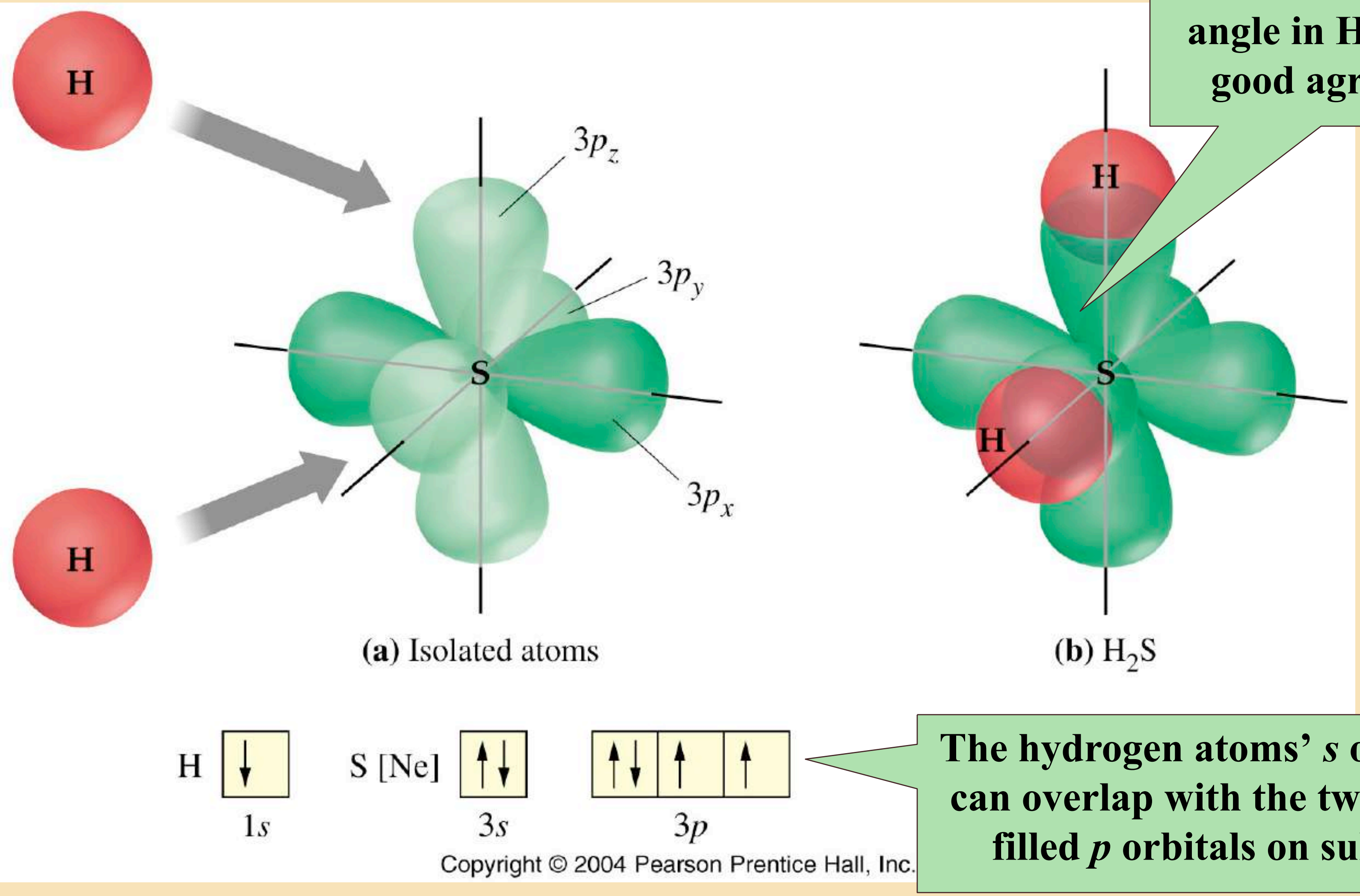
Atomic Orbital Overlap

- ***Valence Bond (VB)*** theory states that a covalent bond is formed when atomic orbitals (AOs) overlap.
- In the overlap region, electrons with opposing spins produce a high electron charge density.
- In general, the more extensive the overlap between two orbitals, the stronger is the bond between two atoms.



Overlap region between nuclei has high electron density

Bonding in H_2S



The measured bond angle in H_2S is 92°; good agreement.

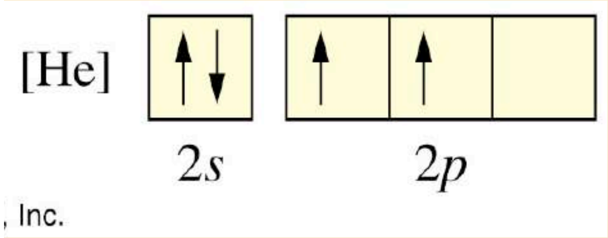
The hydrogen atoms' *s* orbitals can overlap with the two half-filled *p* orbitals on sulfur.

Important Points of VB Theory

- Most of the electrons in a molecule remain in the same orbital locations that they occupied in the separated atoms.
- Bonding electrons are ***localized*** in the region of AO overlap.
- For AOs with directional lobes (such as *p* orbitals), maximum overlap occurs when the AOs overlap ***end to end***.
- VB theory is not without its problems …

Hybridization of Atomic Orbitals

VB theory: carbon should have just ***two*** bonds, and they should be about 90° apart.
But CH_4 has *four* C—H bonds, 109° apart.

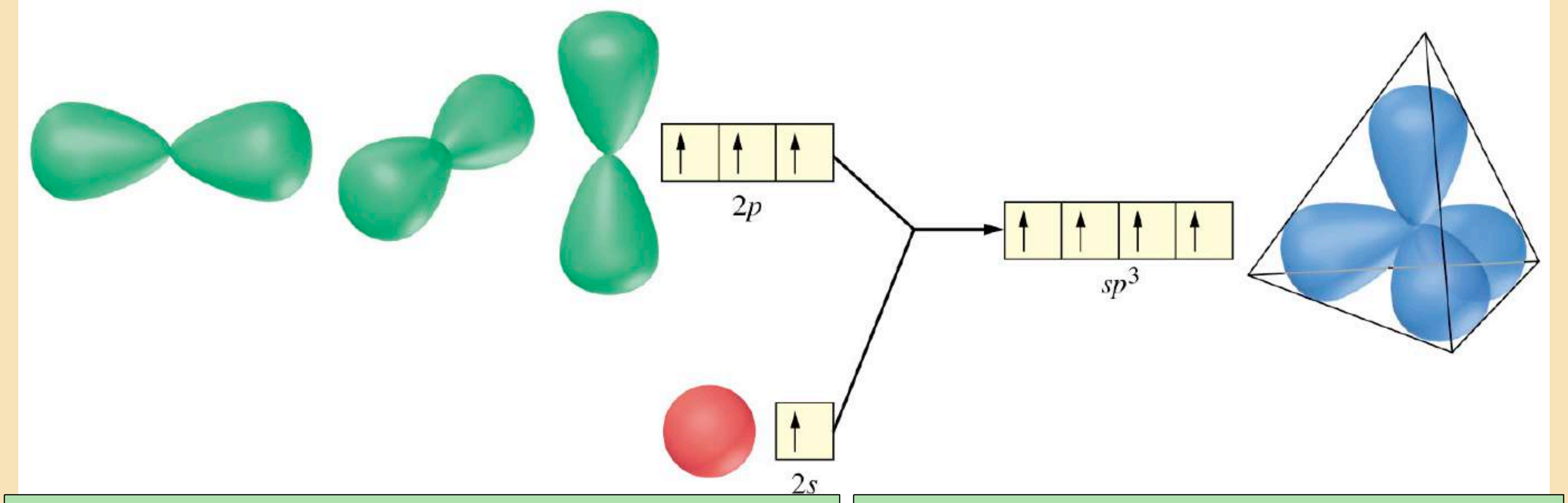


- We can ***hybridize*** the four orbitals holding valence electrons; mathematically combine the wave functions for the 2*s* orbital and the three 2*p* orbitals on carbon.
- The four AOs combine to form four new ***hybrid*** AOs.
- The four hybrid AOs are degenerate (same energy) and each has a single electron (Hund's rule).

sp^3 Hybridization

- Hybridizing one *s* orbital with three *p* orbitals gives rise to four hybrid orbitals called ***sp*^{3}** orbitals.
- The number of hybrid orbitals is equal to the number of atomic orbitals combined.
- The four hybrid orbitals, being equivalent, are about 109° apart.

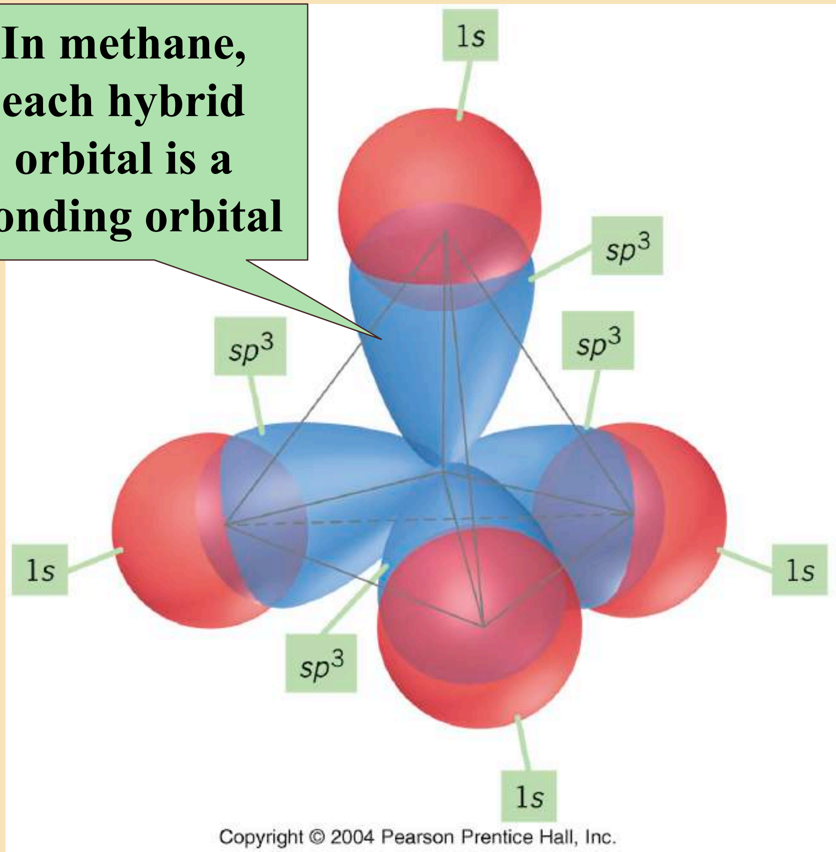
The sp^3 Hybridization Scheme



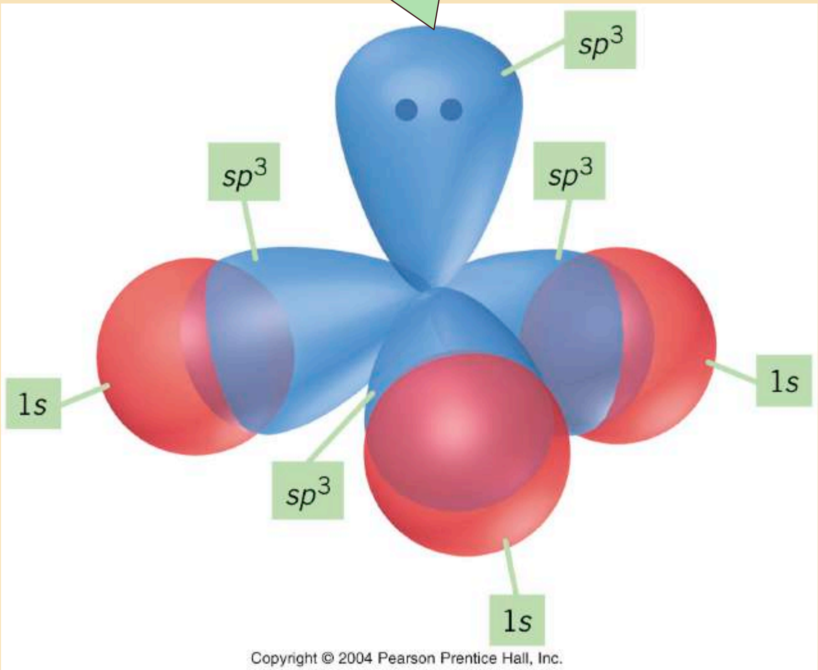
Four AOs … **… form four new hybrid AOs.**

Methane and Ammonia

In methane, each hybrid orbital is a bonding orbital



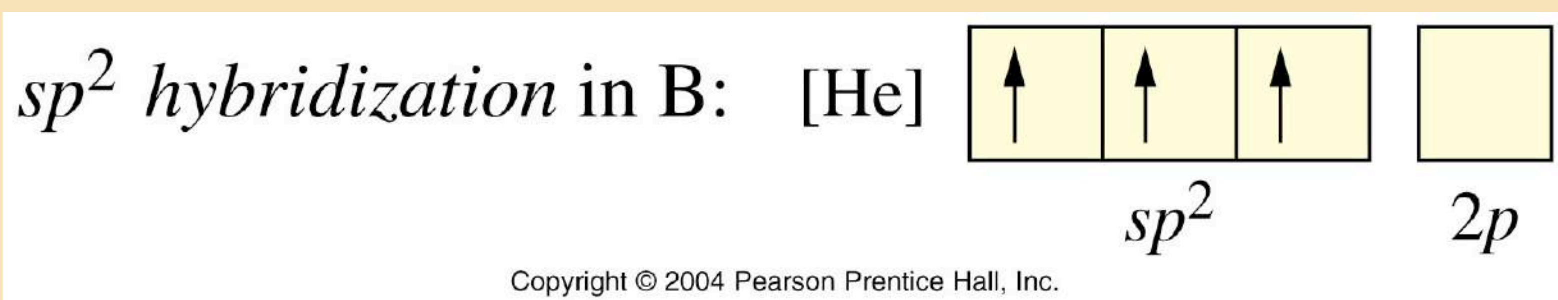
In ammonia, one of the hybrid orbitals contains the lone pair that is on the nitrogen atom



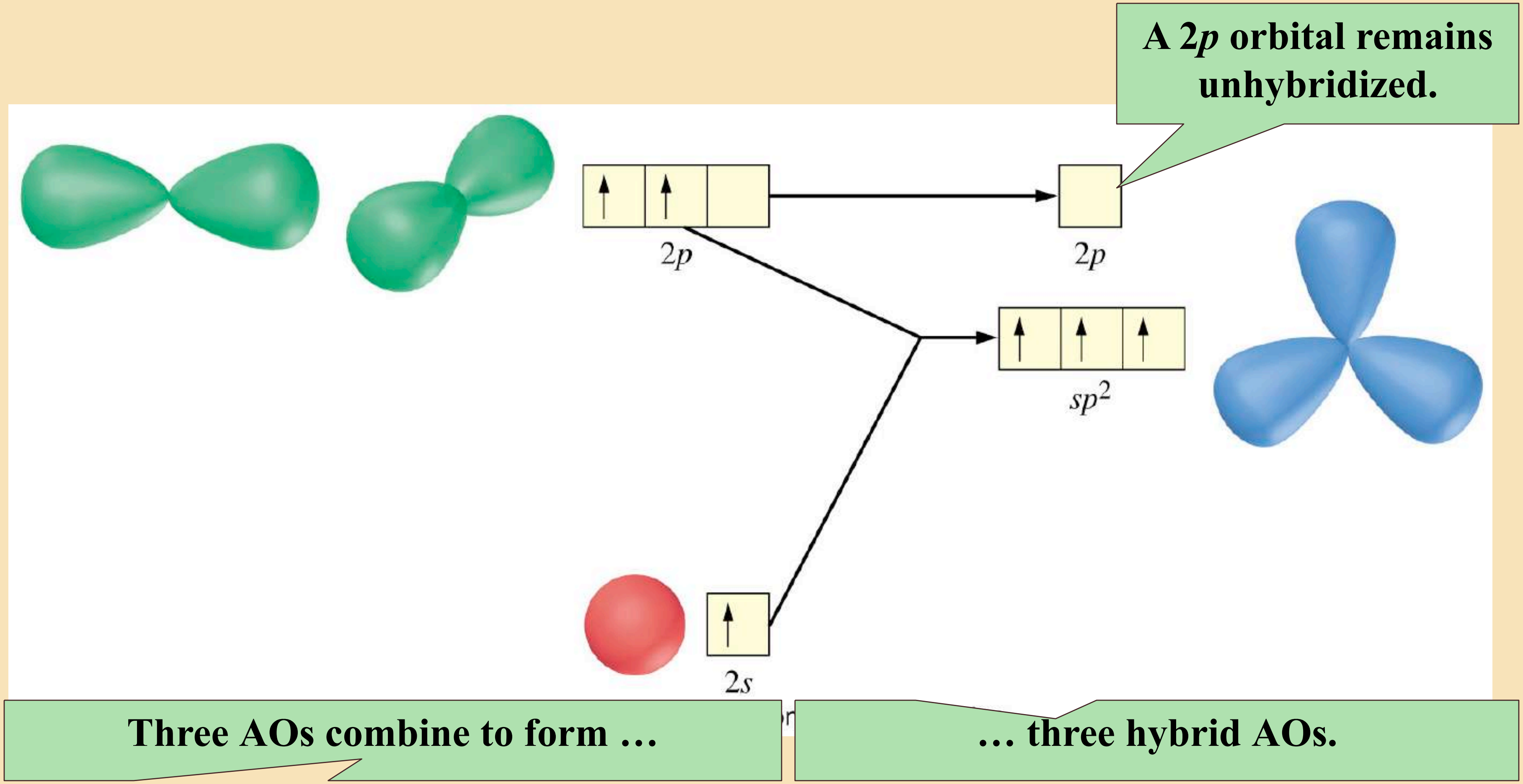
Four *sp*^{3} hybrid orbitals: tetrahedral
Four electron groups: tetrahedral
Coincidence? Hardly.

sp^2 Hybridization

- Three ***sp*²** hybrid orbitals are formed from an *s* orbital and two *p* orbitals.
- The empty *p* orbital remains unhybridized. It may be used in a multiple bond.
- The sp^2 hybrid orbitals are in a plane, 120° apart.
- This distribution gives a ***trigonal planar*** molecular geometry, as predicted by VSEPR.

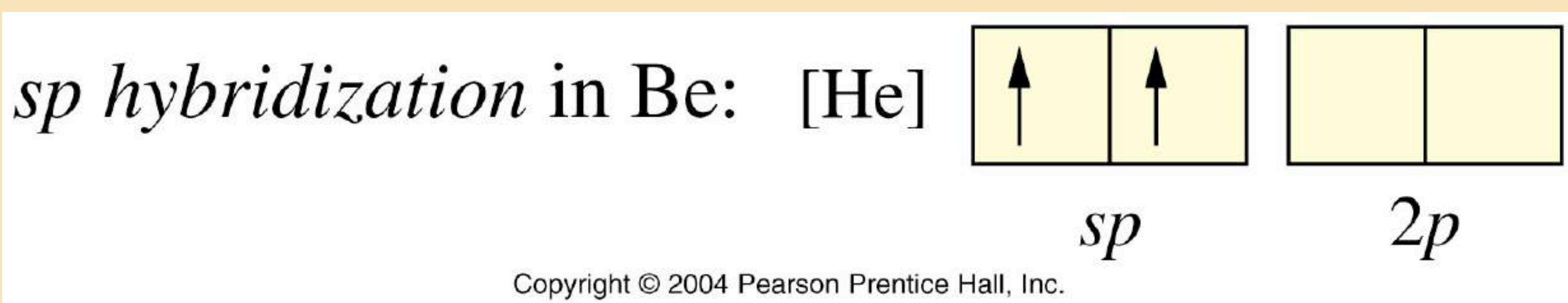


The sp^2 Hybridization Scheme in Boron



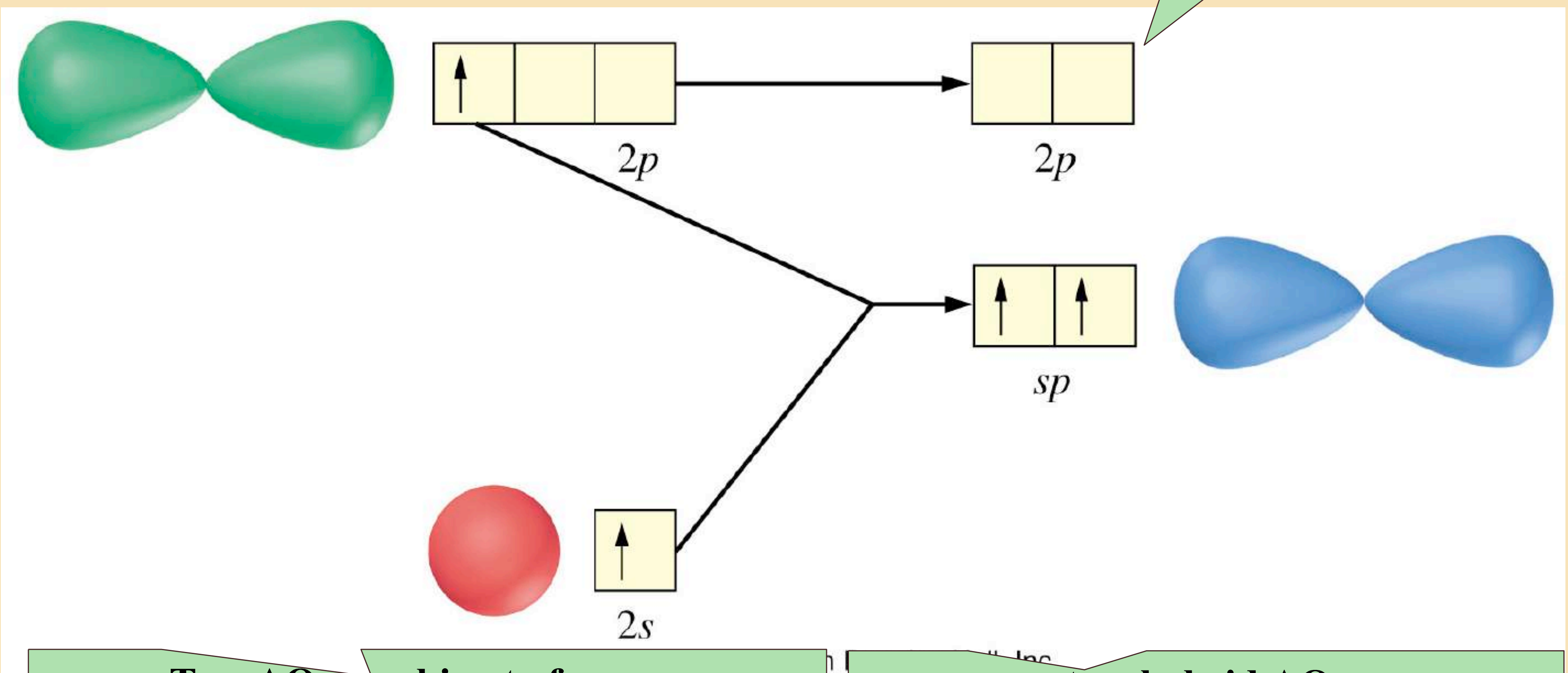
sp Hybridization

- Two ***sp*** hybrid orbitals are formed from an *s* orbital and a *p* orbital.
- Two empty *p* orbitals remains unhybridized; the *p* orbitals may be used in a multiple bond.
- The *sp* hybrid orbitals are 180^{o} apart.
- The geometry around the hybridized atom is ***linear***, as predicted by VSEPR.



sp Hybridization in Be

… with two unused *p* orbitals.

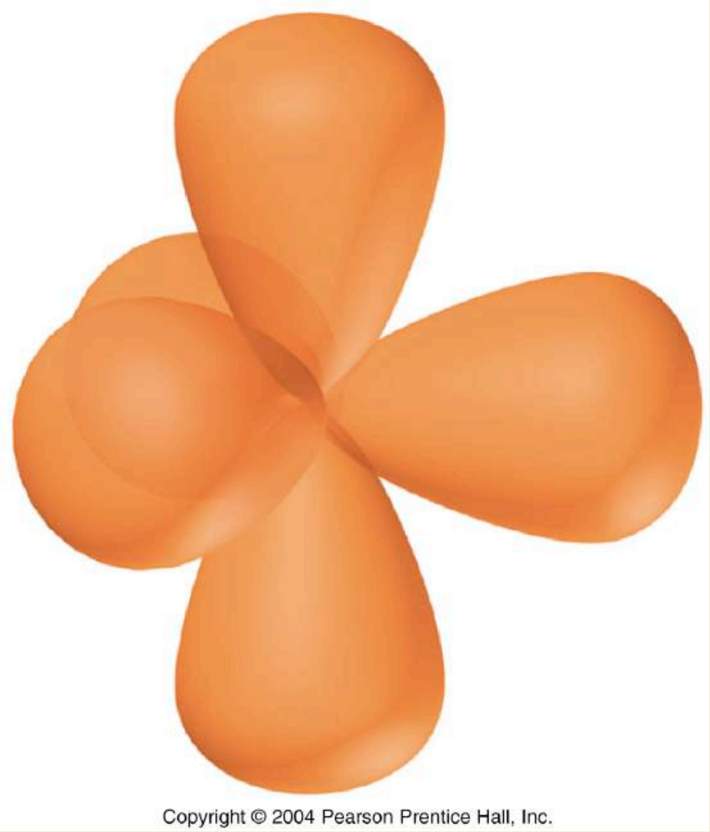


Two AOs combine to form …

… two hybrid AOs …

Hybrid Orbitals Involving *d* Subshells

- This hybridization allows for ***expanded valence shell*** compounds.
- By hybridizing one *s*, three *p*, and one *d* orbital, we get five ***sp^3d*** hybrid orbitals.
- This hybridization scheme gives trigonal bipyramidal electron-group geometry.



Hybrid Orbitals Involving *d* Subshells

- By hybridizing one *s*, three *p*, and two *d* orbitals, we get five ***sp^3d^2*** hybrid orbitals.
- This hybridization scheme gives octahedral geometry.

Predicting Hybridization Schemes

In the absence of experimental evidence, probable hybridization schemes can be predicted:

- Write a plausible Lewis structure for the molecule or ion.
- Use the VSEPR method to predict the electron-group geometry of the central atom.
- Select the hybridization scheme that corresponds to the VSEPR prediction.
- Describe the orbital overlap and molecular geometry.

Table 10.2 Hybrid Orbitals and Their Geometric Orientation

Hybrid Orbitals	Geometric Orientation	Example
sp	Linear	$BeCl_2$
sp^2	Trigonal planar	BF_3
sp^3	Tetrahedral	CH_4
sp^3d	Trigonal bipyramidal	PCl_5
sp^3d^2	Octahedral	SF_6

Example 10.6

Iodine pentafluoride, IF_5, is used commercially as a fluorinating agent—a substance that, via a chemical reaction, introduces fluorine into other compounds. Describe a hybridization scheme for the central atom, and sketch the molecular geometry of the IF_5 molecule.

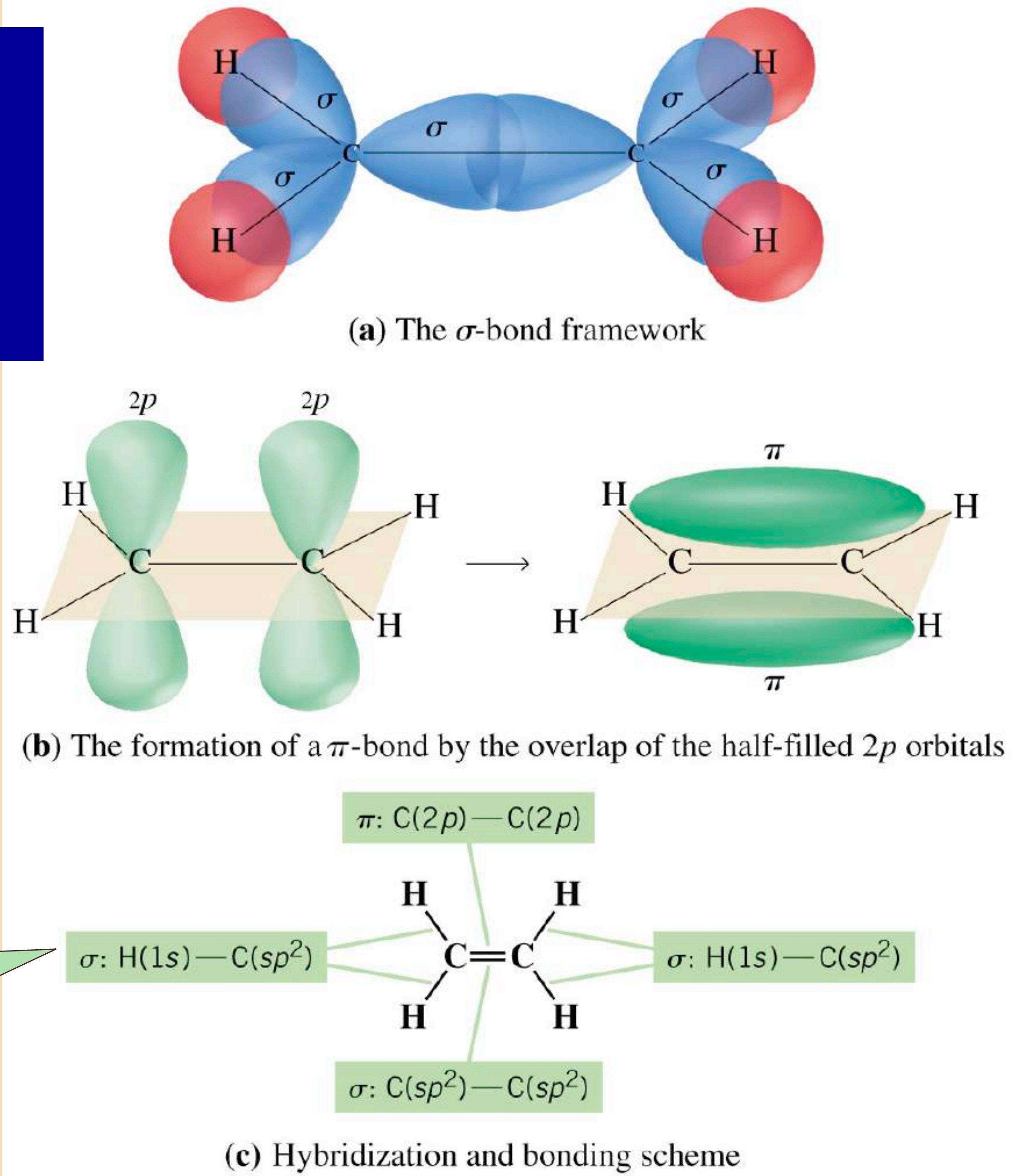
Hybrid Orbitals and Multiple Covalent Bonds

- Covalent bonds formed by the end-to-end overlap of orbitals are called ***sigma (σ) bonds***.
- All single bonds are sigma bonds.
- A bond formed by parallel, or side-by-side, orbital overlap is called a ***pi (π) bond***.
- A double bond is made up of ***one*** sigma bond and ***one*** pi bond.
- A triple bond is made up of ***one*** sigma bond and ***two*** pi bonds.

VB Theory for Ethylene, C_2H_4

π-bond has *two* lobes (above and below plane), but is *one* bond. Side overlap of 2*p*–2*p*.

The hybridization and bonding scheme is described by listing each bond and its overlap.

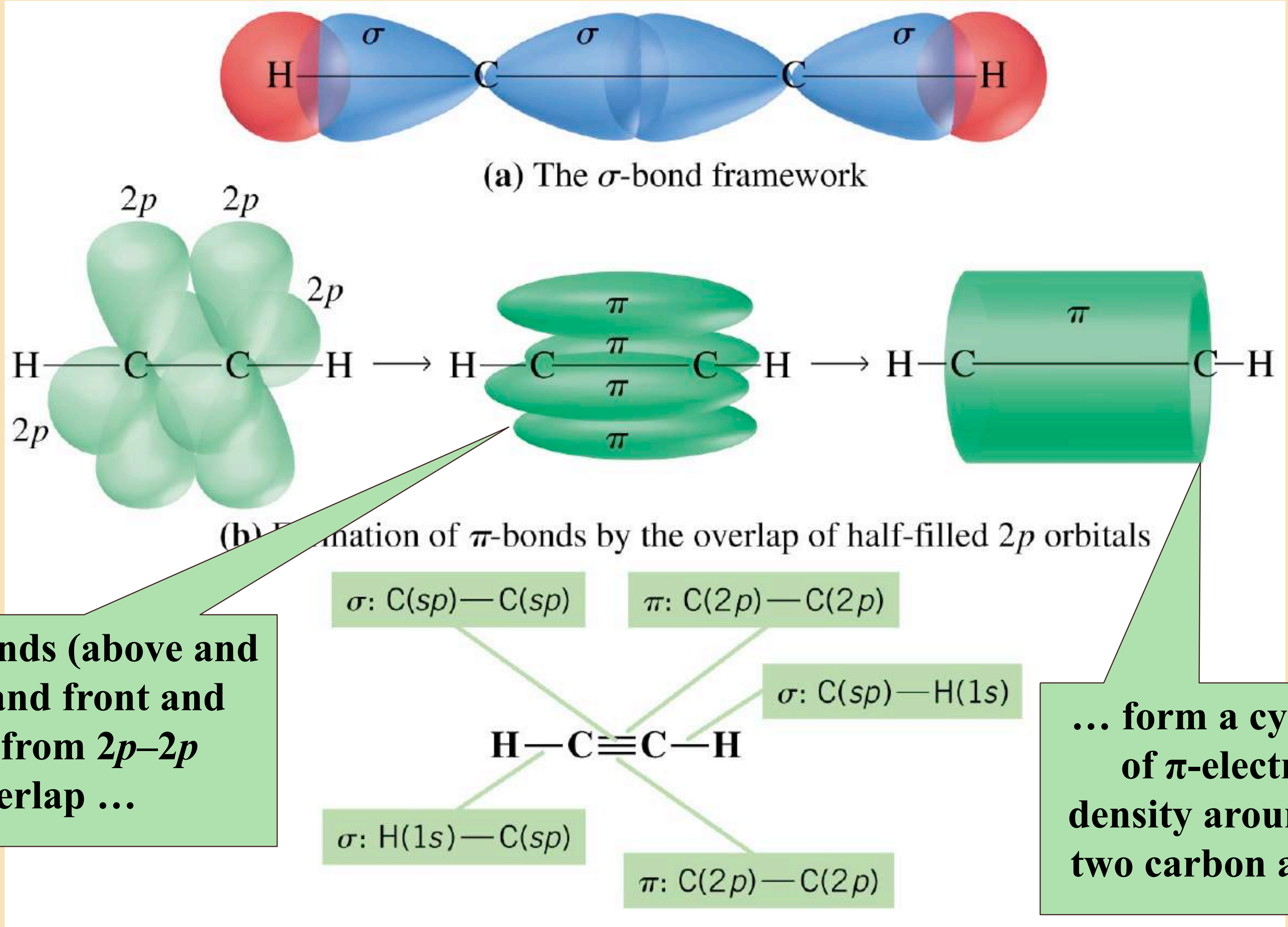


Example 10.7

Formic acid, HCOOH, is the simplest carboxylic acid.

- Predict a plausible molecular geometry for this molecule.
- Propose a hybridization scheme for the central atoms that is consistent with that geometry.
- Sketch a bonding scheme for the molecule.

VB Theory: Acetylene



(a) The σ-bond framework

(b) F[…]mation of π-bonds by the overlap of half-filled 2p orbitals

(c) Hybridization and bonding scheme

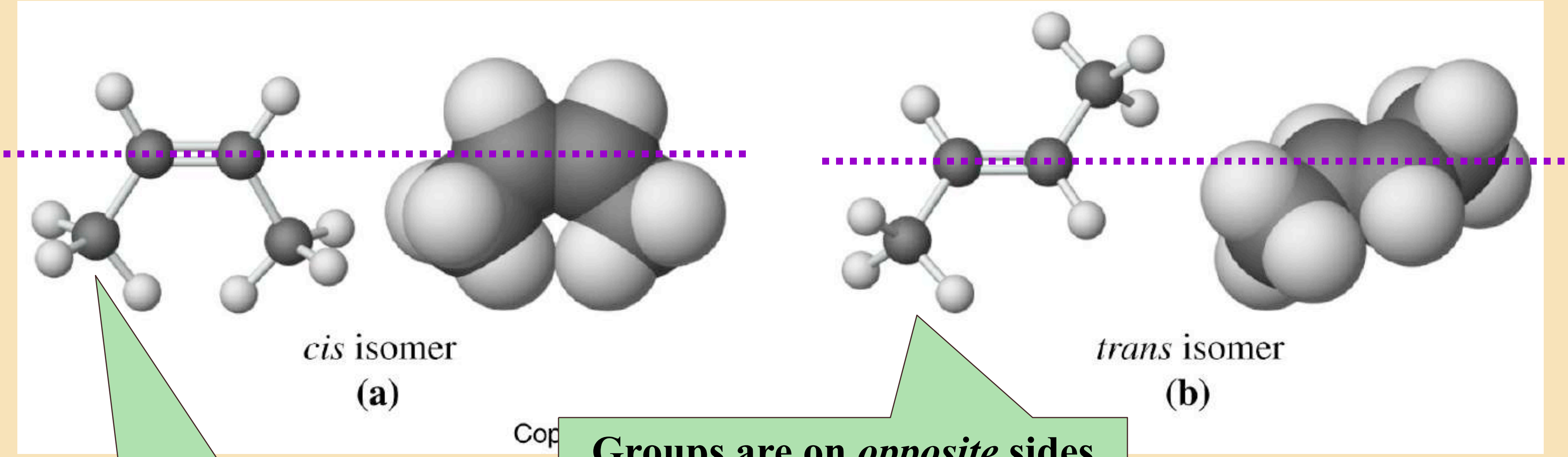
Two π-bonds (above and below, and front and back) from 2*p*–2*p* overlap …

… form a cylinder of π-electron density around the two carbon atoms.

Geometric Isomerism

- ***Geometric isomers*** are isomers that differ only in the geometric arrangement of certain substituent groups.
- Two types of geometric isomers include:
  - ***cis***: substituent groups are on the same side
  - ***trans***: substituent groups are on opposite sides
- *cis*- and *trans*- compounds are distinctly different in both physical and chemical properties.
- Usually formed across double bonds and in square planar compounds.

Geometric Isomerism in 2-Butene



Groups are on *opposite* sides of double bond: *trans*-isomer

Groups are on the *same side* of the double bond: *cis*-isomer

***n-Butane* does not have these isomers; why not??**

Example 10.8 A Conceptual Example

Is it possible to write a unique structural formula for 1,2-dichloroethene if we are told that the molecule is nonpolar?

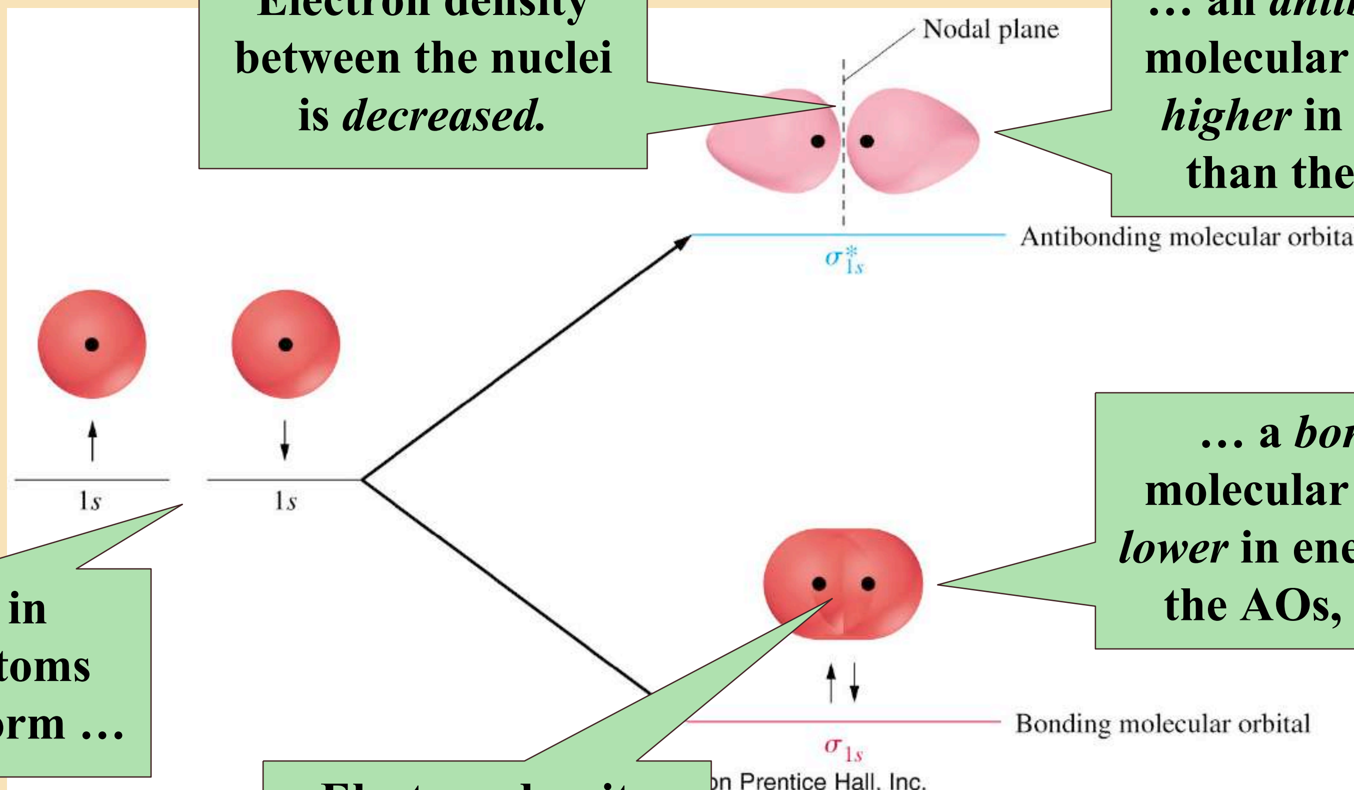
Molecular Orbitals

- An alternative scheme to VB theory uses molecular orbitals.
- A ***molecular orbital (MO)*** is a mathematical description of the region in a ***molecule*** where there is a high probability of finding electrons.
- ***Molecular orbitals*** are to molecules as ________ are to atoms.
- In MO theory, molecular orbitals are formed by the combination of atomic orbitals.

Characteristics of Molecular Orbitals

- Two atomic orbitals combine => two molecular orbitals result.
- Of each pair of molecular orbitals, one is a ***bonding*** molecular orbital.
  - The bonding orbital is at a ***lower*** energy than the separate atomic orbitals.
  - Electrons in a bonding orbital ***increase*** the stability of the molecule.
- The second orbital is an ***antibonding*** orbital.
  - The antibonding orbital is at a ***higher*** energy than the AOs.
  - Electrons in an antibonding orbital ***decrease*** the stability of the molecule.

Types of Molecular Orbitals



Two AOs in hydrogen atoms combine to form …

… a *bonding* molecular orbital, *lower* in energy than the AOs, and …

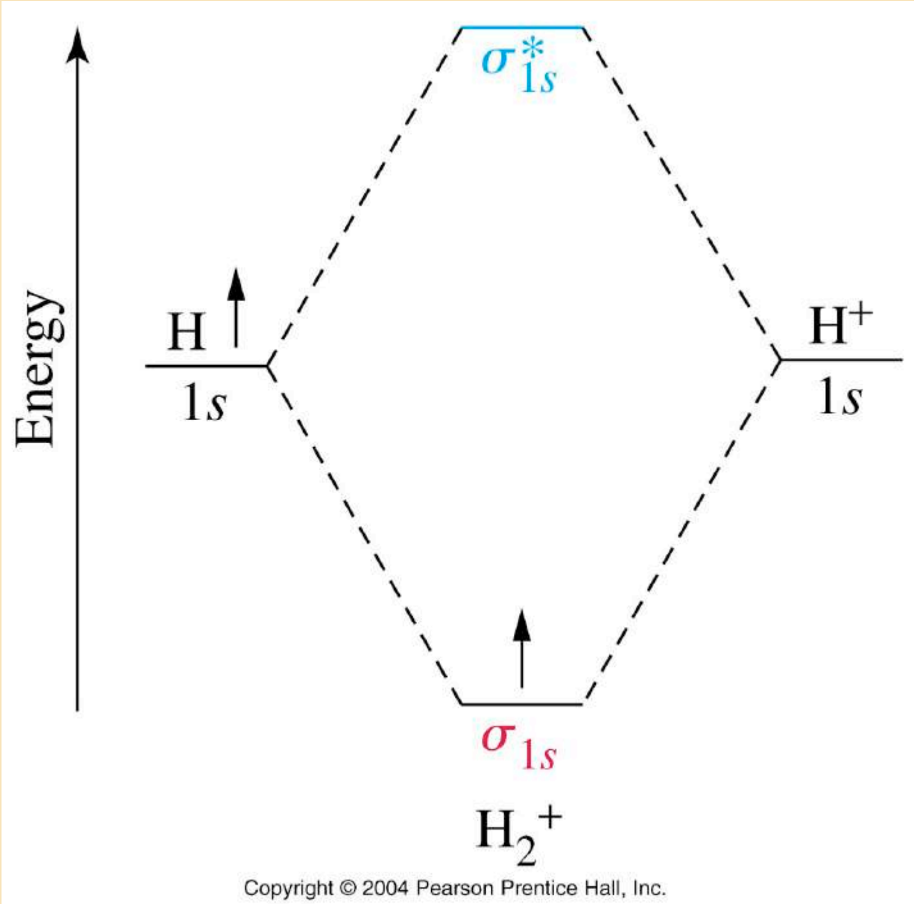
… an *antibonding* molecular orbital, *higher* in energy than the AOs.

Electron density between the nuclei is *increased.*

Electron density between the nuclei is *decreased.*

Example 10.9 A Conceptual Example

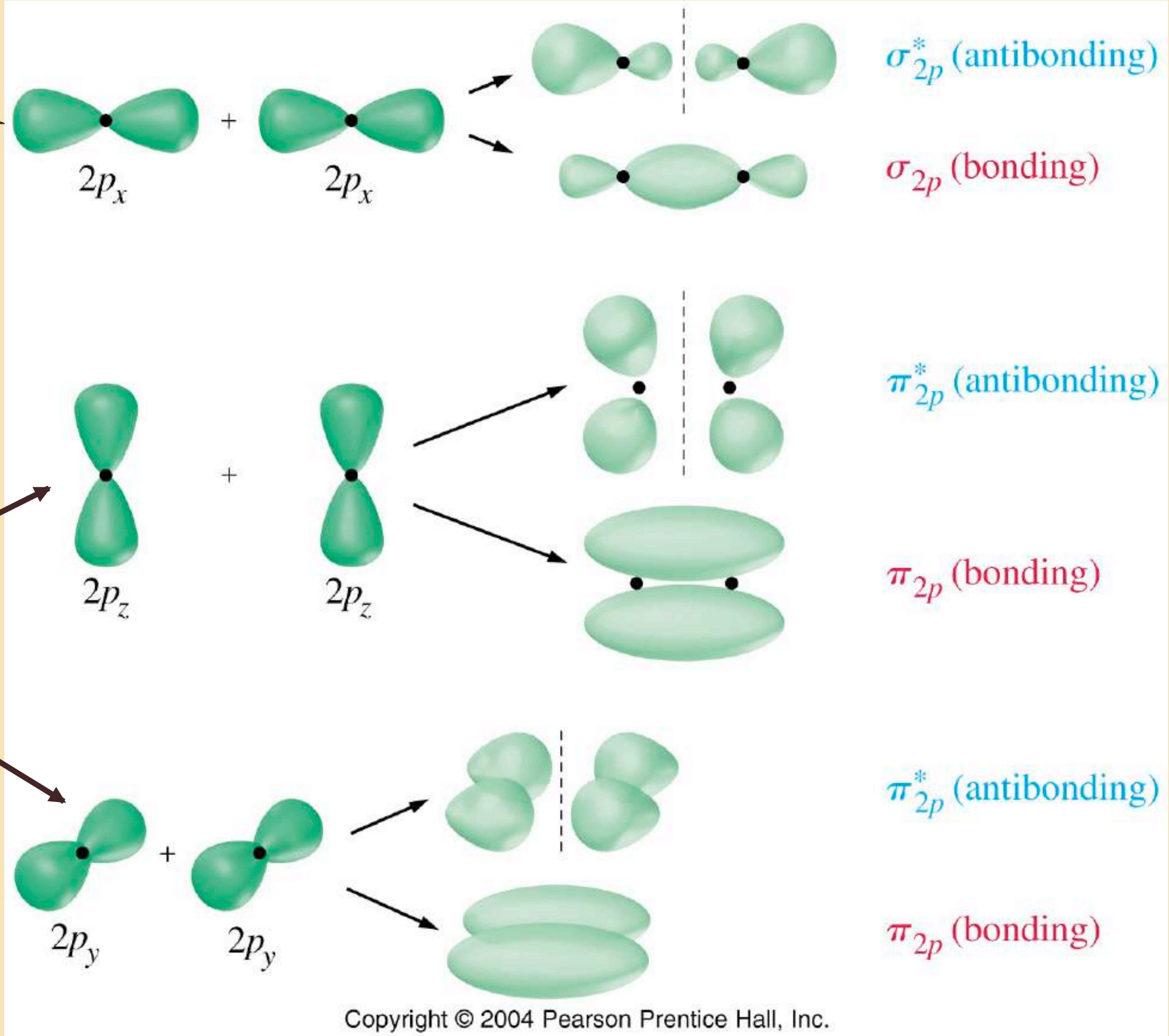
Molecular orbital theory allows for species with a one-electron bond. What does the term “one-electron bond” signify? Cite an example of such a bond.



Homonuclear Diatomic Molecules of the Second-Period Elements

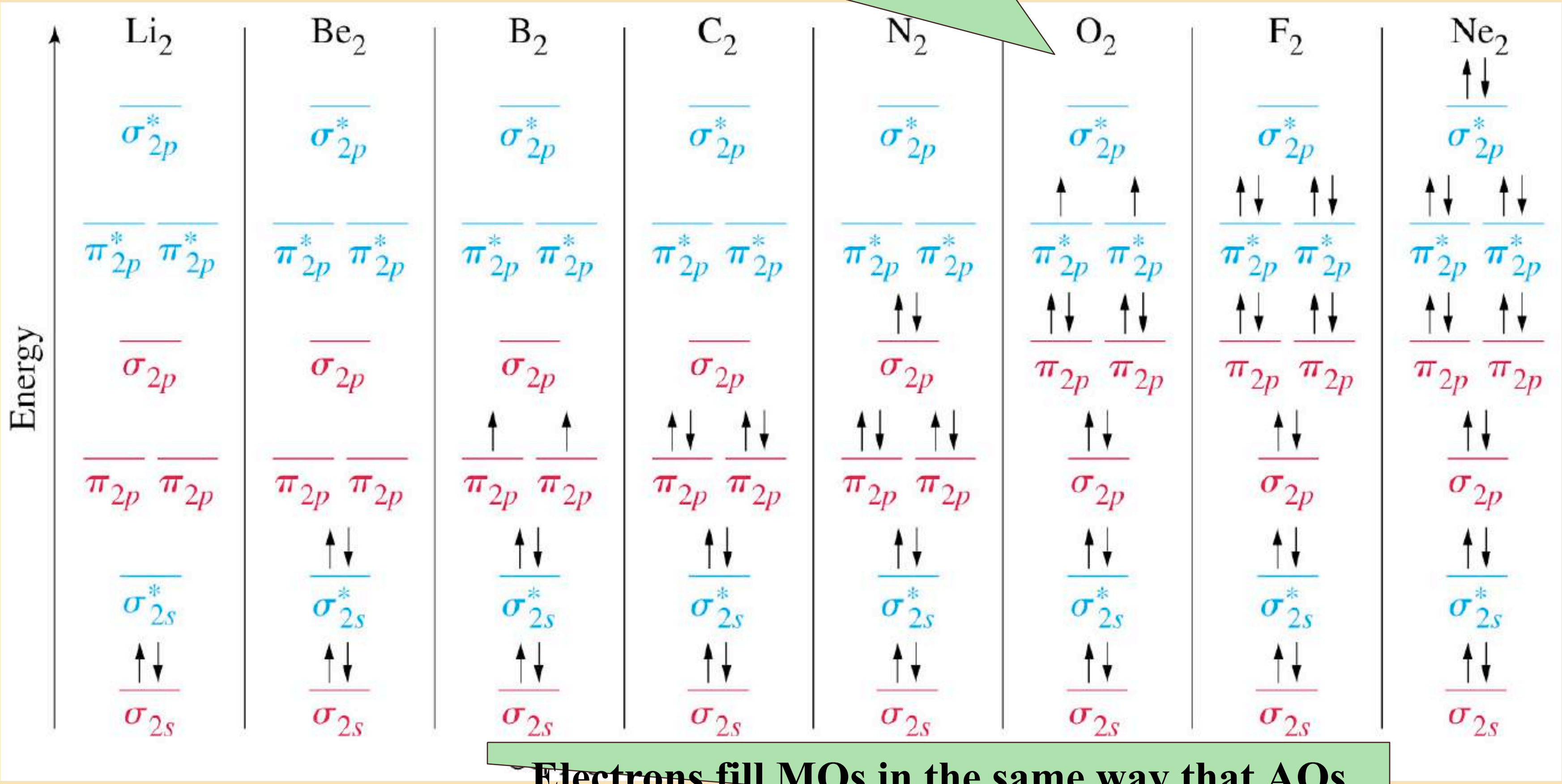
The two p_x orbitals combine to form *sigma* bonding and antibonding MOs.

The two p_y orbitals and the two p_z orbitals give *pi* bonding and antibonding MOs.



Molecular Orbital Diagrams

Just like AOs: there are some irregularities in the filling order …



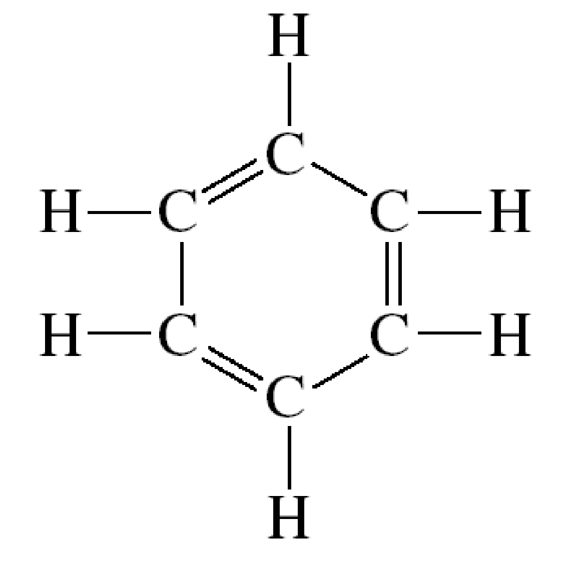
Electrons fill MOs in the same way that AOs are filled – lowest energy to highest energy.

Example 10.10 A Conceptual Example

When an electron is removed from a N_2 molecule, forming an N_2^+ ion, the bond between the N atoms is weakened. When an O_2 molecule is ionized to O_2^+, the bond between the O atoms is strengthened. Explain this difference.

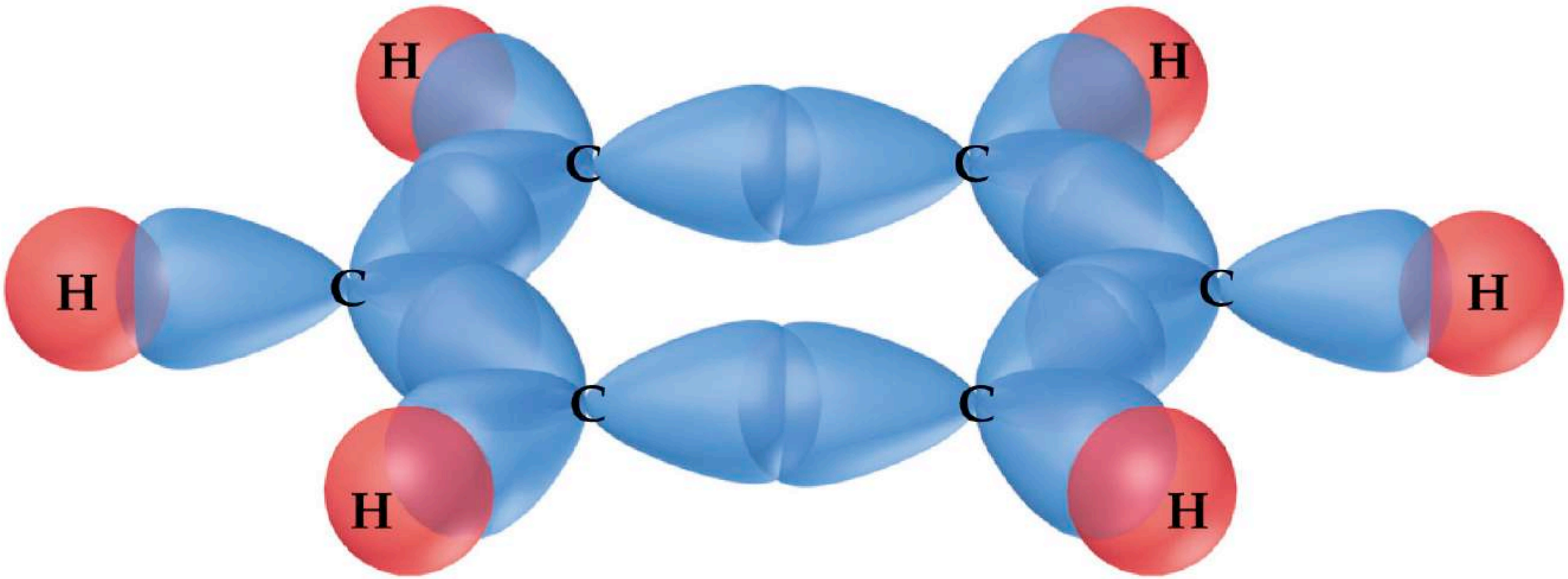
Bonding in Benzene

- In 1865, Kekulé proposed that benzene (C_6H_6) has a *cyclic* structure, with a hydrogen atom attached to each carbon atom. Alternating single and double bonds join the carbon atoms.

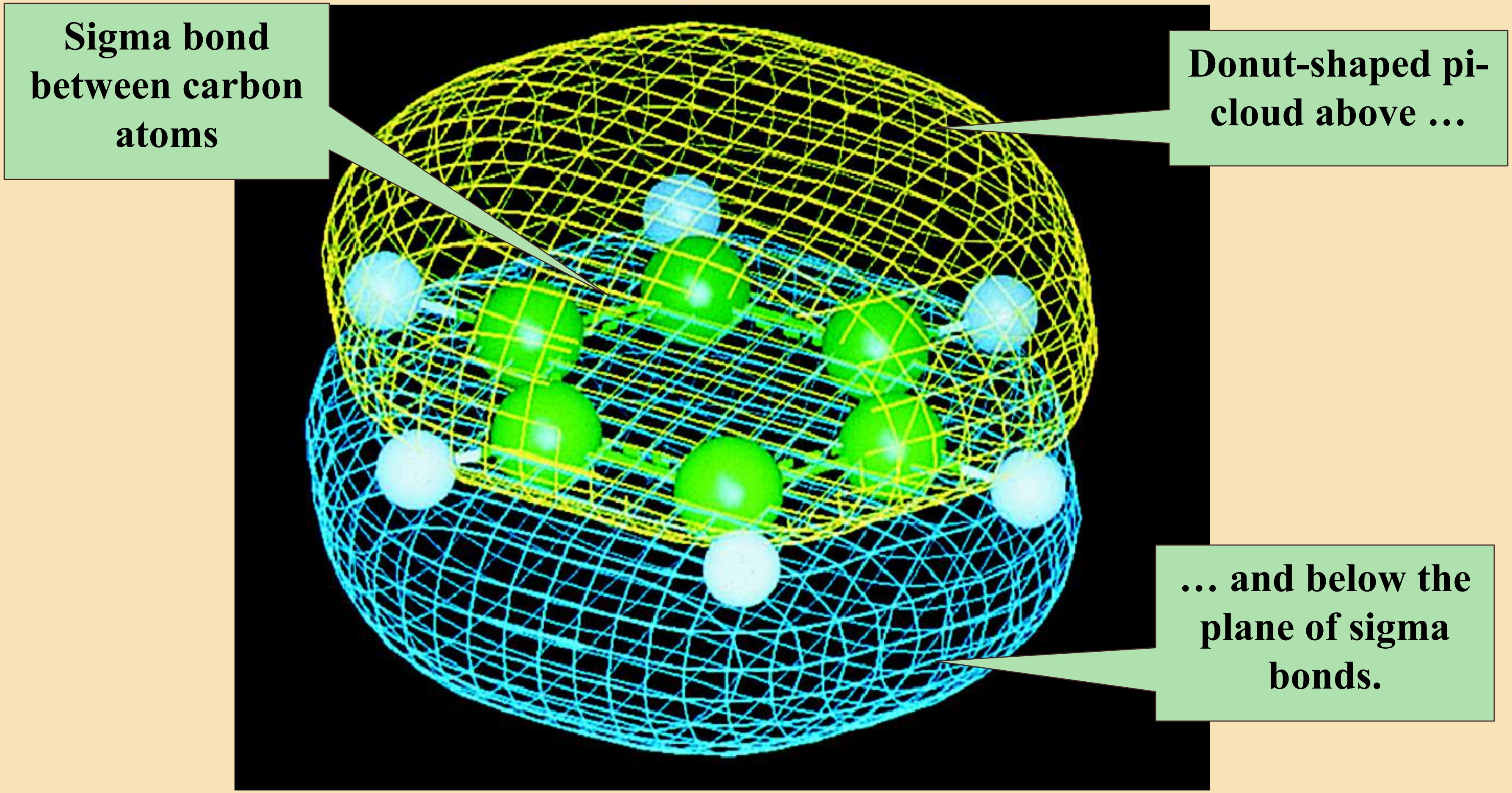


- Modern view: there are two resonance hybrids of benzene.
- The pi-electrons are not localized between any particular carbon atoms, but are ***delocalized*** among all six carbon atoms.

The σ-Bonding Framework



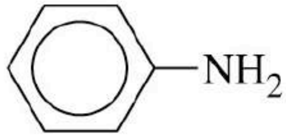
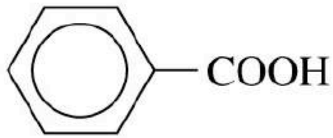
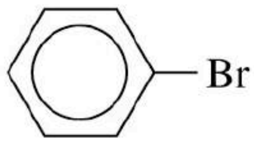
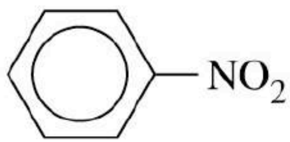
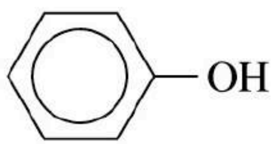
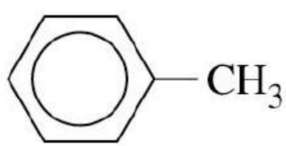
Computer-Generated Structure of Benzene



Aromatic Compounds

- Many of the first benzene-like compounds discovered had pleasant odors, hence the name ***aromatic*** was applied to the compounds.
- Today an ***aromatic compound*** is one that has a ring structure and bonding characteristics related to those of benzene (more in Chapter 23).
- All organic compounds that are not aromatic are called ***aliphatic compounds***.

TABLE 10.3 Some Representative Aromatic Compounds

Name	Structure	Typical Use(s)
Aniline		Starting material for the synthesis of dyes, drugs, resins, varnishes, perfumes; solvent; vulcanizing rubber
Benzoic acid		Food preservative; starting material for the synthesis of dyes and other organic compounds; curing of tobacco
Bromobenzene		Starting material for the synthesis of many other aromatic compounds; solvent; motor oil additive
Nitrobenzene		Starting material for the synthesis of aniline; solvent for cellulose nitrate; in soaps and shoe polish
Phenol		Disinfectant; starting material for the synthesis of resins, drugs, and other organic compounds
Toluene		Solvent; gasoline octane booster; starting material for the synthesis of benzoic acid, benzaldehyde, and many other organic compounds

Cumulative Example

Methyl isocyanate (MIC), used in the manufacture of pesticides and polymers, is a carbon–hydrogen–oxygen–nitrogen compound with a molecular mass of 57.05 u; it is 5.29% H by mass. The nitrogen in a 0.7500-g sample of the compound is converted to $NH_3(g)$, which is neutralized by passing it into 50.00 mL of 0.2800 M $H_2SO_4(aq)$. After neutralization of the $NH_3(g)$, the excess $H_2SO_4(aq)$ requires 36.49 mL of 0.4070 M NaOH(aq) for complete neutralization. Indicate hybridization for the central atoms in the methyl isocyanate molecule, and draw a sketch of the molecule with appropriate bond angles.