Chapter 10-11  The Shapes of Molecules; Theories of Covalent Bonding

Depicting Molecules & Ions with Lewis Structures

Steps for drawing Lewis structures

1. *Sum the valence electrons from all atoms.* For anions, add one electron for each negative charge. For cations, subtract one electron for each positive charge.

2. *Write the symbols for the atoms to show which are connected to which. Connect the atoms with single bonds.* The least electronegative element is usually the central atom. This means that in general, the atom with the lower group number is the central atom. If all atoms are in the same group, the atom lower in the group is the central atom.

3. *For each bond in the skeletal structure from step 1, subtract 2 electrons from the total.*

4. *Complete octets of atoms bonded to the central atom.* Exception: H only can have 2 electrons.

5. *Place any leftover electrons on the central atom,* even if doing so results in the central atom having more than an octet.

6. *If there are not enough electrons to give all atoms octets, start using multiple bonds.*

Examples

- **Draw the Lewis structure for sulfur tetrafluoride, SF₄.**
  1. 1(S) + 4(F) = 1(6) + 4(7) = 34 valence electrons
  2. F S F
  4. F S F (32 e⁻)
  5. F S F (34 e⁻)

- **Draw the Lewis structure for carbon dioxide, CO₂.**
  1. 1(C) + 2(O) = 1(4) + 2(6) = 16 valence electrons
  2. O=C=O
  4. O=C=O
  5. no extra electrons to put on C.
  6. O=C=O (16 e⁻)

- **Draw the Lewis structure for nitrogen triiodide, NI₃.**
Resonance Structures

- Equivalent Lewis structures that differ in the placement of the same number/types of bonds.

- **Draw the Lewis structure for sulfur dioxide, SO₂.**
  1. \(1(S) + 2(O) = 1(6) + 2(6) = 18 \) valence electrons
  2. \( \text{O} \equiv \text{S} \equiv \text{O} \)
  4. \( \text{O} = \equiv \text{S} = \equiv \text{O} \) (16 electrons used)
  5. \( \text{O} \equiv \equiv \text{S} \equiv \equiv \text{O} \) (all 18 electrons used up)
  6. \( \text{O} = \equiv \equiv \text{S} = \equiv \equiv \text{O} \leftrightarrow \text{O} \equiv \equiv \text{S} \equiv \equiv \text{O} \) (two resonance structures of SO₂)

The S-O bond order would be \( \frac{3 \text{ electron pairs}}{2 \text{ atom-to-atom linkages}} = \frac{3}{2} = 1 \frac{1}{2} \)

Finding the “Best” Structure When There Is a Real Choice

- **Draw the Lewis structure for thiocyanate ion, SCN⁻.**
  1. \(1(S) + 1(C) + 1(N) + 1(-1 \text{ charge}) = 6 + 4 + 5 + 1 = 16 \) valence electrons
  2. \( \text{S} \equiv \text{C} \equiv \text{N} \)

...6. \[
\begin{array}{c}
\text{S} \equiv \text{C} \equiv \text{N} \equiv \\
\text{S} \equiv \text{C} \equiv \text{N} \equiv \\
\text{S} \equiv \text{C} \equiv \text{N} \equiv \\
\end{array}
\]

Which Lewis structure of SCN⁻ to choose? Calculate formal charge on each atom in each structure.

**Formal Charge**

Rules for calculating formal charge:
1. All unshared electrons on an atom are assigned to the atom on which they are found.
2. Half of the bonding electrons are assigned to each atom in a bond.
3. \( FC = (\text{number of valence e}^- \text{ in isolated atom}) - (\text{e}^- \text{ assigned}) \)

The preferred (major) Lewis structure will have (1) the smallest magnitude FCs and (2) any negative FCs on atoms with higher electronegativities. Therefore:

\[
\begin{array}{c}
\text{S} \equiv \text{C} \equiv \text{N} \equiv \\
\text{S} \equiv \text{C} \equiv \text{N} \equiv \\
\text{S} \equiv \text{C} \equiv \text{N} \equiv \\
\end{array}
\]

Formal Charge \( +1 \ 0 \ -2 \)
\( 0 \ 0 \ -1 \)
\( -1 \ 0 \ 0 \)

The middle Lewis structure has the smallest FCs and places the negative FC on nitrogen, which is the most electronegative atom of the three. Therefore, the center structure (S=C=N⁻) is preferred if we must pick only one. It is the major contributor to the structure. The right-hand structure is a minor contributor.
Exceptions to the Octet Rule

1. **Odd Number of Electrons**: “free radicals”
   e.g., ClO₂

2. **Electron-Deficient Molecules** (primarily B, Be central atoms)
   e.g., BeF₂(g)  e.g., BF₃

3. **Expanded Valence Shells**
   Seeming use of empty valence d orbitals in addition to s and p orbitals
VSEPR Model & Molecular Shape

Electron pairs are negatively charged and repel each other. The most stable arrangement of electron pairs around an atom will minimize the repulsive forces.

Electron-Group Arrangements (Figure 10.2)

- bond angle: angle formed by nuclei of bonded atoms and nucleus of central atom

Summary of Molecular Shapes (Figure 10.10)

The first three (linear, trigonal planar, tetrahedral group geometries) are most important in organic chemistry.
<table>
<thead>
<tr>
<th>Number of Atoms*</th>
<th>Shape</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>linear A—B</td>
</tr>
<tr>
<td></td>
<td>linear C—A—B</td>
</tr>
<tr>
<td>3</td>
<td>bent</td>
</tr>
<tr>
<td></td>
<td>[B—\overline{A}C] or [B—\overline{A}C]</td>
</tr>
<tr>
<td>4</td>
<td>trigonal planar B—A—C</td>
</tr>
<tr>
<td></td>
<td>trigonal pyramidal B—A—C</td>
</tr>
<tr>
<td></td>
<td>T-shaped</td>
</tr>
<tr>
<td>5</td>
<td>tetrahedral</td>
</tr>
<tr>
<td></td>
<td>square planar</td>
</tr>
<tr>
<td></td>
<td>seesaw</td>
</tr>
<tr>
<td>6</td>
<td>trigonal bipyramidal B—A—C—D</td>
</tr>
<tr>
<td></td>
<td>square pyramidal B—A—C—D</td>
</tr>
<tr>
<td>7</td>
<td>octahedral</td>
</tr>
</tbody>
</table>

*including central atom
Molecular Polarity
Both molecular shape and bond polarity determine if a molecule is polar overall. The dipole moment is a quantitative measurement of the amount of polarity of a molecule. For our purposes, we will only worry about whether a molecule has a NET dipole moment of 0 or not.
- A molecule with a net zero dipole moment is said to be a nonpolar molecule.
- A molecule with a net nonzero dipole moment is said to be a polar molecule.

- If a central atom has the same two atoms bonded to it in a linear geometry, the molecule is nonpolar.
- If a central atom has no lone pairs and only identical atoms bonded to it, the molecule is nonpolar.
- Other nonpolar molecules do exist; this results from like atoms “canceling out” each other’s bond polarities.

Valence Bond Theory & Orbital Hybridization
In bond formation, two orbitals overlap and are occupied by a pair of electrons. Valence orbitals in bonded atoms are different than those in isolated atoms.
Mathematical mixing of quantum mechanical atomic orbitals → Hybrid Orbitals
[SAME NUMBER of hybrid orbitals out as atomic orbitals in]

Types of Hybrid Orbitals & Relationship to Molecular Geometry (Table 11.1)

<table>
<thead>
<tr>
<th>Hybridization</th>
<th>Orientation of hybrid orbitals</th>
<th>Number of ( \sigma ) bonds</th>
<th>Molecular geometries</th>
<th>Theoretical angles between hybrid orbitals</th>
</tr>
</thead>
<tbody>
<tr>
<td>( sp )</td>
<td><img src="image.png" alt="Image" /></td>
<td>2</td>
<td>Linear</td>
<td>180°</td>
</tr>
<tr>
<td>( sp^2 )</td>
<td><img src="image.png" alt="Image" /></td>
<td>3</td>
<td>Trigonal planar</td>
<td>120°</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2</td>
<td>Bent</td>
<td></td>
</tr>
<tr>
<td>( sp^3 )</td>
<td><img src="image.png" alt="Image" /></td>
<td>4</td>
<td>Tetrahedral</td>
<td>109.5°</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3</td>
<td>Trigonal pyramidal</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>2</td>
<td>Bent</td>
<td></td>
</tr>
</tbody>
</table>
Hybrid Orbitals and Multiple Bonds

Two pairs of orbitals overlapping between the same two atoms = double bond (BO = 2)
Three pairs of orbitals overlapping between the same two atoms = triple bond (BO = 3)

- sigma (σ) bond: results from end-to-end overlap of orbitals.
- pi (π) bond: results from side-to-side overlap of orbitals.

Figure 11.11, orbital overlap in ethylene, C₂H₄.

In general:

A double bond consists of one sigma bond and one pi bond.
A triple bond consists of one sigma bond and two pi bonds.

Side-to-side overlap is not as extensive as end-to-end overlap, so pi bonds are generally not as strong as sigma bonds between the same atoms.
Sigma bonds allow free rotation about the bond axis. The extent of overlap is not affected by such rotation.

Pi bonds restrict rotation about the bond because rotation about the bond would require breaking the pi bond overlap. The result is that double-bonded molecules exhibit different structures depending on the orientation of other parts of the molecule with respect to the double bond.

- isomers: molecules with the same formula but different structures

Figure 11.14, two isomers of C₂H₂Cl₂ (of three possible)
Molecular Orbitals

VSEPR and valence-bond theory with hybrid orbitals do not explain all observed properties of molecules. In the molecular orbital model, electrons are delocalized over entire molecules. The simplest approach to MOs is to use linear combinations of atomic orbitals (LCAO-MO).

(a) One-dimensional standing wave

Energy

$1s + 1s \rightarrow \sigma_{1s}$

(b) Atomic orbitals add to make bonding orbital

Energy

$1s - 1s \rightarrow \sigma^*_{1s}$

(c) Atomic orbitals subtract to make antibonding orbital

✓ Figures 11.15-11.16, Standing wave and Linear combinations of 1s atomic orbitals

<table>
<thead>
<tr>
<th>BONDING MO</th>
<th>has more electron density between nuclei</th>
</tr>
</thead>
<tbody>
<tr>
<td>ANTIBONDING* MO</td>
<td>has less electron density between nuclei</td>
</tr>
</tbody>
</table>

✓ Figure 11.20, Linear combinations of 2p atomic orbitals
σ MO is cylindrically symmetrical (i.e., can rotate any amount about bond axis)
π MO is not cylindrically symmetrical but does have plane of symmetry

Just as for atomic orbitals, we can draw orbital diagrams to show the occupancy of MOs in molecules.
We still follow the aufbau principle, the exclusion principle, and Hund’s rule. Still a limit of two electrons with opposite spins per orbital.

\[
\text{BOND ORDER} = \frac{1}{2} [\text{number of bonding } e^- - \text{number of antibonding } e^-]
\]

**MO Treatment of Homonuclear Diatomic Molecules**

**Figure 11.17, MOs in H₂.**

- H₂ bond order = \(\frac{1}{2}(2 - 0) = 1\)
- √ Figure 11.18, MOs in He₂ and He₂⁺.

<table>
<thead>
<tr>
<th>Bond order</th>
<th>Magnetic properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Diamagnetic</td>
</tr>
<tr>
<td>0</td>
<td>Nonexistent</td>
</tr>
<tr>
<td>1</td>
<td>Paramagnetic</td>
</tr>
<tr>
<td>2</td>
<td>Diamagnetic</td>
</tr>
<tr>
<td>3</td>
<td>Diamagnetic</td>
</tr>
<tr>
<td>2</td>
<td>Paramagnetic</td>
</tr>
<tr>
<td>1</td>
<td>Diamagnetic</td>
</tr>
<tr>
<td>0</td>
<td>Nonexistent</td>
</tr>
</tbody>
</table>

**Figure 11.22, MO occupancy in Li₂ through Ne₂.**
MO Treatment of Heteronuclear Diatomic Molecules
- asymmetric MO diagram (unequal AO energies)
- more electronegative atoms have lower AO energies

✓ MO diagram of NO (Figure 11.23B)
- Lewis structure of NO shows a double bond, but experimental bond energy and length consistent with higher bond order
- Note that bonding MOs are closer in energy to oxygen’s AOs since O is the more electronegative atom

Delocalization of Electrons
Molecules such as benzene and ozone were difficult to picture using Lewis structures since resonance structures were required. (Alternating single and double bonds)

MO theory treats such molecules much more elegantly through being able to “spread out” or delocalize electron density over several atom-to-atom connections.

✓ Figure 11.24, Lowest-energy \( \pi \) bonding MOs in benzene and ozone.
MO Treatment of Metallic Bonding (Fig. 12.37)