Chapter 1. Electronic Structure and Covalent Bonding

Learning objectives:

1. Write the ground-state electron configuration.
2. Draw Lewis structure.
3. Use electronegativity to predict polarized and non-polarized bond.
4. Predict the hybridization, bond angles, and geometry of an atom or molecule.
5. Recognize polar and non-polar molecules.
6. Know skeletal structure.
7. Know the property of hydrogen bond.

Content:

1.1 Electron Configuration
1.2 Ionic and Covalent Bonds
1.3 Structure of Molecule
1.4 Atomic Orbitals and Covalent Bonds
1.5 Hybridization and Properties of Molecule
1.6 Hydrogen Bond

1.1 Electron Configuration

A. The structure of an atom

- electron
- neutron
- proton
Proton consists of two up quarks and one down quark.

Neutron consists of two down quarks and one up quark.

**B.** Very small particles have both wave and particle characters
C. Electron Configuration of Atoms

Know the following glossaries:

Atomic number:

Atomic weight (atomic mass)

Isotope:

Atomic orbitals

Know the energy level and number of basic atomic orbitals. (1s, 2s, 2p, 3s and 3p)
Rule of Filing Electrons in Atomic Orbitals (Aufbau principle)

- Each atomic orbital can hold up to two electrons with their spin paired (opposite spin).

- Fill electrons into atomic orbitals in order of increasing energy from lowest to highest.

**Know the shape, relative energy level and number for basic atomic orbitals. (1s, 2s, 2p, 3s and 3p)**

- For orbitals with equivalent energy, fill in one electron to each equivalent orbital before completely filling any one of these equivalent orbitals.
Examples:

H: He:

Li: C:

N: O:

Na: P:

Know the difference between valence and core electrons.

D. Self-assessment Questions

- Do you know the shape, relative energy level and number for basic atomic orbitals (1s, 2s, 2p, 3s and 3p)?
- Do you know how to construct an electron configuration for an atom?
- Do you know the definition of valence orbital and valence electron?
1.2 Ionic and covalent bonds

A. Formation of Ions (Octet rule, Anion and Cation)

Na

Mg

F

B. Formation of Chemical Bond

Ionic bond (charge attraction)

NaCl

Covalent bond (sharing electrons)

CH$_4$

H$_2$

C. Electronegativity and Chemical Bonds

(i) Tendency of electronegativity on periodic table
(ii) Important electronegativity

H: F:

Li: C:

N: O:

(iii) Electronegativity and chemical bonds

Ionic bond

Polar bond

Covalent bond

D. Polarity and Electrostatic potential maps

![Diagram of polar and covalent bonds]
D. Self-assessment Questions

- Can you describe what is octet rule?
- Can you use octet rule to predict the stability of atoms, cations and anions?
- Can you predict the relative electronegativity of atoms based on the positions of those atoms on periodic table?
- Can you describe the general concept for atoms that will form non-polar and polar covalent bonds, and ionic bond?
1.3 Structure of Molecule

A. Lewis Structures of Molecules and Ions

(i) Determine the number of valence electrons

(ii) Know the number of legible (optimal) bonds and lone pair electrons for the commonly seen atoms:

<table>
<thead>
<tr>
<th>Atom</th>
<th>carbon</th>
<th>nitrogen</th>
<th>oxygen</th>
<th>fluorine</th>
</tr>
</thead>
<tbody>
<tr>
<td>No. of bond</td>
<td>4</td>
<td>3</td>
<td>2</td>
<td>1</td>
</tr>
<tr>
<td>No. of LP</td>
<td>0</td>
<td>1</td>
<td>2</td>
<td>3</td>
</tr>
</tbody>
</table>

Possible structure:

- H: \( \cdot \)
- C: \( \cdot \)
- N: \( \cdot \)
- O: \( \cdot \)
- F: \( \cdot \)

(iii) Determine the arrangement of atoms.

Identify the Center Atom(s)

(iv) Show the chemical bond as single line and non-bonding (lone pair) electrons as a pair of Lewis dots.

(v) Use multiple bonds when necessary
double and triple bond
(vi) Pay attention to the octet rule

(vii) Avoid but not exclude O-O, O-X and three membered ring

Examples:

H$_2$O  \hspace{1cm} NH$_3$  \hspace{1cm} CH$_4$

HCl  \hspace{1cm} C$_2$H$_4$  \hspace{1cm} C$_2$H$_2$
B. Formal Charge

(i) Know the number of valence electrons for the commonly seen atoms.

(ii) Know the number of legible (optimal) bonds and the corresponding charge for the commonly seen atoms.

**Quick Guide:**

<table>
<thead>
<tr>
<th>Formal Charge</th>
<th>+1</th>
<th>0</th>
<th>-1</th>
</tr>
</thead>
<tbody>
<tr>
<td>No. of bond</td>
<td>3</td>
<td>4</td>
<td>3</td>
</tr>
<tr>
<td>No. of LP</td>
<td>0</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>Possible structure</td>
<td><img src="image" alt="Possible Structures" /></td>
<td><img src="image" alt="Possible Structures" /></td>
<td><img src="image" alt="Possible Structures" /></td>
</tr>
<tr>
<td></td>
<td>carbocation</td>
<td>carboanion</td>
<td></td>
</tr>
</tbody>
</table>

Carbocations do not meet the octet rule. Carboanion meet the octet rule. Both are unstable in most of the cases.
### Nitrogen: 5 valence e⁻

<table>
<thead>
<tr>
<th>Formal Charge</th>
<th>+1</th>
<th>0</th>
<th>-1</th>
</tr>
</thead>
<tbody>
<tr>
<td>No. of bond</td>
<td>4</td>
<td>3</td>
<td>2</td>
</tr>
<tr>
<td>No. of LP</td>
<td>0</td>
<td>1</td>
<td>2</td>
</tr>
</tbody>
</table>

Possible structure:

- ammonium
- amine
- anionic amine

All these nitrogen atoms meet the octet rule but behave very differently.

### Oxygen: 6 valence e⁻

<table>
<thead>
<tr>
<th>Formal Charge</th>
<th>+1</th>
<th>0</th>
<th>-1</th>
</tr>
</thead>
<tbody>
<tr>
<td>No. of bond</td>
<td>3</td>
<td>2</td>
<td>1</td>
</tr>
<tr>
<td>No. of LP</td>
<td>1</td>
<td>2</td>
<td>3</td>
</tr>
</tbody>
</table>

Possible structure:

- oxonium
- oxo
- oxide

All these oxygen atoms meet the octet rule but behave very differently.

(iii) Arrange atoms according to the guidelines of Lewis structure section.
Examples:

\[ \text{O}_3 \quad \text{HN}_3 \quad \text{HNO}_3 \]

\[ \text{CH}_3\text{O}^- \quad \text{CH}_2\text{N}_2 \quad \text{HCO}_3^- \]

\[ \text{NaHCO}_3 \]
C. Condensed Structures

- Use line to represent chemical bond.
- Lone-pair electron can be omitted.
- Write carbon atom separately.
- Place groups connected to the same carbon to the right.
- Use ( ) for complex or same groups.

Information of atom connectivity is shown.

Examples:

```
H   H   H   H
H—C—C—C—C—H
     H   H   H

H   H   H   H
H—C—C—C—C—H
     H   H   H
       OH

H   H   H   H
H—C—C—C—C—H
     H   H   H
  H—C—H
     H
```
D. Skeletal Structure

- Omit hydrogen atoms attached to carbon.
- Use bent joint to represent carbon.
- Show other atoms and attached hydrogens.

E. Self-assessment Questions

- Can you describe what are the optimal number of chemical bonds and lone pair electrons for carbon, nitrogen and oxygen?
- Can you use octet rule to explain the relationship between the optimal number of chemical bonds and lone pair electrons for carbon, nitrogen and oxygen?
- Can you derive the Lewis structure of a molecule with a given formula?
- Can you calculate the formal charge of an atom in a molecule?
- Can you derive the condensed and skeletal structures of a molecule with a given formula?
1.4 Atomic Orbitals and Covalent Bonds

**P orbitals have different phase.**

A. Formation of Covalent Bond from Overlapping of Atomic Orbital

Overlapping between:

(i) 1s and 1s
(ii) 1s and 2p (head on vs. side way)

(iii) 2p and 2p (head on and side way)

B. $\sigma$ and $\pi$ Bonds
C. Self-assessment Questions

- Can you describe the formation of s bond from overlapping of s and s orbitals, s and p orbitals and p and p orbitals?
- Can you describe the formation of p bond from overlapping of p and p orbitals?
- Can you describe bonding and anti-bonding of s and p bonds?
1.5 Hybridization and Properties of Molecule

*Know the concept of hybridization*

Hybridization provides same number of hybridized orbitals.

Covalent Bonds of Methane (CH$_4$)

A. SP$^3$ hybridization: one S orbital hybridizes with three P orbitals
B. Geometry variation with lone-pair electrons

Examples:

\[ \text{CH}_4 \quad \text{NH}_3 \]

\[ \text{H}_2\text{O} \]
C. SP\(^2\) hybridization: one S orbital hybridizes with two P orbitals

Covalent Bonds in Ethene (CH\(_2\)CH\(_2\))

Molecular Orbitals in Formaldehyde (CH\(_2\)O)
D. SP hybridization: one S orbital hybridizes with one P orbitals

Covalent Bonds in Ethyne (CHCH)

Molecular Orbitals in Hydrogen Cyanide (HCN)
E. Valence Shell Electron Pair Repulsion (VSEPR)

*Know the total number of \( \sigma \) bond(s) and lone-pair electron(s) for the center atom(s)*

(i) Lone-pair electrons will *not* be considered as part of the shape of molecule.

(ii) The total number of \( \sigma \) bond(s) and lone-pair electron(s) for the center atom(s) dictate the arrangement of atoms surrounding the center atom(s) thus shape of molecules around the center atom(s).

<table>
<thead>
<tr>
<th>Total Number</th>
<th>Description of Shape</th>
<th>Predicted Bond Angles</th>
<th>Possible Variation</th>
<th>Hybridization of Center Atom(s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>Linear</td>
<td>180°</td>
<td></td>
<td>SP</td>
</tr>
<tr>
<td>3</td>
<td>Trigonal Planar</td>
<td>120°</td>
<td>Linear-like (two pairs of lone-pair electrons) Bent (planar, one pair of lone-pair electrons)</td>
<td>SP²</td>
</tr>
<tr>
<td>4</td>
<td>Tetrahedral</td>
<td>109.5°</td>
<td>Bent (planar, two pairs of lone-pair electrons) Pyramidal (one pair of lone-pair electrons)</td>
<td>SP³</td>
</tr>
</tbody>
</table>
Examples:
F. Polarity of molecules

*Larger polarity, stronger intermolecular interaction and higher b.p.*

Examples:

(i) \( \text{NH}_3 \)

(ii) \( \text{CO}_2 \)

(iii) \( \text{H}_2\text{O} \)
(iv) CF₄

(v) CHCl₃

G. Self-assessment Questions

- Can you describe SP³, SP², and SP hybridizations, and the information, such as geometry and bond angle associated with these hybridizations?
- Can you use VSEPR theory to predict the hybridization of atoms in a molecule?
- Can you use VSEPR theory to determine the orbital(s) where lone-pair electrons locate?
- Can you determine whether a molecule is polar or non-polar?
1.6 Hydrogen Bond

**Difference in electronegativity**

<table>
<thead>
<tr>
<th>0</th>
<th>Non-polar</th>
<th>0.5</th>
<th>Polar</th>
<th>1.9</th>
<th>Ionic</th>
</tr>
</thead>
</table>

0.9  **H-bond**  1.9

*Hydrogen atoms attached to atoms with high electronegativity.*

\[
\text{N—H} \quad \text{O—H} \quad \text{X—H} \quad \text{S—H}
\]

\[X = \text{F, Cl, Br and I}\]

**Examples:**

- \(\text{NH}_3\)
- \(\text{H}_2\text{O}, \text{CH}_3\text{OH}\)
- \(\text{CH}_3\text{NH}_2\)
- \(\text{CH}_3\text{CO}_2\text{H}\)

A. Properties of Molecules with Hydrogen Bond

*Molecules with hydrogen bond have higher boiling point and solubility in aqueous media.*
van der Waals force \textit{(induced dipole-induced dipole interaction)}

B. Self-assessment Questions

- Can you identify the hydrogen atom that can form hydrogen bond?
- Can you explain the influence of hydrogen bond on the b.p. and the solubility of a molecule?
- Can predict the tendency of b.p. and solubility of molecules?
Homework for Chapter 1 (optional)

Name: A number: