Chapter 1

The Basics
Bonding and Molecular Structure

2B. Valence Electrons
- Electrons that surround the nucleus exist in shells of increasing energy and at increasing distances from the nucleus. The most important shell, called the valence shell, is the outermost shell because the electrons of this shell are the ones that an atom uses in making chemical bonds with other atoms to form compounds.
- The number of electrons in the valence shell (called valence electrons) is equal to the group number of the atom.

- e.g. Carbon is in group IVA
  - Carbon has 4 valence electrons

- e.g. Nitrogen is in group VA
  - Nitrogen has 5 valence electrons

- e.g. Halogens are in group VIIA
  - F, Cl, Br, I all have 7 valence electrons

3. The Structural Theory of Organic Chemistry
- Number of covalent bonds usually formed by some elements typically encountered in organic compounds

<table>
<thead>
<tr>
<th>Element</th>
<th># of covalent bonds</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>1</td>
</tr>
<tr>
<td>C</td>
<td>4</td>
</tr>
<tr>
<td>N</td>
<td>3 (or 4)</td>
</tr>
<tr>
<td>O</td>
<td>2</td>
</tr>
<tr>
<td>F</td>
<td>1</td>
</tr>
<tr>
<td>Cl</td>
<td>1</td>
</tr>
<tr>
<td>Br</td>
<td>1</td>
</tr>
<tr>
<td>I</td>
<td>1</td>
</tr>
</tbody>
</table>
- Thus
  - C is tetravalent
  - O is divalent
  - H and halogens are monovalent

- Important:
  - Do not draw any structure with more than 4 bonds on a carbon

- Carbon–carbon bonds
  - Single bond
  - Double bond
  - Triple bond

- Never draw 5 (or more) bonds on carbon

- However C may make 3 bonds \(\Rightarrow\) but need a charge on carbon

- Oxygen
  - Usually divalent

- \(\text{CH}_3\)(diethyl ether)\(\text{CH}_3\)(methanol)\(\text{CH}_3\)(acetone)
Lone pair electrons on oxygen can donate electrons to a Lewis acid
- 3 bonds on oxygen (with a positive charge on oxygen)

\[
\begin{array}{c}
\text{H}_3\text{C} \quad \text{OH} \\
\text{H} \quad \text{H} \quad \text{H}
\end{array}
\quad \quad \quad
\begin{array}{c}
\text{H}_3\text{C} \quad \text{O}^- \\
\text{H} \quad \text{H} \\
\text{e}^- \quad \text{g} \\
\text{H} \quad \text{H}
\end{array}
\]

dative covalent bond

One bond on oxygen
- Usually need a negative charge on oxygen

\[
\begin{array}{c}
\text{R} \quad \text{O}^\text{=O} \quad \text{H} \\
\text{H} \quad \text{OH}
\end{array}
\quad \quad \quad
\begin{array}{c}
\text{R} \quad \text{O}^- \\
\text{H}
\end{array}
\quad \quad \quad
\begin{array}{c}
\text{H}_2\text{O}
\end{array}
\]

3A. Isomers: The Importance of Structural Formulas
- Different compounds that have the same molecular formula. Such compounds are called isomers
Both have the molecular formula C₄H₁₀O

They are constitutional isomers

Constitutional isomers usually have different physical properties (e.g., melting point, boiling point, and density) and different chemical properties (reactivity)

There are two constitutional isomers with the formula C₂H₆O. Write structural formulas for these isomers.

3B. The Tetrahedral Shape of Methane

4. Chemical Bonds: The Octet Rule

In forming compounds, they gain, lose, or share electrons to give a stable electron configuration characterized by 8 valence electrons

When the octet rule is satisfied for C, N, O, and F, they have an electron configuration analogous to the noble gas Ne
4. Chemical Bonds: The Octet Rule

- **Ionic** (or electrovalent) bonds are formed by the transfer of one or more electrons from one atom to another to create ions.

- **Covalent** bonds result when atoms share electrons.

4A. Ionic Bonds

- Atoms may gain or lose electrons and form charged particles called **ions**.
  - An ionic bond is an attractive force between oppositely charged ions.
Electronegativity (EN)

- The **intrinsic ability** of an atom to **attract the shared electrons** in a covalent bond.

- Electronegativities are based on an arbitrary scale, with F the most electronegative (EN = 4.0) and Cs the least (EN = 0.7).
4B. Covalent Bonds & Lewis Structures

- **Covalent bonds** form by sharing of electrons between atoms of similar electronegativities to achieve the configuration of a noble gas.

- **Molecules** are composed of atoms joined exclusively or predominantly by covalent bonds.

- Example

  
  ![Cl Cl](image)
  
  \[ \text{[Ne]} \ 3s^2 \ 3p^5 \quad \text{[Ne]} \ 3s^2 \ 3p^5 \]

  - Covalent bonding

  \[ \text{Cl} - \text{Cl} \]

  - (3 bonds on N)

- Ions, themselves, may contain covalent bonds. Consider, as an example, the ammonium ion.

  ![Ammonium ion](image)

  - (ammonia)
  - (ammonium cation)
  - (4 bonds on N with a positive charge on N)
5. How to Write Lewis Structures

- Lewis structures show the connections between atoms in a molecule or ion using only the valence electrons of the atoms involved.

- For main group elements, the number of valence electrons a neutral atom brings to a Lewis structure is the same as its group number in the periodic table.

- If the structure we are drawing is a negative ion (an anion), we add one electron for each negative charge to the original count of valence electrons. If the structure is a positive ion (a cation), we subtract one electron for each positive charge.

- In drawing Lewis structures we try to give each atom the electron configuration of a noble gas.

Examples

(1) Lewis structure of CH₃Br

- Total number of all valence electrons:

  C  H  Br

  ↓  ↓  ↓

  4  +  1 × 3  +  7  =  14
(2) Lewis structure of methylamine
\((\text{CH}_3\text{N})\)

- Total number of all valence electrons:

\[
\begin{array}{ccc}
\text{C} & \text{H} & \text{N} \\
4 & 1 \times 5 & 5 \\
\end{array}
\]

\[4 + 1 \times 5 + 5 = 14\]

6. Exceptions to the Octet Rule

- Elements in the 2nd row in the periodic table usually obey the Octet Rule (Li, Be, B, C, N, O, F) since they have one 2s and three 2p orbitals available for bonding.

- Elements in the 3rd row in the periodic table have d orbitals that can be used for bonding and may not obey the Octet Rule.

Examples

- Phosphorus pentachloride
  
  \[
  \text{(PCl}_5\text{)}
  \]
  
  m.p. = 179°C

- \((\text{SiF}_6^{2-}\))
Some highly reactive molecules or ions have atoms with fewer than eight electrons in their outer shell.

Formal charges and how to calculate them:

- Formal charge: number of valence electrons - \( \frac{1}{2} \) number of shared electrons - number of unshared electrons

or

\[
F = Z - \frac{S}{2} - U
\]

where \( F \) is the formal charge, \( Z \) is the group number of the element, \( S \) equals the number of shared electrons, and \( U \) is the number of unshared electrons.

Examples:

(1) The Ammonium ion (NH\(_4^+\))

\[
\begin{array}{c}
\text{H} \\
\text{H} \\
\text{H} \\
\text{H} \\
\end{array}
\]

Recall: \( F = Z - \frac{S}{2} - U \)

Formal charge of H:

\[
= 1 - \frac{2}{2} - 0 = 0
\]

Formal charge of N:

\[
= 5 - \frac{8}{2} - 0 = +1
\]

Charge on ion = 4 x 0 +1 = +1

\Rightarrow\text{ The arithmetic sum of all the formal charges in a molecule or ion will equal the overall charge on the molecule or ion.}
(2) The Nitrate ion (NO$_3^-$)

Recall: $F = Z - S/2 - U$

Formal charge of O:

$$= 6 - 2/2 - 6 = -1$$

Formal charge of N:

$$= 5 - 8/2 - 0 = +1$$

Charge on ion = $2 \times (-1) + 0 + 1 = -1$

(3) Water (H$_2$O)

The sum of the formal charges on each atom making up a molecule must be zero.

Formal charge of O:

$$= 6 - 4/2 - 4 = 0$$

Formal charge of H:

$$= 1 - 1/2 - 0 = 0$$

Charge on molecule = $0 + 2 \times 0 = 0$

7A. A Summary of Formal Charges

<table>
<thead>
<tr>
<th>Group</th>
<th>Formal Charge of +1</th>
<th>Formal Charge of 0</th>
<th>Formal Charge of -1</th>
</tr>
</thead>
<tbody>
<tr>
<td>IIIA</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>IVA</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>VA</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>VIA</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>VIIA</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*For example: $X = F, Cl, Br, or I$*
8. Resonance Theory

- In a Lewis structure, we draw a well-defined location for the electrons in a molecule.

- In many molecules and ions (especially those containing \( \pi \) bonds), more than one equivalent Lewis structures can be drawn which represent the same molecule.

- We can write three different but equivalent structures, 1–3.

- Resonance theory states that whenever a molecule or ion can be represented by two or more Lewis structures that differ only in the positions of the electrons, two things will be true:
  - None of these structures, which we call resonance structures or resonance contributors, will be a realistic representation for the molecule or ion. None will be in complete accord with the physical or chemical properties of the substance.
  - The actual molecule or ion will be better represented by a hybrid (average) of these structures.
• Resonance structures, then, are not real structures for the actual molecule or ion; they exist only on paper.

![Resonance Structures Diagram]

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• It is also important to distinguish between resonance and an equilibrium.

• In an equilibrium between two or more species, it is quite correct to think of different structures and moving (or fluctuating) atoms, but not in the case of resonance (as in the carbonate ion). Here the atoms do not move, and the “structures” exist only on paper.

• An equilibrium is indicated by ⟷ and resonance by ⟷

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8A. How to Write Resonance Structures

• Resonance structures exist only on paper. Although they have no real existence of their own, resonance structures are useful because they allow us to describe molecules and ions for which a single Lewis structure is inadequate.

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• We write two or more Lewis structures, calling them resonance structures or resonance contributors. We connect these structures by double-headed arrows ⟷, and we say that the real molecule or ion is a hybrid of all of them.

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We are only allowed to move electrons in writing resonance structures.

\[ \begin{align*} 
H_3C-CH-CH=CH_2 & \xrightarrow{+} H_3C-CH=CH-CH_2 \\ 
1 & \quad 2 \\
\end{align*} \]

These are resonance structures.

\[ \begin{align*} 
H_2C=CH_2-CH=CH_2 & \xrightarrow{+} H_2C=CH-CH=CH_2 \\
\end{align*} \]

All of the structures must be proper Lewis structures.

\[
\begin{array}{c}
\overset{\scriptscriptstyle H}{\underset{\scriptscriptstyle H}{\text{H}}} \\
\overset{\text{C} \equiv \text{O}}{=}
\end{array}
\]

This is not a proper resonance structure of methanol.

The energy of the resonance hybrid is lower than the energy of any contributing structure.

Resonance stabilizes a molecule or ion. This is especially true when the resonance structures are equivalent. Chemists call this stabilization «resonance stabilization». If the resonance structures are equivalent, then the resonance stabilization is large.

The more stable a structure is (when taken by itself), the greater is its contribution to the hybrid.

The more covalent bonds a structure has, the more stable it is.

Charge separation decreases stability.

Resonance structures for formaldehyde:

Four covalent bonds

More stable

Three covalent bonds

Less stable
Structures in which all the atoms have a complete valence shell of electrons (i.e., the noble gas structure) are more stable.

Examples
1. Benzene
2. Carboxylate ion (RCOO⁻)
3. Ozone (O₃)

10. Atomic Orbitals and Electron Configuration

10A. Electron Configurations
- The relative energies of atomic orbitals in the 1st & 2nd principal shells are as follows:
  - Electrons in 1s orbitals have the lowest energy because they are closest to the positive nucleus.
  - Electrons in 2s orbitals are next lowest in energy.
  - Electrons of the three 2p orbitals have equal but higher energy than the 2s orbital.
  - Orbitals of equal energy (such as the three 2p orbitals) are called degenerate orbitals.
- **Aufbau principle**
  - Orbitals are filled so that those of lowest energy are filled first

- **Pauli exclusion principle**
  - A maximum of two electrons may be placed in each orbital but only when the spins of the electrons are paired

- **Hund’s rule**
  - When we come to orbitals of equal energy (degenerate orbitals) such as the three $p$ orbitals, we add one electron to each with their spins unpaired until each of the degenerate orbitals contains one electron. (This allows the electrons, which repel each other, to be farther apart.) Then we begin adding a second electron to each degenerate orbital so that the spins are paired

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11. **Molecular Orbitals**

- IV Nuclear repulsion
- I No attraction
- III Covalent bonding
- II Attraction between electrons and nuclei

$r = 0.74 \text{ Å}$

436 kilojoules mol$^{-1}$
- We cannot simultaneously know the position and momentum of an electron.

- An atomic orbital represents the region of space where one or two electrons of an isolated atom are likely to be found.

- A molecular orbital (MO) represents the region of space where one or two electrons of a molecule are likely to be found.

- An orbital (atomic or molecular) can contain a maximum of two spin-paired electrons (Pauli exclusion principle).

- When atomic orbitals combine to form molecular orbitals, the number of molecular orbitals that result always equals the number of atomic orbitals that combine.

- A bonding molecular orbital ($\psi_{\text{molec}}$) results when two orbitals of the same phase overlap.

- An antibonding molecular orbital ($\psi^*_{\text{molec}}$) results when two orbitals of opposite phase overlap.
12. The Structure of Methane and Ethane: sp\(^3\) Hybridization

Ground state of a carbon atom

\[
\begin{align*}
C &: \quad 1s \quad 2s \quad 2p_x \quad 2p_y \quad 2p_z
\end{align*}
\]

- Hybridization
  - sp\(^3\)

- Covalent bond
- Hybridized carbon

(line bond structure)

(Tetrahedral structure)

(Carbon with 4 \(\sigma\) bonds)

(Lewis structure)

(3-D structure)
A sigma (σ) bond has a circularly symmetrical orbital cross section when viewed along the bond between two atoms. All purely single bonds are sigma bonds.
Rotation of groups joined by a single bond does not usually require a large amount of energy.

Rotation around sigma bond is free.
13A. Restricted Rotation and the Double Bond

- There is a large energy barrier to rotation associated with groups joined by a double bond
  - $\sim 264 \text{ kJmol}^{-1}$ (strength of the $\pi$ bond)
  - To compare: rotation of groups joined by C-C single bonds $\sim 13$-$26$ kJmol$^{-1}$
13B. Cis–Trans Isomerism

- Stereochemistry of double bonds

\[
\begin{align*}
&\text{identical to} \\
&\text{identical to}
\end{align*}
\]

- Restricted rotation of C=C

- Cis-Trans System
  - Useful for 1,2 disubstituted alkenes
  - e.g.
    - (1) \textit{trans}-1-Bromo-2-chloroethane vs. \textit{cis}-1-Bromo-2-chloroethane
    - (2) \textit{trans}-3-Hexene vs. \textit{cis}-3-Hexene
    - (3) \textit{trans}-1,3-Dibromopropene vs. \textit{cis}-1,3-Dibromopropene
14. The Structure of Ethyne (Acetylene): sp Hybridization

- **sp**
  - 1 σ bond + 2 π bond
  - Linear structure
  - Carbon with (2 σ + 2 π) bonds

![Diagram](image1.png)

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- Ground state
- Excited state
- sp-Hybridized state
- Promotion of electron
- Hybridization

![Diagram](image2.png)

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- sp Orbital
- p Orbitals

![Diagram](image3.png)

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- σ Bond
- π Bond

![Diagram](image4.png)
sp orbital
  ● 50% $s$ character, 50% $p$ character

sp$^2$ orbital
  ● 33% $s$ character, 66% $p$ character

sp$^3$ orbital
  ● 25% $s$ character, 75% $p$ character

15. A Summary of Important Concepts That Come from Quantum Mechanics

1) An atomic orbital (AO) corresponds to a region of space about the nucleus of a single atom where there is a high probability of finding an electron. $s$ orbitals are spherical, $p$ orbitals are like two almost-tangent spheres. Orbitals can hold a maximum of two electrons when their spins are paired.

2) When atomic orbitals overlap, they combine to form molecular orbitals (MOs)

3) When atomic orbitals with the same phase sign interact, they combine to form a bonding molecular orbital

4) An antibonding molecular orbital forms when orbitals of opposite phase sign overlap
5) The energy of electrons in a bonding molecular orbital is less than the energy of the electrons in their separate atomic orbitals.

6) The number of molecular orbitals always equals the number of atomic orbitals from which they are formed.

7) Hybrid atomic orbitals are obtained by mixing (hybridizing) the wave functions for orbitals of different types (i.e., $s$ and $p$ orbitals) but from the same atom.

8) Hybridizing three $p$ orbitals with one $s$ orbital yields four $sp^3$ orbitals and they are tetrahedral.

9) Hybridizing two $p$ orbitals with one $s$ orbital yields three $sp^2$ orbitals and they are trigonal planar.

10) Hybridizing one $p$ orbital with one $s$ orbital yields two $sp$ orbitals, a linear molecule.

11) A sigma ($\sigma$) bond (a type of single bond) is one in which the electron density has circular symmetry when viewed along the bond axis.

12) A pi ($\pi$) bond, part of double and triple carbon–carbon bonds, is one in which the electron densities of two adjacent parallel $p$ orbitals overlap sideways to form a bonding pi molecular orbital.

16. Molecular Geometry: The Valence Shell Electron Pair Repulsion Model

- Valence shell electron pair repulsion (VSEPR) model:
  1) We consider molecules (or ions) in which the central atom is covalently bonded to two or more atoms or groups.
2) We consider all of the valence electron pairs of the central atom—both those that are shared in covalent bonds, called bonding pairs, and those that are unshared, called nonbonding pairs or unshared pairs or lone pairs.

3) Because electron pairs repel each other, the electron pairs of the valence shell tend to stay as far apart as possible. The repulsion between nonbonding pairs is generally greater than that between bonding pairs.

4) We arrive at the geometry of the molecule by considering all of the electron pairs, bonding and nonbonding, but we describe the shape of the molecule or ion by referring to the positions of the nuclei (or atoms) and not by the positions of the electron pairs.

16A. Methane
A tetrahedral arrangement of the electron pairs explains the trigonal pyramidal arrangement of the four atoms. The bond angles are 107° (not 109.5°) because the nonbonding pair occupies more space than the bonding pairs.
16F. Carbon Dioxide

![Diagram of Carbon Dioxide]

The four electrons of each double bond act as a single unit and are maximally separated from each other.

17. How to Interpret and Write Structural Formulas

![Structural Formulas]

17A. Dash Structural Formulas

- Atoms joined by single bonds can rotate relatively freely with respect to one another

![Equivalent Dash Formulas for Propyl Alcohol]
17B. Condensed Structural Formulas

Dash formula

CH₃CH₂CH₂CH₃ or CH₃CHOHCH₂

H₃C

CH₂CH₂CH₂ or CH₂CHOHCH₂

H₂O

H

Dash formula

Condensed formulas

17C. Bond-Line Formulas

Bond-line formula

CH₃CH₂CH₂CH₃ -

\[ \text{Bond-line formula} \]

CH₃CH₂CH₂CH₂ -

\[ \text{Bond-line formula} \]

(CH₂)₃CH₂Cl -

\[ \text{Bond-line formula} \]

17D. Three-Dimensional Formulas

Ethane

OR

C

H

C

H

H

H

H

H

H

Breathing

OR

H

C

H

H

H

H

H

H

Br

Bromomethane

etc.
Examples of bond-line formulas that include three-dimensional representations

An example involving trigonal planar geometry

An example involving linear geometry