Chapter 7. Covalent Bonds & Molecular Structure

- **Covalent bonds** are formed by sharing at least one pair of electrons.
- Size and strength of a bond results from interplay of attraction between opposite charges, and repulsion between like charges.

**Bond Length**

- Every covalent bond has its own characteristic length that leads to maximum stability.
- This is the bond length.
- Bond lengths can be estimated from ionic radii.

**Polar-Covalent Bonds**

- Ionic and covalent bonds represent two extremes of a continuous spectrum. Between these are those known as polar covalent bonds.

**Electronegativity**

- **Pauling Electronegativities.**

**Electron Dot Structures**

- For main group elements, bond formation can be considered a way to simulate a noble gas configuration, i.e. 8 valence electrons (except H).
- Lewis Dot Structures, as they are often called, are named after G. N. Lewis of U.C. Berkeley.
- Using electron dot (Lewis) structures, the valence electrons in an element are represented by dots.

**Lewis Dot Bonding**

- The electron–dot structures provide a simple, but useful way of representing chemical reactions.

"octet"
Multiple Bonds

- **Double Bonds:**
  
  ![Double Bond](image)

- **Triple Bonds:**
  
  ![Triplet Bond](image)

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**Drawing Lewis Structures**

Example: \( \text{NH}_3 \)

**Step 1:** Arrange atoms with single bond connections

(H is never central, halogens rarely. N, C, P often central)

\[
\begin{align*}
\text{H} & - \text{N} \equiv \text{N} \\
\text{H} & - \text{N} \equiv \text{N}
\end{align*}
\]

**Step 2:** Count the total valence electrons for all atoms = \(3(1) + (5) = 8\)

Subtract ones already used for bonds = \(8 - 3(2) = 2\)

**Step 3:** Add extra electrons as lone pairs to
(a) peripheral atoms except H, and
(b) central atom.

\[
\begin{align*}
\text{H} & - \text{N} \equiv \text{N} \\
\text{H} & - \text{N} \equiv \text{N}
\end{align*}
\]

**Step 4:** Check octet rule for each atom (2 for H).

If not satisfied, move lone pair to form a multiple bond.

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**Electron-Group Geometry**

<table>
<thead>
<tr>
<th>total e⁻ pairs</th>
<th>group geometry</th>
<th>Diagram</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>linear</td>
<td><img src="image" alt="Linear" /></td>
</tr>
<tr>
<td>3</td>
<td>trigonal planar</td>
<td><img src="image" alt="Trigonal Planar" /></td>
</tr>
<tr>
<td>4</td>
<td>tetrahedral</td>
<td><img src="image" alt="Tetrahedral" /></td>
</tr>
<tr>
<td>5</td>
<td>trigonal bipyramidal</td>
<td><img src="image" alt="Trigonal Bipyramidal" /></td>
</tr>
<tr>
<td>6</td>
<td>octahedral</td>
<td><img src="image" alt="Octahedral" /></td>
</tr>
</tbody>
</table>

**Two Electron Groups**

- A \( \text{CO}_2 \) molecule is linear, with a bond angle of 180°:
  
  ![CO2](image)

- An \( \text{HCN} \) molecule is linear, with a bond angle of 180°:
  
  ![HCN](image)

**Three Electron Groups**

- Formaldehyde (\( \text{H}_2\text{CO} \)) is **trigonal planar** with bond angle of about 120°:
  
  ![Formaldehyde](image)

- \( \text{SO}_2 \) has electron groups in a trigonal planar geometry.

  Molecule shape is **bent** with a bond angle of about 120°.

**Four Electron Groups**

- Methane (\( \text{CH}_4 \)) is **tetrahedral** with bond angles of 109.5°:
  
  ![Methane](image)

- Ammonia (\( \text{NH}_3 \)) is **trigonal pyramidal** with bond angles of 107°:
  
  ![Ammonia](image)

- Water (\( \text{H}_2\text{O} \)) is **bent** with a bond angle of 104.5°:
  
  ![Water](image)

Lone pairs take up a bit more space than bonding electron pairs.

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Chap 7: Covalent Bonds

Five Electron Groups
- 5 bonds, trigonal bipyramidal
- 4 bonds, see-saw
- 3 bonds, T-shaped
- 2 bonds, linear

Six Electron Groups
- 6 bonds, octahedral
- 5 bonds, square pyramidal
- 4 bonds, square planar

Valence Bond Theory
- Orbitals overlap to form a bond - a region of increased electron density.
- Two electrons (of opposite spin) go into the bond.
- Bonding electrons have a higher probability of being found in the region between bonded nuclei.

Hybrid Orbitals
Consider methane (CH₄). The central carbon atom has one s and three p orbitals to share in its valence shell. However, by symmetry (and from the tetrahedral shape) we know that the four bonds are equivalent.

In 1931 Linus Pauling showed that wavefunctions from s orbitals and p orbitals could be combined to form hybrid atomic orbitals.

Multiple Bonds
- The first bond is a σ bond from end-on overlap of hybridized orbitals.
- The second or third bonds are π bonds from side-by-side overlap of remaining unhybridized p orbitals.

Double Bond Example
Ethene (ethylene): C₂H₄

Predicts that ethylene is planar. True!
Otherwise, the unhybridized p orbitals can’t line up to overlap.
Molecular Orbitals (MO)

• Valence Bond theory is a first approximation where we imagine that each atom retains its own independent orbitals which interact with the orbitals of another atom.
• A more rigorous approach is to use Quantum Mechanics to determine appropriate wavefunctions for the molecule as a whole.
• Combining two Atomic Orbitals gives Two Molecular Orbitals:
  - Subtractive combination
  - Additive combination

H₂ MO Energy Levels

Molecular Orbital Diagram for H₂:

MO Theory Predicts Magnetic Properties

Valence bond theory does not predict that O₂ is paramagnetic.

Orbitals in Solid State Materials (Chap. 21)

Consider a crystalline solid to be the limiting case of a large molecule.

Orbitals clump together so closely, they are regarded as "bands."

Electrical Conductivity

• Filled energy levels are called the valence band.
• Unfilled energy levels are the conduction band.
• In the presence of an electric potential, the electrons are accelerated toward the positive terminal, creating a net current.
• Unfilled energy levels must be accessible in order for current to flow.
• In a metal, unfilled energy levels are directly adjacent to the filled ones, so negligible energy (electrical potential) is required to access them.

Band Gaps

• In an insulator (non-metal) there is a large energy gap between the valence band and the conduction band.
• It is impractical to excite electrons into the conduction band.
• In a semiconductor (Si, Ge, GaAs) there is a small energy gap between the valence band and the conduction band.
• Applying an electrical potential of only a few volts is sufficient to promote electrons into the conduction band and cause current to flow.