Chapter 7: Chemical Bonding and Molecular Structure

- Ionic Bond
- Covalent Bond
- Electronegativity and Bond Polarity
- Lewis Structures
- Orbital Overlap
- Hybrid Orbitals
- The Shapes of Molecules (VSEPR Model)
- Molecular Orbitals

The Interaction of Two Hydrogen Atoms

Optimum distance to achieve lowest overall energy of system

H₂ molecule

H atom

The atoms begin to interact as they move closer together.

H atom

H atom

Sufficiently far apart to have no interaction.
The Interaction of Two Hydrogen Atoms

Models

- Models are attempts to explain how nature operates on the microscopic level based on experiences in the macroscopic world.

Fundamental Properties of Models
- A model does not equal reality.
- Models are oversimplifications, and are therefore often wrong.
- Models become more complicated as they age.
- We must understand the underlying assumptions in a model so that we don’t misuse it.
**Bonding Overview**

- Valence $e^-$ play a fundamental role in chemical bonding.

- $e^-$ transfer leads to *ionic bonds*.

- Sharing of $e^-$ leads to *covalent bonds*.

- $e^-$ are transferred or shared to give each atom a noble gas configuration
  - *the octet.*

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**The Ionic Bond**

- An *ionic bond* is formed by the *electrostatic attraction* of oppositely charged ions.
  
  - Ionic compounds form between metals and nonmetals.
  
  - The greater the difference in metallic/nonmetallic properties (more widely separated in the periodic table), the more likely it is a compound will be ionic.
Formation of Cations

• Metals in the s and p blocks have low ionization energies and form cations with an np^6 electronic configuration.
  – Large jumps in ionization energy occur when removing an electron from an np^6 electronic configuration.

• Cations are smaller than their corresponding neutral atoms.
  – Losing electrons reduces electron-electron repulsion.
  – Remaining electrons are more tightly bound to the nucleus.

Formation of Cations

• Transition metals can form cations with more than one possible charge.
  – Transition metals first lose electrons from the s subshell.
  – Additional electrons are lost from the partially filled d orbitals.
  – A half filled d orbital set is a fairly stable arrangement.
    • Fe^{2+} and Fe^{3+} ions are both stable.
Formation of Anions

- Nonmetals have negative electron affinities and generally form anions with an np⁶ electronic configuration.

- Anions are larger than their corresponding neutral atoms.
  - Gaining electrons increases electron-electron repulsion.
  - Valence electrons less tightly bound to the nucleus.

Formation of Ions

- Sizes (pm) of ions compared to corresponding neutral atoms.
Formation of Ions

• Forming an ionic bond between a metal and nonmetal usually requires energy to form the ion pair.
  – Ionization energies are positive.
  – Electron affinities for nonmetals are negative.
  – Energy input to form the cation is not offset by energy released by forming the anion.

\[ F = \frac{q_1 q_2}{4\pi \varepsilon_0 r^2} \]

– \( F \) is force of attraction, \( q_1 \) and \( q_2 \) are the charges, and \( r \) is the distance between the nuclei of the two ions.

• The potential energy, \( V \), for the ion pair can be calculated using:

\[ V = \frac{k q_1 q_2}{4\pi \varepsilon_0 r} \]

– \( k = 1.389 \times 10^5 \text{ kJ pm/mol} \) (charges expressed in units of electron charge)
Formation of Ions

• The energy released in forming NaF can be calculated.

  – First the ion pair must be formed. \((496 - 328 = +168 \text{ kJ/mol})\)
    • The ionization energy for Na is 496 kJ/mol.
    • The electron affinity for F is -328 kJ/mol.

  – Second the potential energy from coulombic attraction is calculated.
    Use the ionic radii to calculate \(V\).
    • \(V = -591 \text{ kJ/mol}\).

• The energy released from the coulombic attraction is much greater than the energy required to form the NaF ion pair.
  – The formation of the NaF ionic bond releases energy.

Formation of Ions

• In ionic solids, the ions are arranged in a crystal lattice.

  – Ions experience attractive and repulsive interactions in three dimensions.

  – Strength of interaction decreases with distance.
• In a solid lattice, any given ion experiences a large number of attractive and repulsive interactions.

**Formation of Ions**

- The *lattice energy* is the overall result of the attractive and repulsive forces a crystal contains.
  - Small ions with large charges form ionic compounds with large lattice energies.
  - Large ions with small charges form ionic compounds with small lattice energies.
Ionic Bond Example Problem

• In each of the following pairs of ionic solids, the ions are arranged into similar lattices. Which one has the largest lattice energy?

  – NaCl or KCl
  – Mg(OH)$_2$ or MgO
  – MgO or BaS

The Covalent Bond

• A *covalent bond* is based on the sharing of pairs of electrons between two atoms.

• Driving force behind bond formation is lowering of overall energy.

  – Ionic bonding lowers energy by transferring electrons between a metal and a nonmetal.

  – Covalent bonding lowers energy by sharing electrons between two nonmetals.
**Chemical Bonds and Energy**

- *Bond energy* - energy released when isolated atoms form a covalent bond.

- *Bond length* - the distance between the nuclei of the bonding atoms where the potential energy is a minimum.

- Electron density distribution is different for isolated atoms and covalently bonded atoms.
  - Isolated atoms have spherical electron density around the nucleus.
  - Covalently bonded atoms have a build up of electron density between bonded atoms.

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**Chemical Bonds and Energy**

- When two atoms approach one another, the negatively charged electron clouds are attracted to the other atom’s positively charged nucleus.

- The diagram represents electron density during bond formation.
**Chemical Bonds and Energy**

- Formation of bonds always releases energy.
  - Once a bond is formed, the same amount of energy, the *bond energy*, is needed to break the bond apart.
  - Bond energies vary depending on the bonding atoms involved.

- Chemical reactions involve rearranging bonds, turning reactants into products.
  - Reactions are energetically favored if the energy required to break reactant bonds is less than energy released making product bonds.

**Chemical Bonds and Reactions**

- Bond energies for covalent bond types in Teflon.
  - For the combustion of Teflon, the weak O–F bonds of OF₂ compared to the strong C-F bonds in Teflon accounts for Teflon’s resistance to burning.

<table>
<thead>
<tr>
<th>Type of Bond</th>
<th>Bond Energy (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C—F</td>
<td>485</td>
</tr>
<tr>
<td>C—H</td>
<td>415</td>
</tr>
<tr>
<td>O—F</td>
<td>190</td>
</tr>
<tr>
<td>O—H</td>
<td>460</td>
</tr>
</tbody>
</table>

\[
\Delta H = \sum_{Bonds\ Broken} D - \sum_{Bonds\ Formed} D
\]
Chemical Bonds and the Structure of Molecules

• During ionic bond formation, the cations and anions achieve $np^6$ electronic configurations (noble gas configuration).
  – Metals lose electrons.
  – Nonmetals gain electrons.

• During covalent bond formation, electrons are shared between two atoms.
  – Shared electrons are available to both bonding atoms.
  – Sharing leads to 8 valence electrons around each atom.

Chemical Bonds and the Structure of Molecules

• Octet rule - an atom will form covalent bonds to achieve a complement of eight valence electrons.
  – The valence shell electronic configuration is $ns^2np^6$ for a total of eight electrons.
  – For the $n = 1$ shell, hydrogen violates the octet rule and shares only 2 electrons.
Electronegativity and Bond Polarity

- Bonding between the two ends of the bonding continuum, ionic and covalent bonding, is described using electronegativity and bond polarity.

- **Electronegativity** is the attraction of an atom for the shared electrons in a covalent bond.
  - Electronegativities are not measured quantities.
  - Electronegativities are assigned based on factors such as atomic size, electron affinity, and ionization energy.
  - The higher the electronegativity value, the more likely an element will attract extra electron density during compound formation.

Electronegativity

- Electronegativities increase from left to right across a period and from bottom to top for a group.
- Fluorine is the most electronegative element, with an electronegativity of 4.0.
### Types of Bonds

- Bond character is related to difference in electronegativities: 
  \[ \Delta EN \geq 2.0 \approx \text{Ionic} \]
  \[ \Delta EN < 2.0 \approx \text{Covalent} \]
- Ionic e.g., NaCl
- Polar covalent, \( 0.5 < \Delta EN < 2.0 \), e.g., P-Cl
- Covalent, \( \Delta EN < 0.5 \), e.g., C-S

### Bond Polarity

- Electron density is not shared equally when elements with different electronegativities bond.
  - More than half of the electron density is associated with the more electronegative element.
  - The more electronegative element experiences an increase in electron density and attains a partial negative charge.
  - The less electronegative element experiences a decrease in electron density and attains a partial positive charge.
  - The two points of positive and negative charge constitute a dipole.
  - The bond has an electric field associated with it.
Polar Covalent Bonds

(a) Nonpolar covalent bonds

(b) Polar covalent bond

\[ \text{H} \rightarrow \text{Cl}^{\delta^+} \]

\[ \text{H} - \text{Cl}^{\delta^-} \]

= Atomic nucleus
\[ \text{\textcolor{red}{\textcircled{0}}} \] = Center of negative charge
\[ \text{\textcolor{blue}{\textcircled{0}}} \] = Center of positive charge

The Three Possible Types of Bonds

(a) Covalent

(b) Polar Covalent

(c) Ionic
**Bond Polarity Example**

• Consider the bonds: S–S, S–H, or S–O?
  – Order them in increasing polarity,

  – For each of these bonds, determine which atom has a partial positive charge.

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**Localized Electron Bonding Model**

• A molecule is composed of atoms that are bound together by sharing pairs of electrons using the atomic orbitals of the bound atoms.

  1. Description of valence electron arrangement (Lewis structure).
  2. Prediction of geometry (VSEPR model).
  3. Description of atomic orbital types used to share electrons or hold lone pairs.
Chemical Bonds and the Structure of Molecules

- **Lewis dot symbols** keep track of valence electrons, especially for main group elements, allowing prediction of bonding in molecules.

  - To draw a Lewis dot symbol, the valence electrons are represented by dots and are placed around the element symbol.
  
  - The first four dots are placed singly.
  
  - Starting with the fifth dot, they are paired.

<table>
<thead>
<tr>
<th>Group</th>
<th>1</th>
<th>2</th>
<th>13</th>
<th>14</th>
<th>15</th>
<th>16</th>
<th>17</th>
<th>18</th>
</tr>
</thead>
<tbody>
<tr>
<td>Number of electrons in valence shell</td>
<td>1</td>
<td>2</td>
<td>3</td>
<td>4</td>
<td>5</td>
<td>6</td>
<td>7</td>
<td>8 (except He)</td>
</tr>
<tr>
<td>Period 1</td>
<td>H•</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>F•</td>
</tr>
<tr>
<td>Period 2</td>
<td>Li•</td>
<td>Be•</td>
<td>B•</td>
<td>C•</td>
<td>N•</td>
<td>O•</td>
<td>F•</td>
<td>Ne•</td>
</tr>
<tr>
<td>Period 3</td>
<td>Na•</td>
<td>Mg•</td>
<td>Al•</td>
<td>Si•</td>
<td>P•</td>
<td>S•</td>
<td>Cl•</td>
<td>Ar•</td>
</tr>
<tr>
<td>Period 4</td>
<td>K•</td>
<td>Ca•</td>
<td>Sc•</td>
<td>Ti•</td>
<td>V•</td>
<td>Cr•</td>
<td>Mn•</td>
<td>Ne•</td>
</tr>
<tr>
<td>Period 5</td>
<td>Rb•</td>
<td>Sr•</td>
<td>Y•</td>
<td>Zr•</td>
<td>Nb•</td>
<td>Mo•</td>
<td>Tc•</td>
<td>Rn•</td>
</tr>
<tr>
<td>Period 6</td>
<td>Cs•</td>
<td>Ba•</td>
<td>La•</td>
<td>Pb•</td>
<td>Bi•</td>
<td>Po•</td>
<td>At•</td>
<td>Rn•</td>
</tr>
<tr>
<td>Period 7</td>
<td>Fr•</td>
<td>Ra•</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

- Lewis dot symbols for main group elements.
  
  - Elements within a group have the same number of valence electrons and identical Lewis dot symbols.
Chemical Bonds and the Structure of Molecules

- Lewis dot structures show how electrons are shared in a molecule.
  - A pair of shared electrons between two atoms is a bonding pair.
  - Bonding pairs represented by a line between two atomic symbols.
  - Pairs of electrons associated with one atom are nonbonding or lone pair electrons.
- Reflects central idea that stability of a compound relates to noble gas electron configuration.

Lewis Structures for Ionic Compounds

\[
\begin{align*}
\text{BaO} & \quad \text{Ba}^+ \quad \text{O}^2- \\
\text{MgCl}_2 & \quad \text{Mg}^{2+} \quad 2\text{Cl}^- \\
\end{align*}
\]
Chemical Bonds and the Structure of Molecules

- By sharing an electron from each atom, two hydrogen atoms can form a covalent bond. H-H
  - Hydrogen violates the octet rule by sharing only two electrons.
    \[ H \cdot + \cdot H \rightarrow H : H \text{ or } H - H \]

- When two fluorine atoms combine, they form a stable covalent bond.
  - By sharing a pair of electrons, each atom is surrounded by eight valence electrons.
    \[
    \begin{array}{c}
    \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots \\
    :F \cdot + \cdot F & \rightarrow & :F : F & \text{ or } & :F - F \\
    \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots 
    \end{array}
    \]

Chemical Bonds and the Structure of Molecules

- Bonding atoms in molecules can share more than one bonding pair of electrons.
  - A **double bond** results when two bonding pairs are shared.
  - A **triple bond** results when three bonding pairs are shared.
  - Strength of the covalent bond increases as the number of bonding pairs increases.

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<tr>
<td>C—C</td>
<td>346</td>
</tr>
<tr>
<td>C≡C</td>
<td>602</td>
</tr>
<tr>
<td>C≡C</td>
<td>835</td>
</tr>
</tbody>
</table>
Keeping Track of Bonding: Lewis Structures

- **Step 1** - Count the total valence electrons in the molecule or ion.
  - Sum the number of valence electrons for each element in a molecule.
  - For ions, add or subtract valence electrons to account for the charge.
- **Step 2** - Draw the “skeletal structure” of the molecule.
  - The element written first in the formula is usually the central atom, unless it is hydrogen.
  - Usually, the central atom is the least electronegative.
- **Step 3** - Place single bonds between all connected atoms in the structure by drawing lines between them.
- **Step 4** - Place the remaining valence electrons not accounted for on individual atoms until the octet rule is satisfied. Place electrons as lone pairs whenever possible.
  - Place electrons first on outer atoms, then on central atoms.
- **Step 5** - Create multiple bonds by shifting lone pairs into bonding positions as needed for any atoms that do not have a full octet of valence electrons.

Lewis Structure Examples

Draw a Lewis structure for each of the following molecules:

- HF
- NH₃
- CO₂
- HCN
- CH₃COOH
**Resonance**

- *Resonance* structures can be drawn when the choice of multiple bond location is arbitrary.
  
  – The position of all atoms are identical; only the positions of the electrons are different.
  
  – The actual structure is a *hybrid*, an average of the contributing structures, and NOT a mixture of them.

**Resonance Example**

- More than one valid Lewis structure can be written for $\text{NO}_3^-$.

  $\text{NO}_3^- = 24e^-$

\[
\begin{array}{c}
\begin{array}{c}
\text{O} \\
\text{N} \\
\text{O}
\end{array} & \leftrightarrow & \begin{array}{c}
\text{O} \\
\text{N} \\
\text{O}
\end{array} & \leftrightarrow & \begin{array}{c}
\text{O} \\
\text{N} \\
\text{O}
\end{array}
\end{array}
\]

– The *double arrow* indicates the structures are resonance structures.

– Electrons are really delocalized – they can move around the entire molecule.
Resonance

- The two resonance structures for benzene.
  - Indicates the two ways to distribute 3 double bonds among 6 carbon atoms.
  - The true structure is an average of the two resonance structures.

Orbital Overlap and Chemical Bonding

- Lewis dot structures provide insight into a molecule’s bonding, but does not tell how a covalent bond is formed
  - Electrons are modeled as waves.
  - When two waves occupy the same space, they interfere with each other.
  - Constructive and destructive interference are possible.
Orbital Overlap and Chemical Bonding

• Formation of chemical bonds is an example of constructive interference between electron waves.
  – For interference to occur, electron waves must occupy the same space.
  – Valence orbitals of one atom must be positioned to overlap with the valence orbitals of the other atom.

• Destructive interference between electron waves leads to antibonding orbitals.
Orbital Overlap and Chemical Bonding

- *Valence bond model* of chemical bonding - all chemical bonds are the result of overlap between atomic orbitals.

- For $\text{H}_2$, each H atom has a single valence electron in a $1s$ orbital.
  - The $1s$ orbitals overlap to form the covalent bond.
  - $s$ orbitals are spherical, there is no preferred direction of approach.
**Orbital Overlap and Chemical Bonding**

- Overlap of the 1s orbitals for the covalent bond in molecular hydrogen.
  - Top: Overlap shown by plotting the wave functions for the 1s orbitals.
  - Bottom: Shading to represent the buildup of electron density.

For N₂, the Lewis structure shows a total of 6 electrons shared.

\[ \text{N} \equiv \text{N} \]

- Each N atom has a single valence electron in each 2p orbital.
- The 2p orbital set can overlap in different orientations due to their shapes.
- A 2p orbital on one N overlaps end-to-end with a 2p orbital on the second N forming a sigma, \( \sigma \), bond.
- A sigma bond is the result of constructive interference for end-to-end overlap, where electron density lies along a line between the bonding atoms.
Orbital Overlap and Chemical Bonding

- Formation of a sigma bond by the end-to-end overlap of two $p$ orbitals.
  - Two $p$ orbitals approach each other along the $x$, $y$, or $z$ axis.
  - All $p$ orbitals are described as lying along the $x$, $y$ or $z$ axis.

- The remaining two $2p$ orbitals on each N overlap side-to-side forming pi, $\pi$, bonds.
  - A pi bond is the result of constructive interference for side-to-side overlap, where electron density lies above and below, or in front and in back of a line between the bonding atoms.
  - Two pi bonds can form between the two nuclei.
Bonding in $\text{H}_2\text{S}$

$$\sigma_1 = \Psi(\text{H}_a \ 1s) + \Psi(\text{S} \ 3p_x)$$

$$\sigma_2 = \Psi(\text{H}_b \ 1s) + \Psi(\text{S} \ 3p_z)$$