1 Covalent Bonding & Shapes of Molecules

Chapter 1
Organic Chemistry

The study of the compounds of carbon

Over 10 million structures have been identified
  • about 1000 new ones are 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, and some metals
Structure of atoms

- small dense nucleus, diameter $10^{-14} - 10^{-15}$ m, which contains most of the mass of the atom

- extranuclear space, diameter $10^{-10}$ m, which contains positively-charged electrons
Electronic Structure of Atoms

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

<table>
<thead>
<tr>
<th>Shell</th>
<th>Number of Electrons Shell Can Hold</th>
<th>Relative Energies of Electrons in These Shells</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>32</td>
<td>higher</td>
</tr>
<tr>
<td>3</td>
<td>18</td>
<td>↑↑</td>
</tr>
<tr>
<td>2</td>
<td>8</td>
<td>↑</td>
</tr>
<tr>
<td>1</td>
<td>2</td>
<td>lower</td>
</tr>
</tbody>
</table>
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) ..... 

<table>
<thead>
<tr>
<th>Shell</th>
<th>Orbitals Contained in That Shell</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>3s, 3p_x, 3p_y, 3p_z, plus five 3d orbitals</td>
</tr>
<tr>
<td>2</td>
<td>2s, 2p_x, 2p_y, 2p_z</td>
</tr>
<tr>
<td>1</td>
<td>1s</td>
</tr>
</tbody>
</table>
1 Electron Structure of Atoms

- **Aufbau Principle**: orbitals fill from lowest to highest energy
- **Pauli Exclusion Principle**: only two electrons per orbital
- **Hund’s Rule**: for a set of degenerate orbitals, add one electron in each before a second is added in any one

**Example**: Write the ground-state electron configurations for

(a) Li  
(b) O  
(c) Cl
1 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**
  - the symbol of the atom represents the nucleus and all inner shell electrons
  - dots represent valence electrons
Table 1.4 gives the Lewis structures for elements 1-18 of the periodic table.

<table>
<thead>
<tr>
<th>IA</th>
<th>IIA</th>
<th>IIIA</th>
<th>IVA</th>
<th>VA</th>
<th>VIA</th>
<th>VIIA</th>
<th>Vlla</th>
<th>Vllla</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>He</td>
</tr>
<tr>
<td>Li</td>
<td>Be</td>
<td>B</td>
<td>C</td>
<td>N</td>
<td>O</td>
<td>F</td>
<td>Ne</td>
<td></td>
</tr>
<tr>
<td>Na</td>
<td>Mg</td>
<td>Al</td>
<td>Si</td>
<td>P</td>
<td>S</td>
<td>Cl</td>
<td>Ar</td>
<td></td>
</tr>
</tbody>
</table>
Formation of Chemical Bonds

Atoms bond together so that each atom acquires the electron configuration of the noble gas nearest it in the Periodic Table
- an atom that gains electrons becomes an anion
- an atom that loses electrons becomes a cation

Two extremes of bonding
- 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
1 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 left to right in a row
  - increases bottom to top in a column

\[
\begin{array}{c c}
\delta + & \delta - \\
H & Cl \\
2.1 & 3.0 \\
\end{array}
\]
# Electronegativity

## Table 1.6 Classification of Chemical Bonds

<table>
<thead>
<tr>
<th>Difference in Electronegativity Between Bonded Atoms</th>
<th>Type of Bond</th>
</tr>
</thead>
<tbody>
<tr>
<td>less than 0.5</td>
<td>nonpolar covalent</td>
</tr>
<tr>
<td>0.5 to 1.9</td>
<td>polar covalent</td>
</tr>
<tr>
<td>greater than 1.9</td>
<td>ionic</td>
</tr>
</tbody>
</table>
# Bond Dipoles

## Table 1.7 Average Bond Dipoles of Selected Covalent Bonds

<table>
<thead>
<tr>
<th>Bond</th>
<th>Bond Dipole (D)</th>
<th>Bond</th>
<th>Bond Dipole (D)</th>
<th>Bond</th>
<th>Bond Dipole (D)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H-C</td>
<td>0.3</td>
<td>C-F</td>
<td>1.4</td>
<td>C-O</td>
<td>0.7</td>
</tr>
<tr>
<td>H-N</td>
<td>1.3</td>
<td>C-Cl</td>
<td>1.5</td>
<td>C=O</td>
<td>2.3</td>
</tr>
<tr>
<td>H-O</td>
<td>1.5</td>
<td>C-Br</td>
<td>1.4</td>
<td>C-N</td>
<td>0.2</td>
</tr>
<tr>
<td>H-S</td>
<td>0.7</td>
<td>C-I</td>
<td>1.2</td>
<td>C=N</td>
<td>3.5</td>
</tr>
</tbody>
</table>
1 Lewis Structures

To write a Lewis structure

- determine the number of valence electrons
- determine the arrangement of atoms
- connect the atoms by single bonds
- arrange the remaining electrons so that each atom has a complete valence shell
- show bonding electrons as a single bond (a single line)
- show nonbonding electrons as a pair of dots
1 Lewis Structures

H---O---H
H₂O (8)
Water

H---Cl
HCl (8)
Hydrogen chloride

H---C---H
H---N---H
CH₄ (8)
NH₃ (8)
Methane
Ammonia
1 Lewis Structures

\[ \begin{align*}
\text{H–C≡C–H} & \quad \text{C}_2\text{H}_2 \ (10) \\
\text{Acetylene} & \\
\text{H} & \quad \text{H} \\
\text{C} & \quad \text{C} \\
\text{H} & \quad \text{H} \\
\text{H} & \quad \text{H} \\
\text{C}_2\text{H}_4 \ (12) & \\
\text{Ethylene} & \\
\text{H} & \quad \text{H} \\
\text{C} & \quad \text{C} \\
\text{H} & \quad \text{H} \\
\text{H} & \quad \text{H} \\
\text{CH}_2\text{O} \ (12) & \\
\text{Methanal} & \\
\text{H} & \quad \text{O} \\
\text{O} & \\
\text{H} & \quad \text{H} \\
\text{H}_2\text{CO}_3 \ (24) & \\
\text{Carbonic acid} &
\end{align*} \]
1 Lewis Structures

In neutral molecules
- 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
- halogens have 1 bond and 3 unshared pairs of electrons
Formal Charge

Formal charge: the charge on an atom in a molecule or polyatomic ion

To derive formal charge

1. write a correct Lewis structure for the molecule or ion
2. assign each atom all of its unshared (nonbonding) electrons and one-half its shared (bonding) electrons
3. compare this number with the number of valence electrons in the neutral, unbonded atom
Formal Charge

number of valence electrons in the neutral, unbonded atom

- \left( \text{all unshared electrons} + \frac{1}{2} \text{all shared electrons} \right)

- If the number assigned to the bonded atom 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
Example: Draw Lewis structures and show all formal charges for these molecules and ions

- \( \text{NH}_4^+ \)
- \( \text{CH}_3\text{NH}_3^+ \)
- \( \text{CH}_3\text{OH}_2^+ \)
- \( \text{OH}^- \)
- \( \text{HCO}_3^- \)
- \( \text{CO}_3^{2-} \)
- \( \text{CH}_3^- \)
- \( \text{CH}_3\text{CO}_2^- \)
- \( \text{BF}_4^- \)
Exceptions to the Octet Rule

Molecules containing atoms of Group IIIA elements, particularly boron and aluminum

- Boron trifluoride
- Aluminum chloride

6 electrons in the valence shells of boron and aluminum.
Exceptions to the Octet Rule

Molecules and ions that contain an atom with more than eight electrons in its valence shell, including P, which may contain up to 10 electrons in its valence shell.

- Trimethylphosphine
- Phosphorus pentachloride
- Phosphoric acid
Exceptions to the Octet Rule

H and S, which may contain up to 12 electrons in its valence shell

- Hydrogen sulfide
- Dimethyl sulfoxide
- Sulfuric acid
1 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
  1. the units by which we divide organic compounds into classes
  2. the sites of characteristic chemical reactions
  3. the basis for naming organic compounds
Functional Groups

Alcohols and Ethers

- An alcohol (Ethanol)
- An ether (Dimethyl ether)
1 Functional Groups

• Aldehydes and ketones

An aldehyde

A ketone
1 Functional Groups

- Carboxylic acids

\[
\begin{align*}
\text{O} \\
\text{CH}_3 - \text{C} - \text{O} - \text{H} \quad \text{or} \quad \text{CH}_3 \text{COOH} \quad \text{or} \quad \text{CH}_3 \text{CO}_2 \text{H}
\end{align*}
\]

Acetic acid
VSEPR Model

4 regions of e⁻ density (tetrahedral, 109.5°)

3 regions of e⁻ density (trigonal planar, 120°)

2 regions of e⁻ density (linear, 180°)
1 VSEPR Model

**Example:** predict all bond angles for these molecules and ions

\[
\begin{align*}
\text{NH}_4^+ & \quad \text{CH}_3\text{NH}_2 & \quad \text{CH}_3\text{OH} \\
\text{CH}_3\text{CH}=&\text{CH}_2 & \quad \text{H}_2\text{CO}_3 & \quad \text{HCO}_3^- \\
\text{CH}_3\text{CHO} & \quad \text{CH}_3\text{CO}_2\text{H} & \quad \text{BF}_4^- \\
\end{align*}
\]
Polar and Nonpolar Molecules

To determine if a molecule is polar, we need to determine:
- if the molecule has polar bonds
- the arrangement of these bonds in space

Dipole moment ($\mu$): the vector sum of its individual bond dipoles
These molecules have polar bonds, but each has a zero dipole moment.

Carbon dioxide: \( \mu = 0 \) D

Boron trifluoride: \( \mu = 0 \) D

Carbon tetrachloride: \( \mu = 0 \) D
These molecules have polar bonds, and a dipole moment greater than zero.

Water: \( \mu = 1.85D \)

Ammonia: \( \mu = 1.47D \)
For many molecules and ions, no single Lewis structure provides a truly accurate representation.

Ethanoate ion
(Acetate ion)
1 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
1 Resonance

Examples:

Nitrite ion
(equivalent contributing structures)

Ethanoate ion
(equivalent contributing structures)
1 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 is a survival skill in organic chemistry. Learn it well!
1 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 valence shell of 2nd period elements
     • 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
1 Resonance

Examples of ions and a molecule best represented as resonance hybrids

- carbonate ion \( \text{CO}_3^{2-} \)
- acetate ion \( \text{CH}_3\text{CO}_2^- \)
- acetone \( \text{CH}_3\text{COCH}_3 \)
- nitrate ion \( \text{NO}_3^- \)
Resonance

Preference 1: structures with filled valence shells contribute more than those with unfilled valence shells

Greater contribution; both carbon and oxygen have complete valence shells

Lesser contribution; carbon has only 6 electrons in its valence shell
1 Resonance

Preference 2: structures with a greater number of covalent bonds contribute more than those with fewer covalent bonds

\[ \text{Greater contribution (8 covalent bonds)} \]

\[ \text{Lesser contribution (7 covalent bonds)} \]
1 Resonance

Preference 3: structures with separation of unlike charges contribute less than those with no charge separation

\[
\begin{align*}
\text{CH}_3\text{-C-CH}_3 & \quad \text{Greater contribution} \\
\text{CH}_3\text{-C-CH}_3 & \quad \text{Lesser contribution}
\end{align*}
\]

(no separation of unlike charges) (separation of unlike charges)
Preference 4: structures that carry a negative charge on the more electronegative atom contribute more than those with the negative charge on the less electronegative atom.

Greater contribution

Lesser contribution

Can be ignored
Quantum or Wave Mechanics

- A. Einstein: \( E = hv \) (energy is quantized)
  - light has particle properties

- L. deBroglie: wave / particle duality

- E. Schrödinger wave equation
  - \( \psi^2 \) is the probability of finding an electron in a given region of space
  - 95% probability region is called an atomic orbital
Molecular Orbital Theory

- Electrons in atoms exist in atomic orbitals
- Electrons in molecules exist in molecular orbitals (MOs)
- Using Schrödinger equation, we can calculate the shapes and energies of MOs
Molecular Orbital Theory

Rules:

- combination of n atomic orbitals gives n MO
- MOs are arranged in order of increasing energy
- MOs fill by same rules as for atomic orbitals:
  - Aufbau principle: fill beginning with LUMO
  - Pauli exclusion principle: no more than 2 e\textsuperscript{-} in a MO
  - Hund’s rule: filling of degenerate orbitals
Molecular Orbital Theory

Terminology

- **ground state** = lowest energy
- **excited state** = NOT lowest energy
- $\sigma$ = sigma bonding MO
- $\sigma^*$ = sigma antibonding MO
- $\pi$ = pi bonding MO
- $\pi^*$ = pi antibonding MO
1 Hybrid Orbitals

- Shapes of Atomic Orbitals (s, p, d, f, ...)

- Wave function may be
  - positive or negative
  - or zero at a nodal surface

- Hybridization of orbitals (L. Pauling)
  - the combination of two or more atomic orbitals to form a new set of atomic orbitals, called hybrid atomic orbitals
Hybrid Orbitals

The Problem:
- 2s and 2p atomic orbitals would give bond angles of approximately 90°
- instead we observe 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
1 Hybrid Orbitals

We deal with three types of hybrid atomic orbitals:

- **sp³** (1 s orbital + 3 p orbitals)
- **sp²** (1 s orbital + 2 p orbitals)
- **sp** (1 s orbital + 1 p orbital)

Overlap of hybrid atomic 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” overlay
1 \textit{sp}^3 \textit{Hybrid Orbitals}

- Each \textit{sp}^3 hybrid orbital has two lobes of unequal size.

- The sign of the wave function is positive in one lobe, negative in the other, and zero at the nucleus.

- The four \textit{sp}^3 hybrid orbitals are directed toward the corners of a regular tetrahedron at angles of 109.5°.
**1 sp\(^2\) Hybrid Orbitals**

- Each 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 2p orbital is perpendicular to the plane of the sp\(^2\) hybrid orbitals.
1 sp Hybrid Orbitals

- Each sp hybrid orbital has two lobes of unequal size.
- The sign of the wave function is positive in one lobe, negative in the other, and zero at the nucleus.
- The two sp hybrid orbitals lie in a line at an angle of 180°.
- The two unhybridized 2p orbitals are perpendicular to each other and to the line through the two sp-hybrid orbitals.
## Hybrid Orbitals

<table>
<thead>
<tr>
<th>Hybrid-ization</th>
<th>Types of Bonds to Carbon</th>
<th>Example</th>
<th>Name</th>
</tr>
</thead>
<tbody>
<tr>
<td>$sp^3$</td>
<td>four sigma bonds</td>
<td>H-C-C-H</td>
<td>Ethane</td>
</tr>
<tr>
<td>$sp^2$</td>
<td>three sigma bonds and one pi bond</td>
<td>C=C</td>
<td>Ethylene</td>
</tr>
<tr>
<td>$sp$</td>
<td>two sigma bonds and two pi bonds</td>
<td>H-C ≡C-H</td>
<td>Acetylene</td>
</tr>
</tbody>
</table>
Covalent Bonds & Shapes of Molecules

End Chapter 1