WILLIAM H. BROWN
THOMAS POON

www.wiley.com/college/brown

CHAPTER ONE

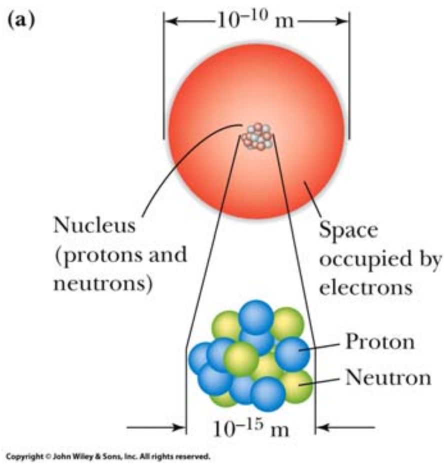
Covalent Bonding and Shapes of Molecules

Organic Chemistry

- **Organic chemistry**: The study of the compounds of carbon.
- Over 10 million organic compounds have been identified.
  - About 1000 new ones are discovered or synthesized and identified each day!
- C is a small atom
  - It forms single, double, and triple bonds.
  - It is intermediate in electronegativity (2.5).
  - It forms strong bonds with C, H, O, N, S, the halogens, and some metals.

Electronic Structure of Atoms

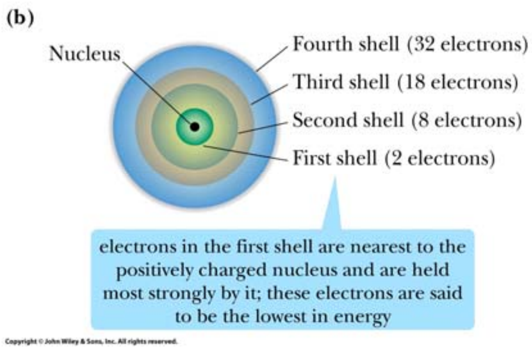
- Figure 1.1 Schematic of an Atom
  - A small dense nucleus, diameter 10^{-14} – 10^{-15} m, which contains positively charged protons, neutrons, and most of the mass of the atom.
  - Extranuclear space, diameter 10^{-10} m, which contains negatively charged electrons.



WILEY 1-3

Electronic Structure of Atoms

- Electrons are confined to regions of space called principle energy levels (shells).
  - Each shell can hold $2n^2$ electrons (n = 1, 2, 3, 4......).



WILEY 1-4

Electronic Structure of Atoms

- Shells are divided into subshells called orbitals, which are designated by the letters *s*, *p*, *d*,…
  - *s* (one per shell)
  - *p* (set of three per shell 2 and higher)
  - *d* (set of five per shell 3 and higher) …

the first shell contains a single orbital called a 1*s* orbital. The second shell contains one 2*s* orbital and three 2*p* orbitals. All *p* orbitals come in sets of three and can hold up to 6 electrons. The third shell contains one 3*s* orbital, three 3*p* orbitals, and five 3*d* orbitals. All *d* orbitals come in sets of five and can hold up to 10 electrons. All *f* orbitals come in sets of seven and can hold up to 14 electrons

TABLE 1.1 Distribution of Orbitals within Shells

Shell	Orbitals Contained in Each Shell	Maximum Number of Electrons Shell Can Hold	Relative Energies of Electrons in Each Shell
4	One 4*s*, three 4*p*, five 4*d*, and seven 4*f* orbitals	2 + 6 + 10 + 14 = 32	Higher
3	One 3*s*, three 3*p*, and five 3*d* orbitals	2 + 6 + 10 = 18	
2	One 2*s* and three 2*p* orbitals	2 + 6 = 8	
1	One 1*s* orbital	2	Lower

Electronic Structure of Atoms

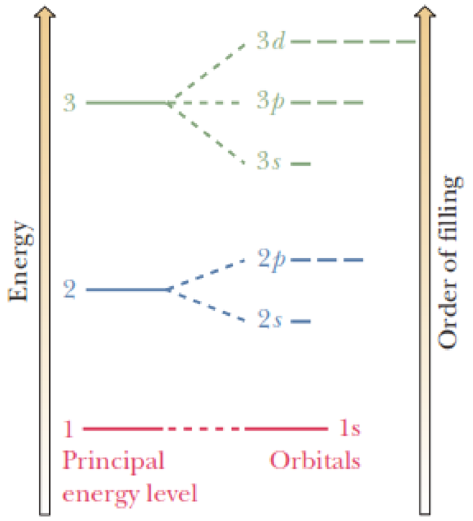
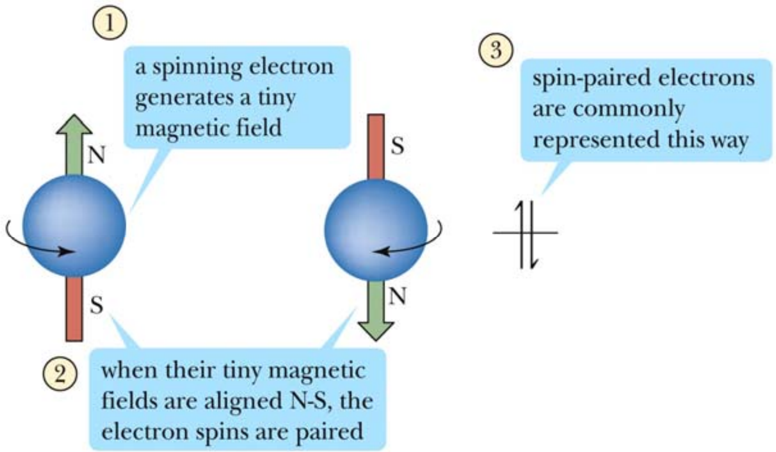
- 

FIGURE 1.2 Relative energies and order of filling of orbitals through the 3*d* orbitals.

Electronic Structure of Atoms

- Figure 1.3 The pairing of electron spins.



Electronic Structure of Atoms

TABLE 1.2 Ground-State Electron Configurations for Elements 1–18*

First Period	H	1	$1s^1$	
	He	2	$1s^2$	
Second Period	Li	3	$1s^2s^1$	[He] $2s^1$
	Be	4	$1s^22s^2$	[He] $2s^2$
	B	5	$1s^22s^22p_x^1$	[He] $2s^22p_x^1$
	C	6	$1s^22s^22p_x^12p_y^1$	[He] $2s^22p_x^12p_y^1$
	N	7	$1s^22s^22p_x^12p_y^12p_z^1$	[He] $2s^22p_x^12p_y^12p_z^1$
	O	8	$1s^22s^22p_x^22p_y^12p_z^1$	[He] $2s^22p_x^22p_y^12p_z^1$
	F	9	$1s^22s^22p_x^22p_y^22p_z^1$	[He] $2s^22p_x^22p_y^22p_z^1$
	Ne	10	$1s^22s^22p_x^22p_y^22p_z^2$	[He] $2s^22p_x^22p_y^22p_z^2$
Third Period	Na	11	$1s^22s^22p_x^22p_y^22p_z^23s^1$	[Ne] $3s^1$
	Mg	12	$1s^22s^22p_x^22p_y^22p_z^23s^2$	[Ne] $3s^2$
	Al	13	$1s^22s^22p_x^22p_y^22p_z^23s^23p_x^1$	[Ne] $3s^23p_x^1$
	Si	14	$1s^22s^22p_x^22p_y^22p_z^23s^23p_x^13p_y^1$	[Ne] $3s^23p_x^13p_y^1$
	P	15	$1s^22s^22p_x^22p_y^22p_z^23s^23p_x^13p_y^13p_z^1$	[Ne] $3s^23p_x^13p_y^13p_z^1$
	S	16	$1s^22s^22p_x^22p_y^22p_z^23s^23p_x^23p_y^13p_z^1$	[Ne] $3s^23p_x^23p_y^13p_z^1$
	Cl	17	$1s^22s^22p_x^22p_y^22p_z^23s^33p_x^23p_y^33p_z^1$	[Ne] $3s^23p_x^23p_y^23p_z^1$
	Ar	18	$1s^22s^22p_x^22p_y^22p_z^23s^23p_x^23p_y^23p_z^2$	[Ne] $3s^23p_x^23p_y^23p_z^2$

*Elements are listed by symbol, atomic number, ground-state electron configuration, and shorthand notation for the ground-state electron configuration, in that order.

Electronic Structure of Atoms

- **Problem**: Write the ground-state electron configuration of each element, given its atomic number, and describe the relationship between an atom's ground-state electron configuration and its position in the Periodic Table.

  (a) Mg (12) and Ar(18)

  (b) P(15) and Cl (17)

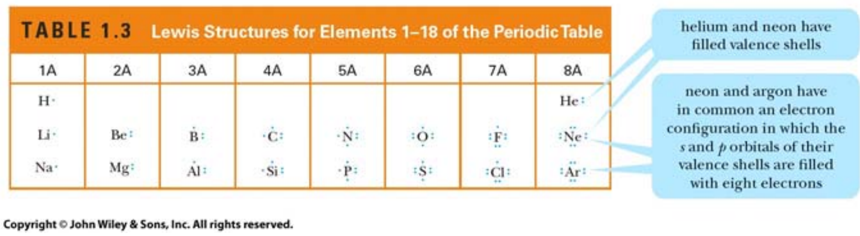
WILEY 1-9

Lewis Structures

- Gilbert N. Lewis
- **Valence shell**: The outermost electron shell of an atom.
- **Valence electrons**: Electrons in the valence shell of an atom. These electrons are used in forming chemical bonds.
- **Lewis structure of an atom**
  - The symbol of the atom represents the nucleus and all inner shell electrons.
  - Dots represent electrons in the valence shell of the atom.

WILEY 1-10

Lewis Structures



WILEY 1-11

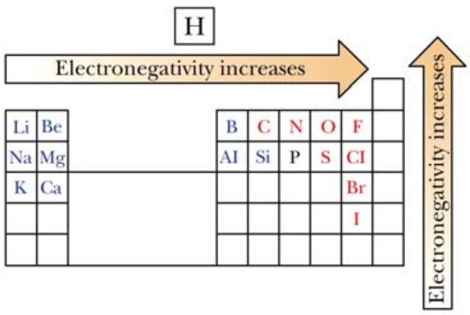
Lewis Model of Bonding

- Atoms bond together so that each atom in the bond acquires the electron configuration of the noble gas nearest it in atomic number.
  - An atom that gains electrons becomes an **anion**.
  - An atom that loses electrons becomes a **cation**.
  - **Ionic bond**: A chemical bond resulting from the electrostatic attraction of an anion and a cation.
  - **Covalent bond**: A chemical bond resulting from two atoms sharing one or more pairs of electrons.
- We classify chemical bonds as ionic, polar covalent, and nonpolar covalent based on the difference in electronegativity between the bonded atoms.

WILEY 1-12

Electronegativity

- **Electronegativity**: A measure of the force of an atom's attraction for the electrons it shares in a chemical bond with another atom.
- Pauling scale
  - Increases from left to right within a period.
  - Increases from bottom to top in a group.



 1-13

Electronegativity

TABLE 1.4 Electronegativity Values for Some Atoms (Pauling Scale)

1A	2A	3B	4B	5B	6B	7B		8B		1B	2B	3A	4A	5A	6A	7A
								H 2.1								
Li 1.0	Be 1.5											B 2.0	C 2.5	N 3.0	O 3.5	F 4.0
Na 0.9	Mg 1.2											Al 1.5	Si 1.8	P 2.1	S 2.5	Cl 3.0
K 0.8	Ca 1.0	Sc 1.3	Ti 1.5	V 1.6	Cr 1.6	Mn 1.5	Fe 1.8	Co 1.8	Ni 1.8	Cu 1.9	Zn 1.6	Ga 1.6	Ge 1.8	As 2.0	Se 2.4	Br 2.8
Rb 0.8	Sr 1.0	Y 1.2	Zr 1.4	Nb 1.6	Mo 1.8	Tc 1.9	Ru 2.2	Rh 2.2	Pd 2.2	Ag 1.9	Cd 1.7	In 1.7	Sn 1.8	Sb 1.9	Te 2.1	I 2.5
Cs 0.7	Ba 0.9	La 1.1	Hf 1.3	Ta 1.5	W 1.7	Re 1.9	Os 2.2	Ir 2.2	Pt 2.2	Au 2.4	Hg 1.9	Tl 1.8	Pb 1.8	Bi 1.9	Po 2.0	At 2.2

<1.0 · 1.0 – 1.4 · 1.5 – 1.9 · 2.0 – 2.4 · 2.5 – 2.9 · 3.0 – 4.0

 1-14

Electronegativity

TABLE 1.5 Classification of Chemical Bonds

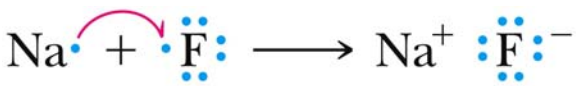
Difference in Electronegativity between Bonded Atoms	Type of Bond	Most Likely Formed Between
Less than 0.5	Nonpolar covalent	Two nonmetals or a nonmetal and a metalloid
0.5 to 1.9	Polar covalent	
Greater than 1.9	Ionic	A metal and a nonmetal

Ionic Bonds

- An ionic bond forms by the transfer of electrons from the valence shell of an atom of lower electronegativity to the valence shell of an atom of higher electronegativity.

$$\mathrm{Na}(1s^2\,2s^2\,2p^6\,3s^1) + \mathrm{F}(1s^2\,2s^2\,2p^5) \longrightarrow \mathrm{Na}^+(1s^2 2s^2 2p^6) + \mathrm{F}^-(1s^2 2s^2\,2p^6)$$

  - We show the transfer of a single electron by a single-headed (barbed) curved arrow.



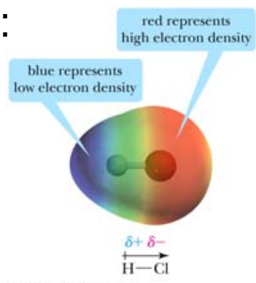
Covalent Bonds

- A covalent bond forms when electron pairs are shared between two atoms whose difference in electronegativity is 1.9 or less.
  - An example is the formation of a covalent bond between two hydrogen atoms.
  - The shared pair of electrons completes the valence shell of each hydrogen.

$$H\cdot + \cdot H \longrightarrow H{-}H \qquad \Delta H^0 = -435\ \text{kJ/mol}\ (-104\ \text{kcal/mol})$$

Polar Covalent Bonds

- In a polar covalent bond:
  - The more electronegative atom has a partial negative charge, indicated by the symbol $\delta-$.
  - The less electronegative atom has a partial positive charge, indicated by the symbol $\delta+$.
- In an electron density model:
  - Red indicates a region
  - of high electron density.
  - Blue indicates a region
  - of low electron density.

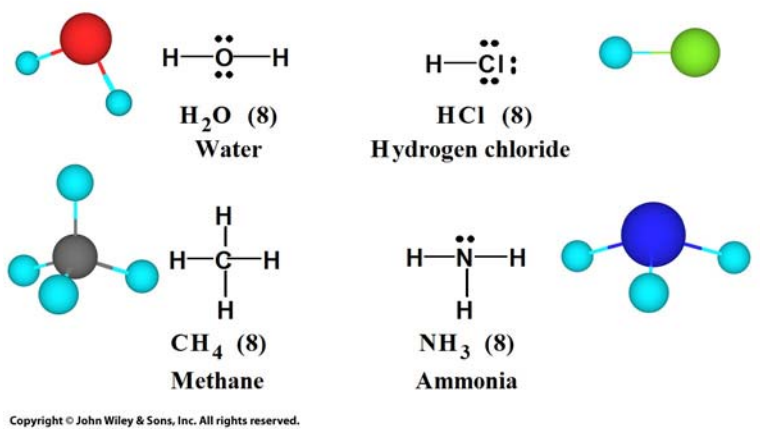


Drawing Lewis Structures

- To draw a Lewis structure:
  - Determine the number of valence electrons in the molecule or ion.
  - Determine the connectivity (arrangement) of atoms.
  - Connect the atoms by single line between atoms.
  - Arrange the remaining electrons so that each atom has a complete valence shell.
  - Show bonding electrons as single lines.
  - Show nonbonding electrons as pairs of dots.
  - Atoms share 1 pair of electrons in a single bond, 2 pairs in a double bond, and 3 pairs in a triple bond.

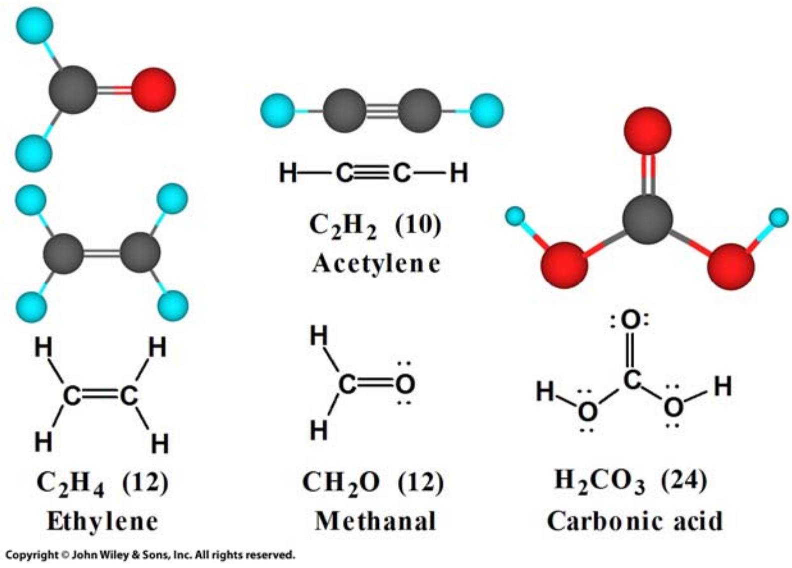
WILEY 1-19

Lewis Structures



WILEY 1-20

Lewis Structures



WILEY 1-21

Lewis Structures

- In neutral molecules containing C, H, N, O, and halogen
  - Hydrogen has one bond.
  - Carbon has 4 bonds and no unshared electrons.
  - Nitrogen has 3 bonds and 1 unshared pair of electrons.
  - Oxygen has 2 bonds and 2 unshared pairs of electrons.
  - Halogen has 1 bond and 3 unshared pairs of electrons.

WILEY 1-22

Formal Charge

- **Formal charge**: the charge on an atom in a molecule or polyatomic ion.
  - Write a Lewis structure for the molecule or ion.
  - Assign each atom all its unshared (nonbonding) electrons and one-half its shared (bonding) electrons.
  - Compare this number with the number of valence electrons in the neutral, unbonded atom.
  - If the number is less than that assigned to the unbonded atom, the atom has a positive formal charge.
  - If the number is greater, the atom has a negative formal charge.

$$\text{Formal charge} = \begin{array}{c}\text{\# of valence}\\ \text{electrons in}\\ \text{unbonded atom}\end{array} - \left(\begin{array}{c}\text{all}\\ \text{unshared}\\ \text{electrons}\end{array} + \begin{array}{c}\text{one-half}\\ \text{of all shared}\\ \text{electrons}\end{array}\right)$$

Lewis Structures

- **Problem**: Draw a Lewis structure for each molecule or ion and show all formal charges.

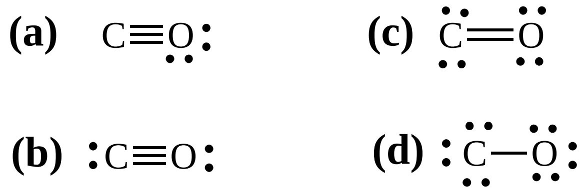
(a) NH_4^+ (b) CO (c) NO_2^+

(d) CH_3^+ (e) N_3^- (f) $CH_3NH_3^+$

(g) BF_4^- (h) CH_3^- (i) $CH_3OH_2^+$

Lewis Structures

- **Problem**: Which is an acceptable Lewis structure (formal charges are not shown) for carbon monoxide, CO? For an acceptable structure, assign formal charges as appropriate.



WILEY 1-25

Valence-shell Electron-Pair Repulsion

- VSEPR is based on two concepts.
  - Atoms are surrounded by regions of electron density.
  - Regions of electron density repel each other.

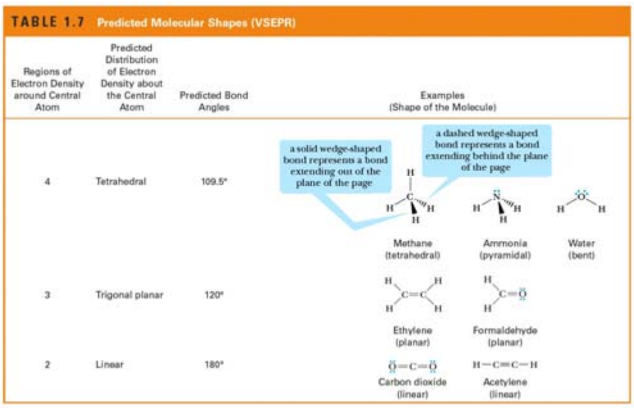


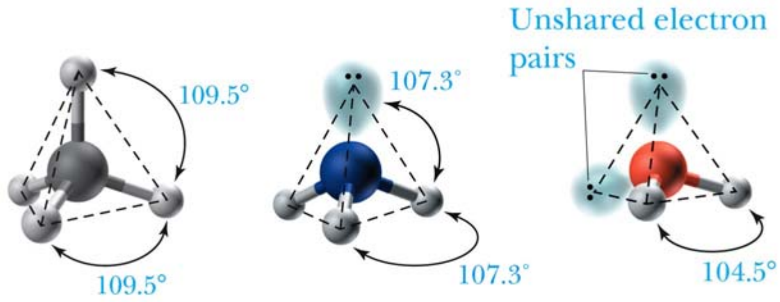
TABLE 1.7 Predicted Molecular Shapes (VSEPR)

Regions of Electron Density around Central Atom	Predicted Distribution of Electron Density about the Central Atom	Predicted Bond Angles	Examples (Shape of the Molecule)		
4	Tetrahedral	109.5°	Methane (tetrahedral)	Ammonia (pyramidal)	Water (bent)
3	Trigonal planar	120°	Ethylene (planar)	Formaldehyde (planar)	
2	Linear	180°	Carbon dioxide (linear)	Acetylene (linear)	

WILEY 1-26

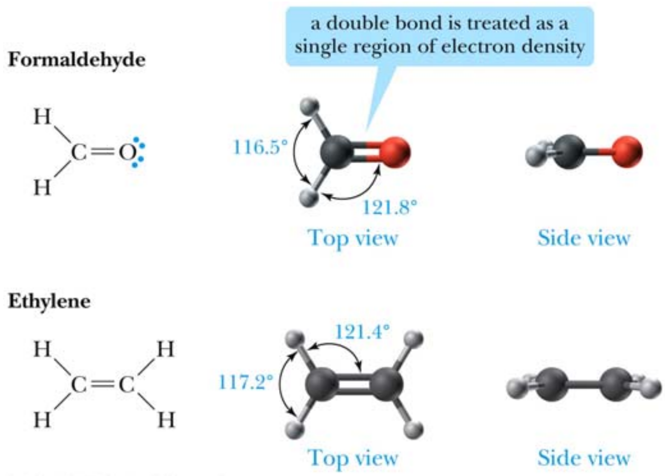
Shapes of Molecules

- Shapes of Methane, Ammonia, and Water molecules.



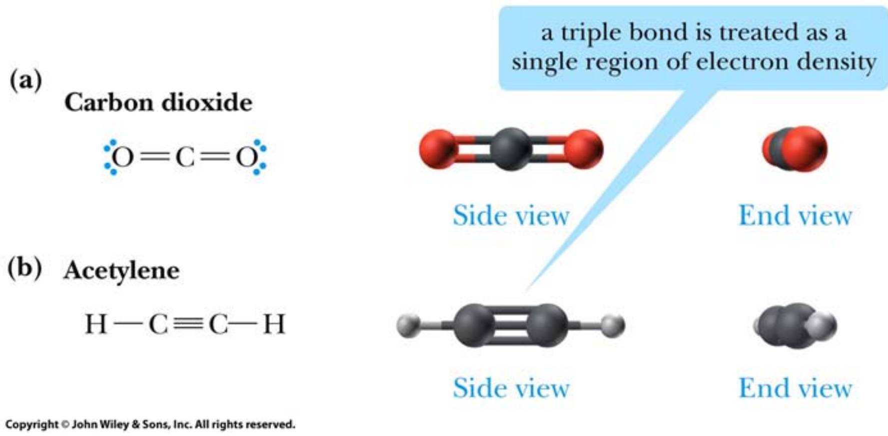
Shapes of Molecules

- Shapes of Formaldehyde and Ethylene.



Shapes of Molecules

- Shapes of carbon dioxide and acetylene.



WILEY 1-29

VSEPR

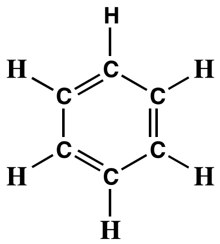
- **Problem**: Draw a Lewis structure and predict all bond angles for these molecules and ions.

(a) NH_4^+	(b) CH_3NH_2	(c) CH_3OH
(d) $CH_3CH{=}CH_2$	(e) H_2CO_3	(f) HCO_3^-
(g) CH_3CHO	(g) CH_3COOH	(h) BF_4^-

WILEY 1-30

Shapes of Molecules

- **Problem**: Following is a structural formula of benzene,C_6H_6, which we will study in Chapter 9.

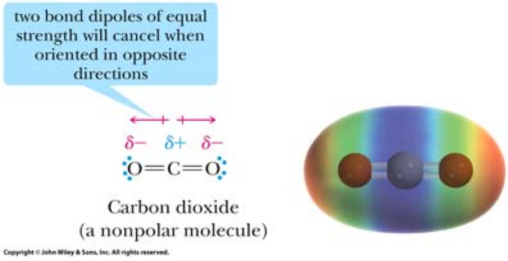


- (a) Using VSEPR, predict each H-C-C and C-C-C bond angle in benzene.
- (b) Predict the shape of a benzene molecule.

WILEY 1-31

Polar and Nonpolar Molecules

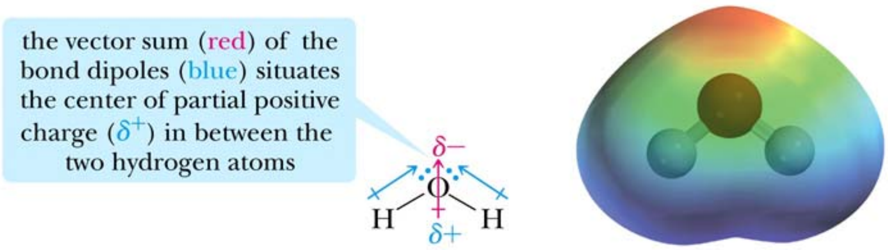
- A molecule is polar if:
  - It has polar bonds and
  - The vector sum of its bonds dipoles is zero (that is, the bond dipoles cancel each other).
  - Carbon dioxide has two polar covalent bonds and because of its geometry, is a nonpolar molecule.



WILEY 1-32

Polar and Nonpolar Molecules

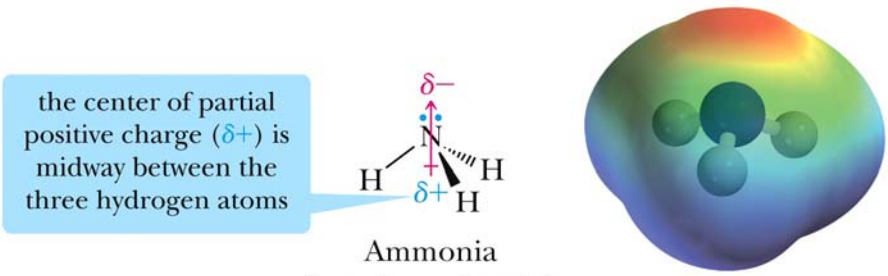
- A water molecule has two polar bonds and, because its geometry, is a polar molecule.



Water
(a polar molecule)

Polar and Nonpolar Molecules

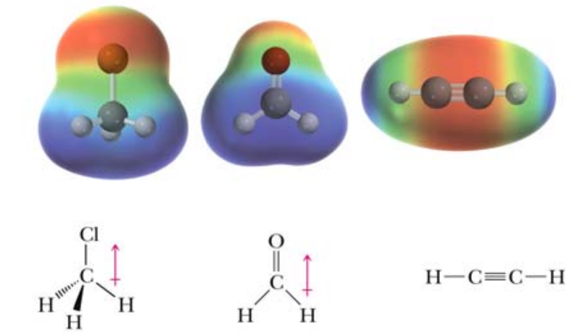
- An ammonia molecule has three polar covalent bonds, and because of its geometry, is a polar molecule.



Ammonia
(a polar molecule)

Polar and Nonpolar Molecules

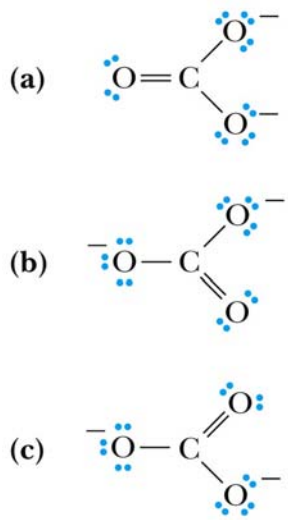
- Chloromethane and formaldehyde are polar molecules.
- Acetylene is a nonpolar molecule.



Chloromethane (polar) | Formaldehyde (polar) | Acetylene (nonpolar)

Resonance

- A way to describe molecules and ions for which no single Lewis structure provides a truly accurate representation. Here are three Lewis structures for the carbonate ion:



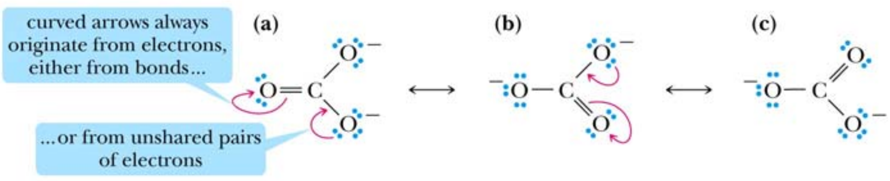
Resonance

- Linus Pauling - 1930s
  - Many molecules and ions are best described by writing two or more Lewis structures.
  - Individual Lewis structures are called **contributing structures**.
  - Connect individual contributing structures by a **double-headed** (resonance) arrow.
  - The molecule or ion is a **hybrid** of the various contributing structures.

WILEY 1-37

Resonance

- Figure 1.12 The carbonate ion as a hybrid of three equivalent contributing structures. Curved arrows show the redistribution of valence electrons between one contributing structure and the next.



WILEY 1-38

Resonance

- **Curved arrow**: A symbol used to show the redistribution of valence electrons.
- In using curved arrows, there are only two allowed types of electron redistribution:
  - from a bond to an adjacent atom.
  - from an atom to an adjacent bond.
- Electron pushing by the use of curved arrows is a survival skill in organic chemistry.
  - learn it well!

WILEY 1-39

Resonance

- All acceptable contributing structures must:

1. Have the same number of valence electrons.
2. Obey the rules of covalent bonding.
   - No more than 2 electrons in the valence shell of H.
   - No more than 8 electrons in the valence shell of a 2nd period element.
   - 3rd period elements may have up to 12 electrons in their valence shells.
3. Differ only in distribution of valence electrons.
4. Have the same number of paired and unpaired electrons.

WILEY 1-40

Resonance

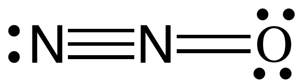
- Examples of ions and a molecule best represented as resonance hybrids. Draw contributing structures for each resonance hybrid.

carbonate ion	CO_3^{2-}
acetate ion	CH_3COO^-
acetone	CH_3COCH_3

WILEY 1-41

Resonance

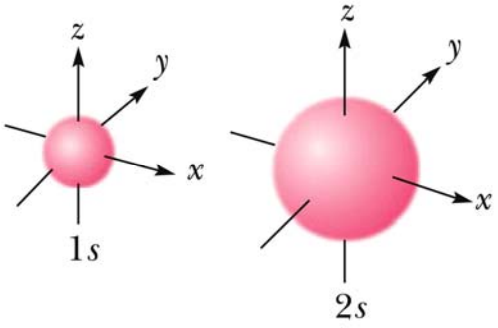
- Problem: Nitrous oxide, N_2O, laughing gas, is a colorless, nontoxic, tasteless, and odorless gas. Because it is soluble in vegetable oils (fats), it is used as a propellant in whipped toppings.
  - (a) How many valence electrons are present in nitrous oxide?
  - (b) Write two equivalent contributing structures for this molecule. The connectivity is N—N—O. Be certain to show formal charges, if any are present.
  - (c) Explain why the following is not an acceptable contributing structure.



WILEY 1-42

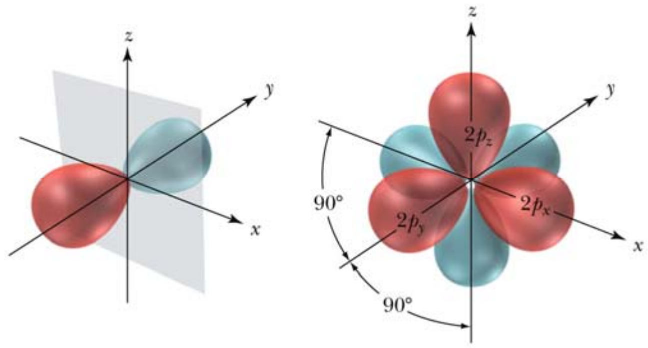
Shapes of Atomic Orbitals

- All *s* orbitals have the shape of a sphere, with its center at the nucleus.
  - Of the *s* orbitals, a 1*s* orbital is the smallest, a 2*s* orbital is larger, and a 3*s* orbital is larger still.



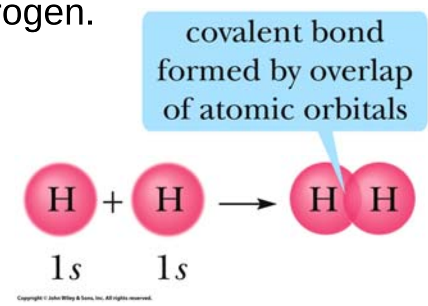
Shapes of Atomic Orbitals

- A *p* orbital consists of two lobes arranged in a straight line with the center at the nucleus.
- *p* orbitals come in sets of three: $2p_x$, $2p_y$, and $2p_z$.



Orbital Overlap Model of Bonding

- A covalent bond forms when a portion of an atomic orbital of one atom overlaps a portion of an atomic orbital of another atom.
  - In forming the covalent bond in H–H, for example, there is overlap of the 1*s* orbitals of each hydrogen.



WILEY 1-45

Hybrid Orbitals

- The Problem:
  - Overlap of 2*s* atomic orbitals of one atom and 2*p* atomic orbitals of another atom would give bond angles of approximately 90°.
  - Instead we observe bond angles of approximately 109.5°, 120°, and 180°.
- A Solution
  - Hybridization of atomic orbitals.
  - 2nd row elements use sp^3, sp^2, and *sp* hybrid orbitals for bonding.

WILEY 1-46

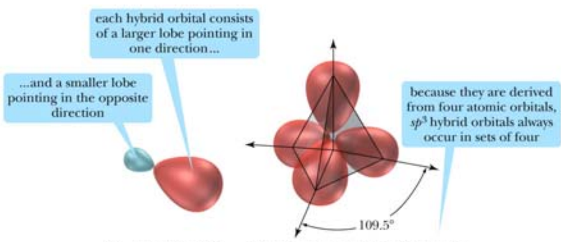
Hybrid Orbitals

- We study three types of hybrid atomic orbitals:
  - *sp^3* (one *s* orbital + three *p* orbitals give four *sp^3* hybrid orbitals).
  - *sp^2* (one *s* orbital + two *p* orbitals give three *sp^2* hybrid orbitals).
  - *sp* (one *s* orbital + one *p* orbital give two *sp* hybrid orbitals).
- Overlap of hybrid orbitals can form two types of bonds, depending on the geometry of the overlap:
  - **σ bonds** are formed by "direct" overlap.
  - **π bonds** are formed by "parallel" overlap.

WILEY

sp^3 Hybrid Orbitals

- Each *sp^3* hybrid orbital has two lobes of unequal size.
- The four *sp^3* hybrid orbitals are directed toward the corners of a regular tetrahedron at angles of 109.5°.
- Figure 1.16 *sp^3* hybrid orbitals.

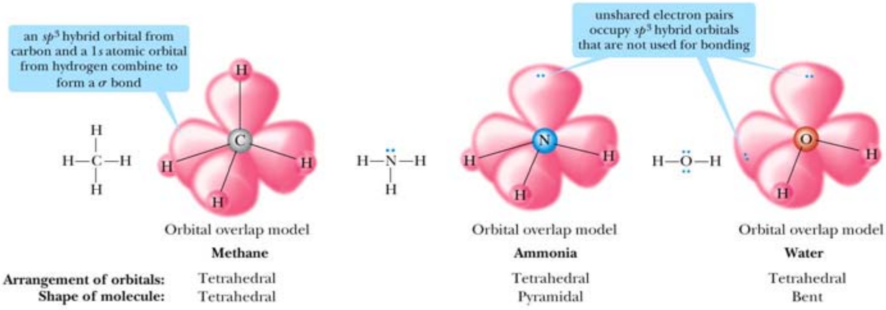


(a) An sp^3 orbital (b) Four tetrahedral sp^3 orbitals

WILEY

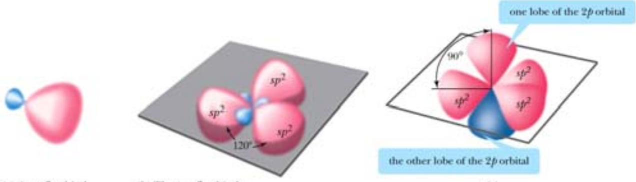
*sp*³ Hybrid Orbitals

– Figure 1.17 Orbital overlap picture of methane, ammonia, and water.



*sp*² Hybrid Orbitals

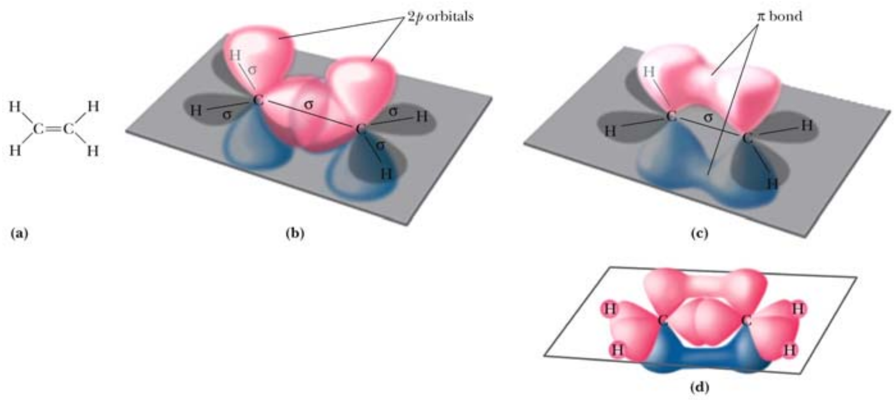
- A single *sp*² hybrid orbital has two lobes of unequal size.
  - The three *sp*² hybrid orbitals are directed toward the corners of an equilateral triangle at angles of 120°.
  - The unhybridized 2*p* orbital is perpendicular to the plane of the three *sp*² hybrid orbitals.



(a) An sp^2 orbital (b) Three sp^2 orbitals (c)

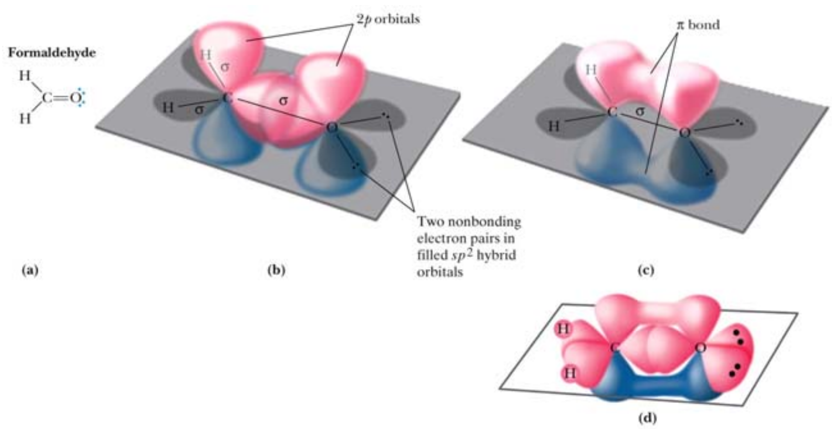
sp^2 Hybrid Orbitals

– Figure 1.19 Covalent bonding in ethylene. Ethylene is a planar molecule.



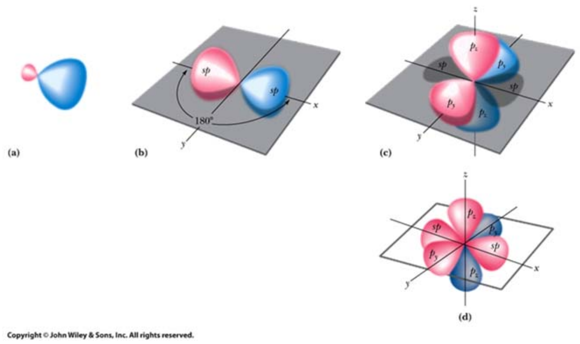
sp^2 Hybrid Orbitals

– Figure 1.20 A carbon-oxygen double bond consists of one sigma (σ) bond and one pi (π) bond.



sp Hybrid Orbitals

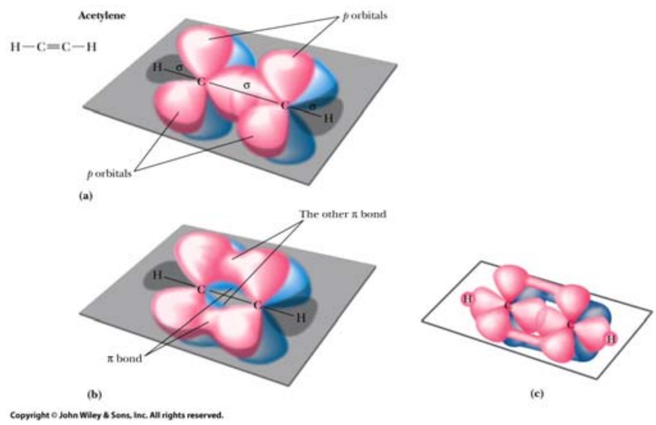
- A single *sp* hybrid orbital has two lobes of unequal size.
  - The two *sp* hybrid orbitals lie in a line at an angle of 180°.
  - The two unhybridized 2*p* orbitals are perpendicular to each other and to the line through the two *sp* hybrid orbitals.



1-53

sp Hybrid Orbitals

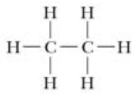
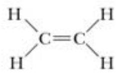
- Figure 1.22 Covalent bonding in acetylene. A carbon-carbon triple bond consists of one sigma (σ) bond and two pi (π) bonds.



1-54

Hybrid Orbitals

TABLE 1.8 Covalent Bonding of Carbon

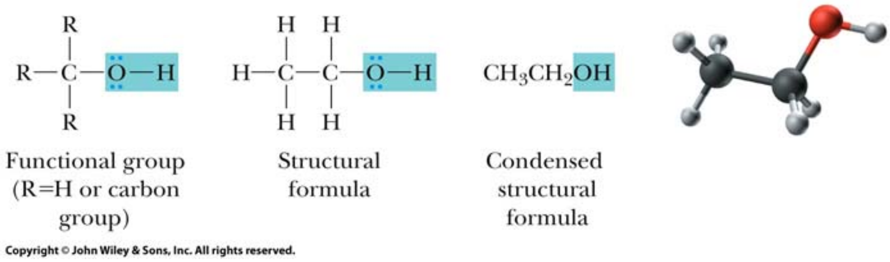
Groups Bonded to Carbon	Orbital Hybridization	Predicted Bond Angles	Types of Bonds to Carbon	Example	Name
4	sp^3	109.5°	four sigma bonds		ethane
3	sp^2	120°	three sigma bonds and one pi bond		ethylene
2	sp	180°	two sigma bonds and two pi bonds	H—C≡C—H	acetylene

Functional Groups

- **Functional Group**: An atom or group of atoms within a molecule that shows a characteristic set of physical and chemical properties.
- Functional groups are important for three reasons, they are:
  - The units by which we divide organic compounds into classes.
  - The sites of characteristic chemical reactions.
  - The basis for naming organic compounds.

Functional Groups

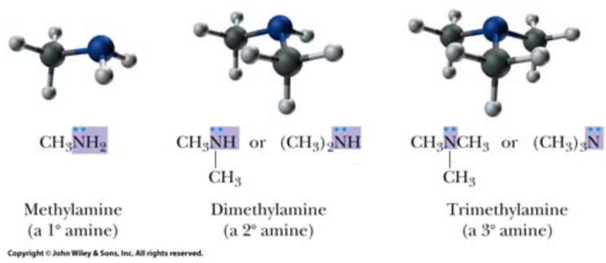
- **Alcohol**: A compound that contains an –OH (**hydroxyl group**) bonded to a tetrahedral carbon atom.



WILEY 1-57

Functional Groups

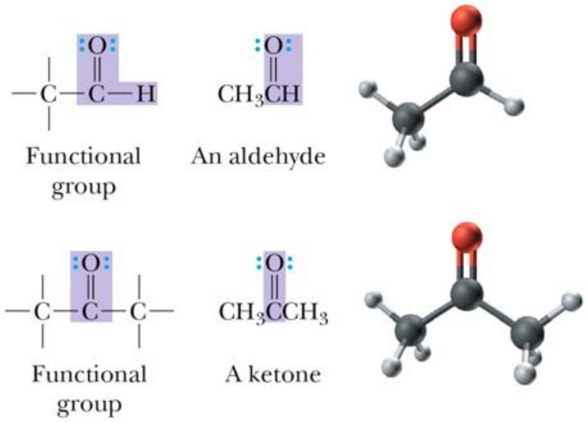
- **Amine**: A compound that contains an amino group—a nitrogen atom bonded to one, two, or three carbon atoms.
  - Amines are classified as 1°, 2°, and 3° according to the number of carbon atoms bonded directly to the nitrogen atom.



WILEY 1-58

Functional Groups

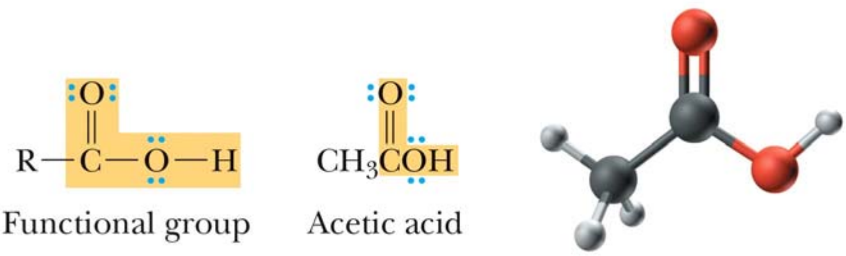
- **Carbonyl group (C=O)** of aldehydes and ketones.



WILEY 1-59

Functional Groups

- **Carboxyl group** of carboxylic acids.



WILEY 1-60