

Chapter: Chemical Bonding

Chemical bonding explains how atoms come together to form molecules and compounds, holding them together with varying strengths. Understanding the different types of bonding and associated theories is critical to predicting the structure, stability, and properties of chemical compounds.

1. Covalent Bond

A covalent bond is formed when two atoms share one or more pairs of electrons. This sharing generally occurs between nonmetal atoms with similar electronegativities.

1.1 Valence Bond Theory (VBT)

Introduction:

Valence Bond Theory was introduced by Heitler and London and further developed by Linus Pauling to describe the quantum mechanical nature of chemical bonds. It provides insights into the formation of covalent bonds through atomic orbital overlap.

Key Features:

1. Orbital Overlap:

- A covalent bond forms when two atomic orbitals overlap, resulting in a region of increased electron density between the two nuclei.
- The extent of overlap determines the bond strength.
- For example, in H_2 , the 1s orbitals of two hydrogen atoms overlap to form a sigma (σ) bond.

2. Nature of Orbitals:

- Bonds can form from the overlap of $s-s$, $s-p$, or $p-p$ orbitals.
- σ -bonds result from head-on overlap, while π -bonds result from side-to-side overlap.

3. Spin Pairing:

- The interacting electrons must have opposite spins.

4. Energy Minimization:

- Bond formation lowers the system's overall energy, leading to a stable molecule.

Directional Nature of Bonds:

Covalent bonds are directional because the atomic orbitals involved in the overlap are oriented in specific directions. This results in molecules with definite shapes, e.g., linear, tetrahedral, etc.

Example:

- In CH_4 (methane), carbon undergoes sp^3 hybridization, forming four equivalent bonds oriented tetrahedrally around the central atom.

Limitations of VBT:

1. It does not explain delocalized bonding in molecules like benzene (C_6H_6).
2. It cannot predict the magnetic behavior of O_2 , which is paramagnetic according to experimental observations.
3. It does not consider molecular orbitals that describe delocalized electron distributions.

1.2 Hybridization and Molecular Shapes

Hybridization:

Hybridization is the mixing of atomic orbitals to form new, equivalent hybrid orbitals that explain molecular shapes and bond angles.

Types of Hybridization:

1. sp :
 - Linear geometry with a bond angle of 180° .
 - Example: BeCl_2 .
2. sp^2 :
 - Trigonal planar geometry with a bond angle of 120° .
 - Example: BF_3 .
3. sp^3 :
 - Tetrahedral geometry with a bond angle of 109.5° .
 - Example: CH_4 .
4. sp^3d :
 - Trigonal bipyramidal geometry.
 - Example: PCl_5 .
5. sp^3d^2 :
 - Octahedral geometry.
 - Example: SF_6 .

1.3 Valence Shell Electron Pair Repulsion (VSEPR) Theory

Concept:

The VSEPR theory explains the shapes of molecules by assuming that electron pairs around the central atom (bonding or lone pairs) repel each other and orient themselves to minimize repulsion.

Key Points:

1. Lone pairs repel more strongly than bonding pairs.
2. The geometry depends on the number of bonding and lone pairs.

Examples:

- NH_3 : One lone pair and three bonding pairs result in a trigonal pyramidal shape.
- H_2O : Two lone pairs and two bonding pairs result in a bent shape.

1.4 Molecular Orbital (MO) Theory

Molecular Orbital Theory (MOT) is a quantum mechanical approach to bonding that describes the formation of molecular orbitals from atomic orbitals.

Key Features:

1. Bonding and Anti-Bonding Orbitals:

- When atomic orbitals combine, they form bonding (lower energy) and anti-bonding (higher energy) molecular orbitals.

2. Bond Order:

Bond order determines the strength and stability of the bond:

$$\text{Bond Order} = \frac{\text{Number of bonding electrons} - \text{Number of anti-bonding electrons}}{2}$$

3. Delocalized Electrons:

MOT explains delocalized bonding in molecules like benzene.

Example:

- O_2 : MOT predicts a bond order of 2 and accounts for its paramagnetism due to unpaired electrons in anti-bonding orbitals.

2. Ionic Solids

An ionic bond is formed when there is a complete transfer of electrons from one atom to another, resulting in oppositely charged ions held together by electrostatic forces.

2.1 Structure and Radius Ratio

The arrangement of ions in ionic solids depends on the relative sizes of the cations and anions.

Radius Ratio Rule:

$$\text{Radius Ratio} = \frac{\text{Radius of cation}}{\text{Radius of anion}}$$

The radius ratio determines the coordination number:

- **NaCl:** Coordination number = 6 (octahedral).
 - **CsCl:** Coordination number = 8 (cubic).
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2.2 Lattice Energy and Born-Haber Cycle

Lattice Energy:

The lattice energy is the energy required to completely separate one mole of an ionic solid into its gaseous ions.

Born-Haber Cycle:

A thermodynamic cycle relates lattice energy to ionization energy, electron affinity, and other parameters.

For NaCl:

$$\Delta H = \text{Sublimation energy} + \text{Ionization energy} + \text{Bond dissociation energy} + \text{Electron affinity} - \text{Lattice energy}$$

2.3 Polarization and Fajan's Rule

Polarization:

Polarization refers to the distortion of an anion's electron cloud by a cation.

Fajan's Rule:

Ionic compounds with significant polarization exhibit covalent character.

Factors increasing polarization:

1. High charge and small size of the cation.
2. Large size of the anion.

3. Metallic Bond

A metallic bond is formed by the delocalized "sea of electrons" in a lattice of metal cations.

1. Free Electron Theory

The free electron theory is one of the earliest quantum mechanical models to describe the behavior of electrons in metals. It is based on the idea that valence electrons in a metal are free to move throughout the solid, like a "gas" of electrons.

Assumptions of Free Electron Theory:

1. Electron Behavior:

- The valence electrons in a metal are free to move throughout the crystal lattice, forming a "sea of electrons."
- These electrons are not bound to any particular atom but are delocalized.

2. Metal Lattice:

- The metal ions (cations) are fixed in a regular lattice arrangement, while the electrons move freely around them.

3. No Electron-Electron Interaction:

- Interactions between electrons are ignored; only the interactions with the positively charged lattice are considered.

4. Electrons as a Gas:

- The electrons behave like an ideal gas of particles that follow the principles of classical mechanics (in the simplest version).

5. Electrons Obey Quantum Rules:

- Electrons follow Fermi-Dirac statistics and quantum mechanical laws in the more advanced version (e.g., Sommerfeld model).

Key Features:

1. Electrical Conductivity:

- The free electrons allow metals to conduct electricity. When an electric field is applied, the electrons move in the direction opposite to the field, resulting in current flow.

2. Thermal Conductivity:

- Free electrons also conduct heat by transferring kinetic energy through the lattice.

3. Density of States:

- Not all electron states are available for occupancy. The density of states represents the number of available energy states at a given energy level.

4. Ohm's Law:

- The movement of free electrons explains Ohm's law ($V = IR$) as resistance arises due to scattering of electrons by lattice vibrations (phonons) and impurities.

Limitations of Free Electron Theory:

1. Fails to Explain Bonding:

- It does not describe the bonding between atoms in a metal.

2. Ignores Electron Interaction:

- Interactions between electrons and the periodic lattice potential are not considered.

3. Inability to Predict Band Gaps:

- Cannot explain why some materials are insulators, semiconductors, or metals.

To address these limitations, **Band Theory** was developed.

2. Band Theory

Band theory is a more sophisticated model derived from quantum mechanics that describes the electronic structure of solids, particularly metals, insulators, and semiconductors. It explains the formation of energy bands due to the interaction of atomic orbitals in a crystal lattice.

Formation of Energy Bands:

1. Atomic Orbitals in Isolation:

- In isolated atoms, electrons occupy discrete energy levels.

2. Interaction in a Solid:

- When atoms are brought close together in a solid, their atomic orbitals overlap.
- This overlap leads to the splitting of energy levels into many closely spaced levels, forming **energy bands**.

3. Energy Bands:

- Two main bands form in solids:
 - **Valence Band:** Occupied by valence electrons.
 - **Conduction Band:** Higher energy levels where electrons can move freely.

4. Band Gap:

- The energy difference between the valence band and conduction band is the **band gap** (E_g):
 - **Metals:** No band gap; the conduction band overlaps the valence band.
 - **Semiconductors:** Small band gap (e.g., silicon, $E_g = 1.1 \text{ eV}$).
 - **Insulators:** Large band gap (e.g., diamond, $E_g \approx 5 \text{ eV}$).

Key Features of Band Theory:

1. Conductors, Semiconductors, and Insulators:

- **Metals:**
 - The conduction band is partially filled, allowing electrons to move freely and conduct electricity.
- **Semiconductors:**
 - Electrons can jump from the valence band to the conduction band if provided with sufficient energy (thermal or light).
- **Insulators:**
 - The large band gap prevents electrons from moving to the conduction band, making the material non-conductive.

2. Electron Motion:

- In metals, electrons in the conduction band are free to move under an electric field, resulting in conductivity.

3. Density of States:

- The distribution of available electronic states in the energy bands determines the material's electronic properties.

4. Band Structure:

- The band structure is represented as $E(k)$, where k is the wave vector. It shows how electron energy varies with momentum.
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Applications of Band Theory:

1. Electrical Conductivity:

- Band theory explains why metals are good conductors and insulators do not conduct electricity.

2. Semiconductors:

- The small band gap in semiconductors enables their use in electronic devices like diodes, transistors, and solar cells.

3. **Optical Properties:**

- The absorption and emission of light in materials depend on the band gap.

4. **Magnetic Materials:**

- Band theory helps understand magnetic materials, spintronics, and quantum computing.

Comparison of Free Electron Theory and Band Theory

Feature	Free Electron Theory	Band Theory
Key Concept	Electrons move freely in a "sea" of electrons.	Electrons occupy energy bands formed by atomic orbital overlap.
Electron Interaction	Ignores electron-lattice and electron-electron interactions.	Considers interaction with the periodic potential of the lattice.
Materials Explained	Metals only.	Metals, semiconductors, and insulators.
Mechanism for Conductivity	Based on free movement of electrons.	Based on the presence of partially filled conduction bands.
Band Gap	Not addressed.	Explains the band gap between valence and conduction bands.

Illustrative Examples

1. **Metal (Copper):**

- No band gap; electrons from the valence band easily move into the conduction band, allowing free electron movement.

2. **Semiconductor (Silicon):**

- Small band gap (1.1 eV). At room temperature, thermal energy excites electrons into the conduction band, enabling conductivity.

3. **Insulator (Diamond):**

- Large band gap (> 5 eV). Electrons cannot move into the conduction band under normal conditions, preventing conductivity.

4. Weak Interactions

4.1 Hydrogen Bonding

A hydrogen bond forms when hydrogen is bonded to a highly electronegative atom (N, O, F) and interacts with another electronegative atom.

4.2 Van der Waals Forces

Van der Waals forces include:

1. **Dispersion Forces:** Temporary dipoles induced in atoms/molecules.
 2. **Dipole-Dipole Forces:** Interactions between polar molecules.
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Applications and Practice Problems

1. Predict the geometry of SF_4 using VSEPR theory.
 2. Explain the delocalized bonding in C_6H_6 using MO theory.
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Disclaimer:

These notes are designed as a quick reference and revision tool to help you recall important concepts efficiently. They provide a summary of key topics to aid in understanding and retention.

For a deeper and more thorough understanding, it is strongly recommended to consult standard textbooks, authoritative sources, or seek guidance from subject matter experts.

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Wishing you success in your learning journey!