Lewis Structures
(The Localized Electron Model)

Using electron-dot symbols, G. N. Lewis developed the Localized Electron Model of chemical bonding (1916) in which valence electrons exist as lone pairs of electrons on an individual atom or as individual electrons seeking to form an electron pairing localized between the nuclei of two atoms in order to achieve an octet.

In Lewis’s Localized Electron Model, molecules are described as being composed of atoms that are bound together by sharing pairs of electrons. He was able to show that the arrangement of atoms in molecules could be predicted based on the arrangements of valence electrons of all atoms involved in the molecule.

Later, Lewis would come to recognize instances where one specific L.S. could not be used to describe the bonding in a molecule; but rather, some molecules should be described as somewhere in between these L.S.

Walter Heitler and Fritz London (1927) were the first to solidify Lewis’s idea by linking atomic orbital overlap to Schrödinger’s wave equation (1925) to show how two hydrogen atom wave functions join together to form a covalent bond.

Linus Pauling soon recognized the existence of more than one predicted L.S. could better be accounted for by one or more pairs of delocalized electrons.

Eventually, Linus Pauling would expand Lewis’s Localized Electron Model by adding Resonance Theory (1928) to explain the delocalized electrons predicted by multiple L.S. molecules. Furthermore, Pauling introduced Orbital Hybridization Theory (1930) to predict the electron behavior in covalently bonded atoms with in a molecule according to the principles set fourth in the Localized Electron Model.

Ronald Nyholm and Ronald Gillespie added VSEPR Theory (1957) to predict molecular geometry, also helping to describe any resulting molecular polarity.

Collectively, Localized Electron Model, Resonance Theory, Orbital Hybridization Theory and VSEPR Theory have been combined into what we call today Valence Bond Theory.

To describe the arrangement of atoms and bonds in molecules, we write Lewis structures following the thoughts of G.N. Lewis. Valence electrons seek pairings. From his Lewis Dot structures, we identify paired electrons are non-bonding and unpaired electrons tend to form bonds.

\[
\text{\{ } \text{Lone Pair (unshared pair)} \text{\}}
\]

\[
\sim \text{Bonding electron (unpaired electron)} \text{\} handout}
\]

Lewis Structures

Lewis structures are representations of molecules showing all electrons, bonding and nonbonding.
**DRAWING LEWIS STRUCTURES**

1. Draw the correct skeletal arrangement using single bonds
   a. Smaller, more electronegative, atoms surround larger, less electronegative, atoms
   b. Oxygen, hydrogen, and/or halogen atoms typically surround a central atom in a symmetrical arrangement
   c. Carbon atoms are usually bonded to each other
   d. Oxygen atoms are bonded to each other only in peroxides ($O_2^2$) or superoxide ($O_2^-$) which reacts with large, heavy alkali metals: K, Rb, Cs.
   e. In most oxyacids (like HNO$_3$) and most other compounds with both O and H, the H-atoms are all bonded to O-atoms

2. Determine the total number of valence electrons in the chemical species
   a. Neutral species: sum of valence electrons VE of all atoms
   b. Positive ion: sum of VE of all atoms minus ionic charge
   c. Negative ion: sum of VE of all atoms plus ionic charge
   d. Subtract two (2) electrons for each single bond in the skeleton structure
   e. Distribute the remaining electrons [in pairs as long as you can] to the connected outer species [attempt to satisfy the “octet rule” (EXCEPT for H)]
     a. If electron pairs are left over and all atoms have an octet, place remaining electrons on the central atom.
     b. If insufficient electron pairs are available to satisfy the octet rule for the central atom, move electron pair(s) from the outer atom(s) to form multiple bond(s) between the central atom and an outer atom
     1. It is quite common for C, N, O, S, P, Se to form multiple bonds
     2. Metals are rarely in covalent compounds and do not typically form multiple bonds
     c. Place polyatomic ionic compounds in brackets [ ] with the charge.

3. Identify possible resonance structures and formal charges to determine the most “likely” Lewis structure.
Important Note When Writing Lewis Structures:
The “Octet Rule” holds true for connecting atoms, but may not for the central atom.

We will discuss exceptions to the octet rule next lecture

1. Using the Lewis structure reference sheet, follow the steps to build the Lewis structure for the following:
   \[ \text{C}_2\text{H}_5\text{Cl.}, \]
   \[ \text{NH}_4^+, \]
   \[ \text{SO}_4^{2-}, \]
   \[ \text{O}_3 \]

Notice that two L.S. can be drawn correctly for ozone, \( \text{O}_3 \)

**RESONANCE**
Resonance theory, developed by Pauling (1928), is a key component of valence bond theory and arises when no single conventional model using only even number of electrons shared exclusively by two atoms can actually represent the observed molecule. Resonance involves modeling the structure of a molecule as an intermediate, or average, between several simpler but incorrect structures.

Resonance
- One Lewis structure cannot accurately depict a molecule such as ozone.
- We use multiple structures, resonance structures, to describe the molecule.
- Resonance is denoted by a double headed arrow separating the different Lewis Structures:

Resonance
- Observe \( \text{HCO}_2^- \):

  \[
  \begin{align*}
  \text{Resonance structure} & \quad \text{Resonance structure} \\
  \text{H} & \quad \text{H} \\
  \text{C} & \quad \text{C} \\
  \text{O} & \quad \text{O} \\
  \text{O} & \quad \text{O} \\
  \end{align*}
  \]

  - In truth, the electrons that form the second C—O bond in the double bonds below do not always sit between that C and that O, but rather can move among the two oxygens and the carbon.
  - They are not localized, but rather are delocalized.
**Delocalized Electrons** =

electrons that move over a number of atoms in a molecule, rather than being localized on or between a pair of atoms.

Resonance is denoted by the use of a double headed arrow between all contributing resonance structures (sometimes written in brackets).

2. Draw all resonance structures for the nitrate ion.

| Double bonds in resonance are generally longer than normal double bonds due to the delocalized electrons, which in turn are shorter than single bonds |
| How does the energy of resonance bonds compare to regular double and single bonds? |

Previously, we defined oxidation states as the charge an atom would have in a molecule as an ion.

This is a gross overestimation of an atom’s ability to attract electrons.

To account for the actual movement of valence electrons in forming a molecule, we use formal charges.

| **FORMAL CHARGE** |
| The difference in the number of valence electrons an atom would have as a free atom compared to the number of valence electrons assigned to the atom in a molecule or polyatomic ion |

| **Assignment of e⁻ in determining formal charges** |
| 1. Lone pairs belong exclusively to atom in question |
| 2. Shared e⁻ are divided equally between the two sharing atoms |
**Example:**

\[ \ddot{O} = \ddot{O} - \ddot{O}^- \]

<table>
<thead>
<tr>
<th>Should Have</th>
<th>6</th>
<th>6</th>
<th>6</th>
</tr>
</thead>
<tbody>
<tr>
<td>Has</td>
<td>6</td>
<td>5</td>
<td>7</td>
</tr>
<tr>
<td>Formal Charge</td>
<td>0</td>
<td>+</td>
<td>-</td>
</tr>
</tbody>
</table>

Therefore: \[ \ddot{O} = \ddot{O}^+ - \ddot{O}^- \]

**Important note:**
The sum of the formal charges in a molecule or polyatomic ion must equal the total charge on the molecule or ion.

This might be a good time to point out the difference between Oxidation states, Formal charges and partial charges:

a. Oxidation numbers treat all bonds as ionic giving the more E.N. atom the electrons of the covalent bond.

b. Formal charges treat all bonds as non-polar covalent disregarding the E.N. of the two atoms of the bond.

c. Partial charges attempt to describe the true electron distribution within a covalent bond.

3. Identify any formal charges for the examples on the worksheet.

**Comparing Lewis Structures**

- The best Lewis structure...
  - ...is the one with the fewest charges.
  - ...puts a negative charge on the most electronegative atom.

\[ \left[ \begin{array}{c} N \equiv C \equiv O \end{array} \right]^- \]

4. Draw all possible Lewis structures for COS, identify any resonance structures, formal charges and the most probable structure.