Chapter 2. Molecular structure and bonding

Lewis structures

2.1 The octet rule

Lewis structures: a review

Lewis Theory

3.1 The octet rule

All elements except hydrogen (hydrogen have a duet of electrons) have octet of electrons once they from ions and covalent compounds. The Lewis dot symbols for atoms and ions shows how many electrons are need for a atom to fill the octet. Normally there are octet of electrons on most monatomic ions.

Basic rules drawing Lewis dot symbols:
1. Draw the atomic symbol.
2. Treat each side as a box that can hold up to two electrons.
3. Count the electrons in the valence shell.
Start filling box - don’t make pairs unless you need to.

**Lewis symbols of second period elements**

Elements try to complete their valence shell to achieve noble-gas electron configurations. The stability of noble/inert gases must be due to their filled valence shell. Elements either loose/gain or share electrons for this purpose. Electron transfer is associated with the formation of ionic compounds. Covalent compounds are formed when electrons are shared between atoms.

A **Lewis symbol** is a symbol in which the electrons in the valence shell of an atom or simple ion are represented by dots placed around the letter symbol of the element. Each dot represents one electron.

- **Hydrogen**
  \[ 1s^1 \quad \text{H}\cdot \]

- **Oxygen**
  \[ 1s^2 \ 2s^2 \ 2p^4 \quad \cdot \cdot \]

- **Chlorine**
  \[ 1s^2 \ 2s^2 \ 2p^6 \ 3s^2 \ 3p^5 \quad :\text{Cl}\cdot \]

- **Chloride ion**
  \[ 1s^2 \ 2s^2 \ 2p^6 \ 3s^2 \ 3p^6 \quad :\text{Cl}^\cdot \]

A **covalent bond** is a chemical bond formed by the sharing of a pair of electrons between two atoms.

The **Lewis structure** of a covalent compound or polyatomic ion shows how the valence electrons are arranged among the atoms in the molecule to show the connectivity of the atoms.
Instead of using two dots to indicate the two electrons that comprise the covalent bond, a line is substituted for the two dots that represent the two electrons.

Below is shown the Lewis structure for water. Two hydrogens (H) are separately covalently bonded to the central oxygen (O) atom. The bonding electrons are indicated by the dashes between the oxygen (O) and each hydrogen (H) and the other two pairs of electrons that constitute oxygens octet, are called non-bonding electrons as they are not involved in a covalent bond.

H₂S has the same Lewis Structure as H₂O since S is in the same group as O.

As a rule if an elements from the period 2 is replaced by another element from the period 3 and same group in the periodic table they will have same lewis structure.

**Drawing Lewis Structures**

**Rules for getting Lewis Structures**

1. Determine whether the compound is covalent or ionic. If covalent, treat the entire molecule. If ionic, treat each ion separately. Compounds of low electronegativity metals with high electronegativity nonmetals (ΔEN 1.6) are ionic as are compounds of metals with polyatomic anions. For a monoatomic ion, the electronic configuration of the ion represents the correct Lewis structure. For compounds containing complex ions, you must learn to recognize the formulas of cations and anions.
2. Determine the total number of valence electrons available to the molecule or ion by:
   (a) summing the valence electrons of all the atoms in the unit and
   (b) adding one electron for each net negative charge or subtracting one electron for each net positive charge. Then divide the total number of available electrons by 2 to obtain the number of electron pairs (E.P.) available.

3. Organize the atoms so there is a central atom (usually the least electronegative) surrounded by ligand (outer) atoms. Hydrogen is never the central atom.

4. Determine a provisional electron distribution by arranging the electron pairs (E.P.) in the following manner until all available pairs have been distributed:
   a) One pair between the central atom and each ligand atom.
   b) Three more pairs on each outer atom (except hydrogen, which has no additional pairs), yielding 4 E.P. (i.e., an octet) around each ligand atom when the bonding pair is included in the count.
   c) Remaining electron pairs (if any) on the central atom.

**Types of Electrons Pairs**

- **Bond pair:** electron pair shared between two atoms.
- **Lone pair:** electron pair found on a single atom.

**Molecules obeying the octet rule.**

In many molecules, each atom (except hydrogen) is surrounded by eight bonding or lone-pair electrons. There is a special stability associated with this configuration. Examples are water, ammonia and methane.

- **Nitrogen (g.s.)**
  
  ![Lewis Structure of Nitrogen](image)

  The ground state (g.s.) configuration of N has three unpaired electrons. Each hydrogen atom has one. No rearrangement is necessary to make the three N-H bonds. Be sure to mark the lone pair on the Lewis diagram.

- **Carbon (g.s.)**

  ![Lewis Structure of Carbon](image)

  The ground state of carbon has only two unpaired electrons, but it is necessary to make four bonds to the hydrogens. The solution, in this case, is to promote a 2s electron to the empty p orbital. Then four bonds can be made. SiH₄ has the same Lewis Structure as CH₄ since Si and C are in the same group.

- **Lewis structure of CCl₄**

  ![Lewis Structure of CCl₄](image)
Lewis Structure of $\text{CCl}_4$,

- Valence electrons: $4 + 28 = 32 = 16$ electron pairs
- Central atom
- Octet on C is already complete
- Count electrons
  - $4 \times 3$ lone pairs = 12 pairs
  - $4 \times 4$ bond pairs = 4 pairs
  - 16 electron pairs

Lewis Structure of $\text{PCl}_3$,

- Valence electrons: $5 + 3 \times 7 = 26 = 13$ pairs
- Central atom
- Connect to terminal atoms to central atom
- Give octet to P and give octets to Cl
- Count electron pairs:
  - 3 bond pairs = 3 pairs
  - $1 + 3 \times 3 = 10$ lone pairs = 10 pairs
  - 13 pairs

1. Connect the central atom to the other atoms in the molecule with single bonds.

Carbon is the central atom, the two oxygens are bound to it and electrons are added to fulfill the octets of the outer atoms.
2. Complete the valence shell of the outer atoms in the molecule.

\[ \text{\( \cdot\cdot\cdot C\cdot\cdot\cdot \)} \]

3. Place any remaining electrons on the central atom.

There are no more electrons available in this example.

4. If the valence shell of the central atom is complete, you have drawn an acceptable Lewis structure.

Carbon is electron deficient - it only has four electrons around it. This is not an acceptable Lewis structure.

5. If the valence shell of the central atom is not complete, use a lone pair on one of the outer atoms to form a double bond between that outer atom and the central atom. Continue this process of making multiple bonds between the outer atoms and the central atom until the valence shell of the central atom is complete.

The best Lewis structure that can be drawn for carbon dioxide is: \[ \text{\( \cdot\cdot\cdot C\cdot\cdot\cdot \)} \]

**Lewis Structure of nitrosyl chloride NOCl**

Setting up the bonding in this molecule is straight forward. Note the lone pairs, especially the one on the nitrogen.

Neutral nitrogen has 3 unpaired electrons, while one negatively charged oxygen and two neutral ones would have 5 unpaired electrons between them. You must move one electron from nitrogen to a neutral oxygen to get the configurations shown. Notice the formal charges marked where they belong on the Lewis structure.
**Bond Order and Bond Length**

The **bond order** is equal to the number of bonds between two atoms.

\[
\text{Bond Order (BO)} = \text{# bonds between two atoms}
\]

\[
\begin{align*}
\text{BO} &= 1 \quad \text{BO} = 2 \quad \text{BO} = 3 \\
\end{align*}
\]

The **bond length** is the distance between those two atoms. The greater the number of electrons between two atoms, the closer the atoms can be brought towards one another, and the shorter the bond.

The BO is an indication of the bond length, the greater the bond order, the shorter the bond.

\[
\begin{align*}
\text{BO} &= 1 \quad \text{BO} = 2 \quad \text{BO} = 3 \\
\end{align*}
\]

**Formal charge**

Formal charge is an accounting procedure. It allows chemists to determine the location of charge in a molecule as well as compare how good a Lewis structure might be. The formula for calculating formal charge is shown below:

\[
\text{Formal Charge} = \# \text{ valence } \varepsilon - (\# \text{ non-bonding } \varepsilon + 1/2 \# \text{ bonding } \varepsilon)
\]

Consider the molecule \(\text{H}_2\text{CO}_2\). There are two possible Lewis structures for this molecule. Each has the same number of bonds. We can determine which is better by determining which has the least formal charge. It takes energy to get a separation of charge in the molecule (as indicated by the formal charge) so the structure with the least formal charge should be lower in energy and thereby be the better Lewis structure. There are two possible Lewis structures for this molecule. Each has the same number of bonds. We can determine which is better by determining which has the least formal charge. It takes energy to get a separation of charge in the molecule (as indicated by the formal charge) so the structure with the least formal charge should be lower in energy and thereby be the better Lewis structure. The two possible Lewis structures are shown below. They are connected by a double headed arrow and placed in brackets. The non-zero formal charge on any atoms in the molecule have been written near the atom.
Electron deficient molecules: atoms have less than octet of electrons

Do not have enough electrons to satisfy the octet rule. Simple examples are beryllium hydride and boron trichloride:

**Lewis Structure of BeCl₂**

Beryllium, an element of the second column of the periodic classification, has for electronical configuration: \([\text{He}] \, 2s^2\). It has two single bonds with two atoms in BeCl₂.

Berillium do not have a octet, therefore, BeCl₂ is an electron deficient compound. Be has only four electrons. BeCl₂ violate octet rule.

**Lewis Structure of BCl₃**

The boron must be in a suitable valence state to bind to the three chlorines. In the molecule the boron is associated with only six electrons. Much of the chemistry of this molecule and ones like it is connected with the resulting strong electrophilic nature. Other examples include the boron
hydrides such as diborane and alkyl-lithium, beryllium and aluminum compounds, which will be described later.

**Lewis Structure of BF₃**

Fill octet to fluorene first

\[
\begin{array}{c}
F - B - F \\
\end{array} \quad \rightarrow \quad \begin{array}{c}
\text{F} \\
\text{F}
\end{array}
\]

- **F** is the most electronegative

i) Count total valence electrons: \(3 + 3 \times 7 = 24\) (12 electron pairs)
ii) Central atom is **B**
iii) Connect central atom terminal atoms:
iv) 3 bonds pairs on **B**.
   - 3 lone pairs on **F**
   - \(3 + 3 \times 3 = 12\) pairs

Boron do not have a octet, therfore, BF₃ is an electron deficient compound. BF₃ violates octet rule.

**Lewis Structure of BH₃**

Similarly BH₃ has the Lewis Structure:

- B has on 3 electron pairs. BH₃ violates octet rule. It exists as diborane B₂H₆

**Lewis Structure of AlCl₃**

Similarly AlCl₃ has the Lewis Structure:
Al has only 3 electron pairs. AlCl$_3$ also violates octet rule and exists as a dimer Al$_2$Cl$_6$.

**Atoms having odd numbers of electrons.**

**Example, nitrogen dioxide NO$_2$**

Total of 17 valence electrons are present.
24 electrons would be needed to satisfy the valencies independently.

$24 - 17 = 7$. The odd number of electrons is a signal that there will be a place where we would normally expect to find another electron. When you have some experience with these situations, you probably will have no problem in assigning the Lewis structure directly. If this is a problem for you, the easiest way to treat these is to assume that we have one extra valence electron to begin with and remove that electron at the end. In this case, it means drawing the Lewis diagram for NO$_2^-$. For NO$_2^-$ the answer to question 1 is 18 valence electrons and the answer to 3 become 6 electrons, or 3 bonds.

We draw one N-O single bond and one N=O double bond in order to achieve the correct number of bonds.

For NO$_2^-$ there will be 12 electrons left to make into nonbonding pairs that can be assigned as shown in the picture below. This will give octets at each atom. To derive the Lewis structure for NO$_2$, the neutral molecule, we must then remove one electron from NO$_2^-$. The choice preferred is to remove the electron from the lone pair that resides on the least electronegative atom. Since N is less electronegative than O, we will take the electron from the N lone pair.

The Lewis diagram for NO$_2$ is consistent with its reaction chemistry. NO$_2$ undergoes a dimerization (two molecules joining to form one) which gives N$_2$O$_4$. The structure of N$_2$O$_4$ is simple two NO$_2$ molecules joined to form an N-N bond by pairing the odd electrons.

**Molecules with expanded valence shells: Hypervalent compounds** occur for central atoms beyond period 2. Such atoms often have more than their octet. Examples are phosphorus trichloride, chlorine trifluoride and xenon difluoride:
Chlorine in its ground state has only one unpaired electron. In order to form the three required bonds, valence bond theory requires the promotion of an electron to an empty d-orbital to form the valence state shown. While it is customary to invoke a valence state using some d-orbitals to rationalize the bonding there is an alternative approach which is best described using molecular orbital theory.

**Lewis Structure of SF$_6$**

i) Count total valence electrons: $6 + 6 \times 7 = 48$ (24 pairs)

ii) S is the central atom:
sulfur already have excess of 4 electrons to octet

iii) fill octet to Fs

iv) count electrons:

$$S - 6 \text{ bond pairs} = 6$$

$$6F - 3 \times 6 \text{ lone pairs} = 18$$

$$24 \text{ pairs}$$

Sulfur violates octet rule, is an exception to octet rule having more than eight electrons on S. S has 12 electrons.

**Lewis Structure of PCl$_5$**

i) Count the total valence electrons: $5 + 5 \times 7 = 40$ (20 pairs)

ii) P is central atom:

iii) P already have 5 electron pairs then give octets to Cls

iv) count electron pairs.

$$5 \text{ pairs on P} = 5$$

$$5 \times 3 \text{ pairs on Cl} = 15$$

$$20 \text{ electron pairs}$$
AsCl₅ have similar structure. PCl₅ and AsCl₅ violates octet rule having 10 electrons on P and As.

**Resonance Structures**

There are a number of compounds and polyatomic ions that cannot be written using one single structure. This was known even back to the early beginnings of structural chemistry in the mid-1850s. These substances must be described in terms of "intermediate" structures, possessing non-integral bonds such as one and one-half bonds or one and one-third bonds.

For example, certain molecules it is necessary to draw several Lewis structures (resonance structures) to adequately describe the structures of the molecules: Examples are CO₃²⁻, NO₃⁻, NO₂⁻.

**Resonance Lewis Structures of CO₃²⁻:**

i) valence electrons: 4 + 3 x 6 + 2(negative charge) = 24 (12 pairs)

ii) central atom is carbon

![Resonance Lewis Structures of CO₃²⁻](image)

iii) fill octet to C; fill octet to O

One oxygen does not have an octet. Share lone pair on C with the oxygens. The double bond could be on any other oxygen atoms.

\[
\begin{align*}
\text{[O=C=O]}^2- & \quad \leftrightarrow \quad \text{[O=C=O]}^2- \\
\text{[O=C=O]}^2- & \quad \leftrightarrow \quad \text{[O=C=O]}^2-
\end{align*}
\]

Therefore, there are three resonance structures for CO₃²⁻ ion

**Resonance Lewis Structures of NO₃⁻:**

i) valence electrons:

\[
5 + 3 \times 6 + 1(\text{negative charge}) = 24 (12 \text{ pairs})
\]

iii) N is the central atom:
iii) Fill octet to N; Fill octet to O

one oxygen has only 6 electrons
share lone pair on N with the oxygen
The double bond could be on any other oxygen atoms. Therefore, there are three resonance structures for the NO$_3^-$ ion.

$$\begin{align*}
\text{Resonance Lewis Structure of NO}_3^- \\
i) \text{valence electrons:} & \quad 5 + 2 \times 6 + 1(\text{negative charge}) = 18 \, (9 \text{ pairs}) \\
ii) \text{central atom is nitrogen.} \\
iii) \text{Fill octet to N; Fill octet to O} \\
one oxygen has only six electrons \\
share lone pair on N with oxygen.
\end{align*}$$

The double bond could be on any of the two oxygen atoms. Therefore, there are two resonance structures for NO$_2^-$ ion.

$$\begin{align*}
\text{Resonance Lewis Structure of NO}_2^- \\
&\quad \begin{array}{c}
\text{O–N–O} \rightarrow \text{[O–N=O]}^-
\end{array}
\end{align*}$$

Resonance Lewis Structure of PO$_4^{3-}$

$$\begin{align*}
\text{O}^{-} \text{P}^{-} \text{O}^{-} & \leftrightarrow \text{O}^{-} \text{P}=\text{O}^{-} & \leftrightarrow & \text{O}^{-} \text{P}^{-} \text{O}^{-} & \leftrightarrow & \text{O}=\text{P}^{-} \text{O}^{-} \\
\text{O}^{-} & & & \text{O}^{-} & \text{B. O.} = 5/4
\end{align*}$$
Resonance structures of Benzene Ring
Any compound with the benzene ring is an aromatic compound. Since the benzene ring looks very much like a triene (alkene with three double bonds), it should be expected that its properties would be like one, but it is not. It does not undergo the addition reactions that alkenes do, and it is unusually stable to oxidizing agents. The reason why is because the benzene ring is a resonance structure. When one Lewis Structure fails to explain the bonding and properties of molecule have to draw more structures.

[Diagram of resonance structures of benzene]

2.2 Structure and bond properties

2.3 The VSEPR model
Valence-bond theory
2.4 The hydrogen molecule
2.5 Homonuclear diatomic molecules
2.6 Polyatomic molecules
Molecular orbital theory
2.7 An introduction to the theory
2.8 Homonuclear diatomic molecules
2.9 Heteronuclear diatomic molecules
2.10 Bond properties

Chapter 2. Molecular Structure and Bonding

3.2 Structure and bond properties
3.3 The VSEPR model
Valence Shell Electron Pair Repulsion is a simple but effective model for predicting molecular geometry. VSEPR assumes a molecule adopts the geometry that minimizes the repulsive force among a given number of electron pairs.

**Applying VSEPR**

Draw the Lewis structure of the molecule.

Count the number of electron pairs around the central atom. Multiple bonds count as one electron pair.

The arrangement of electron pairs that minimizes repulsion is called the electron-pair geometry. The arrangement of atoms is called the molecular geometry.

**Electron-Pair Geometries**

**Basic Geometry.** Once a Lewis structure of a molecule has been constructed, a basic geometry can be inferred for each non-terminal atom in a molecule by counting the number of objects surrounding it. An "object" is a lone-pair or a bonded atom (regardless of the bond order - single, double, triple or fractional).

<table>
<thead>
<tr>
<th>Objects</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Geometry</strong></td>
<td>Linear</td>
<td>Trigonal planar</td>
<td>Tetrahedral</td>
<td>Trigonal bipyramid</td>
<td>Octahedral</td>
<td>Pentagonal bipyramid</td>
</tr>
</tbody>
</table>
Refinements to molecular geometry. The details of the predicted geometry can be further refined by considering what the objects are more carefully. Is another atom bound by a single bond or higher bond order? Is the bond polar? What about the difference between a lone pair and a bond pair? The table below shows how these questions and others can be answered.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Lewis Structure</th>
<th>EP Geometry</th>
<th>Bond Angle</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂</td>
<td>O=C=O</td>
<td>2 - Linear</td>
<td>180°</td>
</tr>
<tr>
<td>SO₂</td>
<td>O=S=O</td>
<td>3 - Trigonal Planar</td>
<td>120°</td>
</tr>
<tr>
<td>CO₃²⁻</td>
<td>O=C-O-</td>
<td>3 - Trigonal Planar</td>
<td>120°</td>
</tr>
<tr>
<td>CH₄</td>
<td>H-C-H</td>
<td>4 - Tetrahedral</td>
<td>109.5°</td>
</tr>
<tr>
<td>NH₃</td>
<td>H-N-H</td>
<td>4 - Tetrahedral</td>
<td>109.5°</td>
</tr>
<tr>
<td>SF₆</td>
<td>S-F</td>
<td>5 - Trigonal Biplanar</td>
<td>90°, 120°</td>
</tr>
<tr>
<td>XeF₄</td>
<td>Xe-F</td>
<td>6 - Octahedral</td>
<td>90°</td>
</tr>
<tr>
<td>Multiple or shorter bonds or bonds polarized towards the centre atom</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>---------------------------------------------------------------</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Medium Repulsion</strong></td>
<td>Normal single bonds</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Smallest Repulsion</strong></td>
<td>Longer single bonds and bonds polarized away from the central atom</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Polarity of Molecules**

The "charge distribution" of a molecule is determined by
- The shape of the molecule
- The polarity of its bonds

A **Polar** Molecule:

- The center of the overall negative charge on the molecule does not coincide with the center of overall positive charge on the molecule
- The molecule can be oriented such that one end has a net negative charge and the other a net positive charge, i.e. the molecule is a **dipole**

A **Nonpolar** molecule

- Has no charges on the opposite ends of the molecule
- Or, has charges of the **same sign** on the opposite ends of the molecule
- Molecule is **not** a dipole

*Any diatomic molecule with a polar bond is a polar molecule (dipole)*

\[ \text{H - F} \]

Polar molecules align themselves:

- in an electric field
- with respect to one another
- with respect to ions
The degree of polarity of a molecule is described by its *dipole moment*, \( \mu = Q \times r \)

where

- \( Q \) equals the charge on either end of the dipole
- \( r \) is the distance between the charges

*the greater the distance or the higher the charge, the greater the magnitude of the dipole*

Dipole moments are generally reported in **Debye** units

\[
1 \text{ debye} = 3.33 \times 10^{-30} \text{ coulomb meters (C m)}
\]

Example: H-Cl a **covalent polar** compound

- The H-Cl bond distance is 1.27Å
- +1 and -1 charges in a dipole produce 1.60 \( \times \) 10\(^{-19} \) C

\[
\mu = Qr = (1.60 \times 10^{-19} \text{ C})(1.27 \times 10^{-10} \text{ m})
\]
\[
\mu = 2.03 \times 10^{-29} \text{ C m}
\]
\[
\mu = 2.03 \times 10^{-29} \text{ C m} \text{ (1 debye/3.33 x 10^{-30}) = 6.10 debye}
\]

The actual dipole of H-Cl is **1.08 debye**. The reason for this is that the compound is covalent and not ionic, thus the charges of the dipole are less that +1, and -1 (values expected for a fully ionic compound)

<table>
<thead>
<tr>
<th>Compound</th>
<th>Bond Length (Å)</th>
<th>Electronegativity Difference</th>
<th>Dipole Moment (D)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HF</td>
<td>0.92</td>
<td>1.9</td>
<td>1.82</td>
</tr>
<tr>
<td>HCl</td>
<td>1.27</td>
<td>0.9</td>
<td>1.08</td>
</tr>
<tr>
<td>HBr</td>
<td>1.41</td>
<td>0.7</td>
<td>0.82</td>
</tr>
<tr>
<td>HI</td>
<td>1.61</td>
<td>0.4</td>
<td>0.44</td>
</tr>
</tbody>
</table>
Although the bond length is increasing, the dipole is decreasing as you move down the halogen group. The electronegativity decreases as we move down the group. Thus, the greater influence is the electronegativity of the two atoms (which influences the charge at the ends of the dipole).

**The Polarity of Polyatomic Molecules**

- Each polar bond in a polyatomic molecule will have an associated dipole
- The overall dipole of the molecule will be the sum of the individual dipoles

**Dipoles**

![Dipoles](image)

**Overall Dipole:** (none)

- Although in carbon dioxide the oxygens have a partial negative charge and the carbon a partial positive charge, the molecule has no dipole - it will not orient in an electrical field
- Water has a dipole and will orient in an electrical field

*Although a polar bond is a prerequisite for a molecule to have a dipole, not all molecules with polar bonds exhibit dipoles*

**ABn molecules and non-polar geometries**

For AB$_n$ molecules, where the central atom A is surrounded by identical atoms for B, there are certain molecular geometries which result in no effective dipole, regardless of how polar the individual bonds may be. These geometries are: