Lewis Structures and Bonding: A Review

Organic chemistry would still be alchemy without Lewis structures! Understanding how atoms are connected is the foundation for functional groups and their reactivity. In addition, knowing the 3-dimensional molecular shapes will help you to visualize how molecules come together in a reaction, and what the orientation of the product may be. It is imperative that you draw good Lewis structures, can translate structural formulas to sound Lewis Structures, and can visualize molecules in your head (with, and ultimately without, the aid of molecules). This is something that comes with practice!

“Rules” for drawing Lewis structures

1. All valence electrons should be represented, including an adjustment for charge. They will be represented as either bonds or lone pairs, where lone pairs are indicated by 2 dots. (Ultimately, we will get “lazy” and omit lone pairs unless they are needed)

2. The molecule should have the correct atom arrangement. Typically, the less electronegative element is central, and Hydrogen is always terminal. Functional groups also help determine the arrangement. Hydrogen is never a central atom

3. For neutral molecules, carbon, nitrogen, oxygen and fluorine must have an octet of electrons surrounding them. For all other atoms (except hydrogen), an octet is a good goal, but not a rule!

   ⇒ B, C, N, O and F cannot exceed an octet ever. Cations of these elements may have less than an octet.

   ⇒ Atoms in the 3rd period (or lower) often exceed 8 electrons (they have d orbitals!)

4. Bonding is maximized.

5. Formal charge is minimized, and non-zero formal charges are listed.

   ⇒ FC = # valence e^- - # bonds - # lone pair e^-  

   ⇒ In general, formal charges should not exceed ±1.

6. Show equivalent resonance structures, where appropriate.

To draw a good Lewis Structure, the following procedure is utilized:

1. Determine the total number of electrons in the molecule, from the valence electrons and charge.

2. Determine the arrangement of atoms, considering functional groups.

3. Connect atoms with single bonds

4. Arrange remaining electrons using typical bonding patterns and formal charges to optimize the structure.

5. Draw appropriate resonance structures, connected with double-sided arrows.

Let’s consider two examples, one that is “inorganic” and one that is “organic”.
Example 1: the sulfate ion, $\text{SO}_4^{2-} \rightarrow S (6 \text{ e}^-) + 4 \text{ O (4 x 6 e}^-) + \text{ charge (2 e}) = 32 \text{ e}^- \text{ total in the structure.}$

Because sulfur is the least electronegative, it is the central atom. I'll put sulfur in the middle and the four oxygens around sulfur, connecting them all with single bonds.

\[
\begin{array}{c}
\text{O} \\
\text{O} \\
\text{O} \\
\text{O}
\end{array}
\rightarrow
\begin{array}{c}
\text{O} \\
\text{O} \\
\text{O} \\
\text{O}
\end{array}
\]

Adding lone pairs to the oxygens satisfies all octets, and now all 32 e$^-$ are represented.

Is that the optimal structure for the sulfate ion? Assigning formal charges will assist in that determination.

\[
\begin{array}{c}
\text{S}^{+2} \\
\text{O} \\
\text{O} \\
\text{O}
\end{array}
\rightarrow
\begin{array}{c}
\text{S}^{+2} \\
\text{O} \\
\text{O} \\
\text{O}
\end{array}
\]

After assigning formal charge, it is clear that this is not an ideal structure! There are too many formal charges on this molecule! Whenever a positive and a negative charge are next to each other, electrons can be shared to make multiple bonds. This can be done in the case of sulfate since sulfur can have an expanded octet.

\[
\begin{array}{c}
\text{O} \\
\text{O} \\
\text{O} \\
\text{O}
\end{array}
\rightarrow
\begin{array}{c}
\text{O} \\
\text{O} \\
\text{O} \\
\text{O}
\end{array}
\]

Does it matter which two oxygens the double bonds go to? No! When multiple structures can be drawn that are all identical, that sets up resonance structures!

The "complete" Lewis structure for the sulfate is the amalgam of all six resonance structures:

\[
\begin{array}{c}
\text{O} \\
\text{O} \\
\text{O} \\
\text{O}
\end{array}
\leftarrow
\begin{array}{c}
\text{O} \\
\text{O} \\
\text{O} \\
\text{O}
\end{array}
\leftarrow
\begin{array}{c}
\text{O} \\
\text{O} \\
\text{O} \\
\text{O}
\end{array}
\leftarrow
\begin{array}{c}
\text{O} \\
\text{O} \\
\text{O} \\
\text{O}
\end{array}
\leftarrow
\begin{array}{c}
\text{O} \\
\text{O} \\
\text{O} \\
\text{O}
\end{array}
\leftarrow
\begin{array}{c}
\text{O} \\
\text{O} \\
\text{O} \\
\text{O}
\end{array}
\]

*Lone pairs omitted for simplicity

The "true structure" of the sulfate ion has 1.5 bonds (6 bonds/4 bonding regions) between sulfur and each oxygen. Since there is no way to represent a "1.5" bond, resonance structures are used to show the sharing of electrons among atoms.


Example 2: 2-chloropropanoic Acid

Recalling some nomenclature from general chemistry (don't worry, we will go over this!), the "prop" prefix indicates 3 carbons in the backbone. The "-oic acid" ending indicates a carboxylic acid functional group, and that functional group defines the #1 carbon. "2-Chloro" indicates a chlorine off of the second carbon. That information results in the following skeleton structure:

Carboxylic acid functional group

Looking at this structure, The atoms are represented, and all carbons have an octet. We are still missing electrons and octets on the oxygens and chlorine. Some lone pairs may help!

The finished structure, with lone pairs!

Once a Lewis structure has been drawn for a molecule, the hybridization of atoms and the geometries can be determined.

Hybridization

Hybridization is the process by which pure atomic orbital (s, p, d etc…) are combined to form bonding atomic orbitals. The hybridization is dependent on the steric number, or the number of groups (bonding pairs, lone pairs) arranged around an atom, so a good Lewis structure is necessary to determine the hybridization. For every group that surrounds the atom of interest, one hybrid orbital is needed, and for every hybrid orbital, one pure atomic orbital is needed. Therefore, if three groups surround a particular atom, three hybrid orbitals are needed. Those three hybrid orbitals are formed from a combination of three pure atomic orbitals \( s + p + p = sp^3 \) hybridization is the result.

Example: formaldehyde: \( \text{CH}_2\text{O} \)

The oxygen has three groups around it - the double bond and 2 lone pairs.

Hybridization = \( s + p + p = sp^2 \) hybridization

The carbon has three groups around it - the double bond and 2 single bonds.

Hybridization = \( s + p + p = sp^2 \) hybridization

Molecular Shape

The number of groups surrounding a particular atom also dictates its electronic and molecular geometries. These geometries are developed by Valence Shell Electron Pair Repulsion (VSEPR) theory, which is based on the fact that "like" charges repel each other. Each electron region surrounding a central atom repels another electron region, such that the regions distribute themselves with maximum distance attainable within a sphere. All electron-containing regions are considered for the electronic geometry, the molecular geometry is a subset of the electronic geometry based only on the bonding electrons. The electronic geometry represents what electrons are there, and the molecular geometry represents what you can actually see. The following chart shows common geometries for 2, 3 and 4 groups around a central atom, and will represent the majority of the molecules that we will encounter in organic chemistry.
<table>
<thead>
<tr>
<th>Steric Number</th>
<th>Electronic Geometry</th>
<th># of Lone pairs</th>
<th>Molecular geometry</th>
<th>Shape</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>Linear</td>
<td>0</td>
<td>Linear</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>1</td>
<td>Linear</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>Trigonal Planar</td>
<td>0</td>
<td>Trigonal Planar</td>
<td></td>
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<tr>
<td></td>
<td></td>
<td>1</td>
<td>Bent</td>
<td></td>
</tr>
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</tr>
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<td></td>
<td></td>
<td>1</td>
<td>Pyramidal</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>2</td>
<td>Bent</td>
<td></td>
</tr>
</tbody>
</table>

### Orbitals and Bonding

Now that we have determined the shape of a molecule and the hybridization of the atoms within the molecule, we can consider how these orbitals interact to create a bond. We must remember that an orbital is a mathematical function that describes the probability distribution of electron density, or a mathematical function that describes the shape of an orbital. Bonds occur when 2 orbitals overlap. Mathematically, when we consider combining 2 orbitals, we must consider both constructively and destructively combining the orbitals. Let's consider the simple case of two s orbitals:

![Image of orbitals and bonding](image-url)

When two s orbitals approach each other and combine, 2 outcomes are possible. The lower energy combination is constructive, and a *bonding* orbital is formed; all electron density is shared and bridges both nuclei. The higher energy combination is destructive, and an *antibonding* orbital is formed; the electron density in each orbital repels the other, and a *node*, or a region of zero electron density, exists between the nuclei. These orbitals are all sigma (σ) orbitals, as only one region of electron density can be seen when viewed down the internuclear axis (one nucleus in front of the other). The bonding orbital is just a σ orbital, and the antibonding orbital is indicated as a σ* (sigma-star) orbital.
When two p orbitals combine, different types of orbitals can be formed depending on their orientation. If the orbitals meet head-to-head, in a linear fashion, sigma-type orbitals are formed. However, if the orbitals interact in a parallel, face-to-face fashion, a new type of orbital, the pi (π) orbital forms. The figure below gives a pictorial representation of these orbitals.

![Diagram of Sigma and Pi Orbitals](image)

All pi orbitals have a node that runs along the internuclear axis, connecting the nuclei. This creates two regions of electron density, one above and one below the internuclear axis and is consistent with the two lobes of a p orbital. Like the σ*, the π* orbital also has a node between the two nuclei.

**Putting it all Together**

The discussion of structures, hybridization and orbitals allows us to complete a mental picture of the orbital landscape within a molecule. When we understand and can visualize where orbitals start out, we can visualize how they change during the sequence of a reaction. Let’s consider the example of formaldehyde once more. Because the carbon is sp²-hybridized, the molecule itself adopts a trigonal planar geometry. That geometry is defined by the sp²-hybrid orbitals, and sets up all of the single bonds within the molecule. At the same time, the oxygen is also sp²-hybridized, which provides locations for the lone pairs. The left-over, unhybridized p-orbitals are then used to make the double bond.

- Hybrid orbitals define the overall molecular shape, and are used to make single, σ bonds and to house lone pairs.
- Unhybridized p orbitals are used to form π bonds that are perpendicular to hybrid orbitals.
- Multiple bonds are formed from one σ and additional π orbitals.