Atoms combine with other atoms to make molecules. These molecules are more stable, that is at lower total energy, than the separated atoms. Completely describing the shared electron density of molecules requires complex computations that are beyond the scope of this course. We will use several types of simple bonding models. In the first model we will use dots represent valence electrons on an atom and lines to represent covalent bonds. In making Lewis structures, we combine the valence electrons on atoms and make bonds until the total electron count around each atom is equal to the number of electrons in the filled shell configuration for that atom. Electron-electron repulsion between the regions of electron density explains the 3-dimensional structure of molecules.

Outline

- Atoms and Electron Count
- Lewis Structures
- Molecular Shape
- Homework

At right you can see how 3 oxygen atoms can combine to form the ozone molecule.

The 18 valance electrons from the atoms give rise to 3, 2-electron bonds (6 electrons) and 6 lone pairs of electrons (12 electrons) in the molecule. There are 2 equally good Lewis structures so a good picture of the electron density comes from the average.

Around the central oxygen atom are 2 bonds with other oxygen atoms and a lone pair of electrons. These clouds of electron density repel each other and give ozone its bent shape.

Atoms and Electron Count

Valence Electrons and Orbitals

In a covalent bond between 2 atoms, each atom provides one electron. Both electrons in the bond associate with each of these atoms. By forming chemical bonds, atoms increase the number of electrons around them up to their filled shell electron number. The filled shell number of electrons around each atom gives the maximum stability.

Here again is the periodic table. Each row of the table represents another principle quantum number, n. For atoms, the ordering of orbitals is 1s < 2s < 2p < 3s < 3p < 4s < 3d < 4p < 5s < 4d < 5p...
Electrons in an atom's s, p, and d valence orbitals can be used to make covalent bonds. The f orbitals are not usually involved in making chemical bonds. The number of bonds that an atom can form depends on the number of valence orbitals and the number of electrons it has.

### Electron Dot Structures

Let's examine the hydrogen atom. It has only 1 electron and 1 valence orbital. We can represent the electron in the 1s orbital as a dot next to the symbol for the hydrogen atom.

<table>
<thead>
<tr>
<th>n</th>
<th>Elements</th>
<th>Valence Orbitals</th>
<th>Maximum Electron Number</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>H, He</td>
<td>1s</td>
<td>2</td>
</tr>
<tr>
<td>2</td>
<td>Li-Ne</td>
<td>2s, 2p&lt;sub&gt;x&lt;/sub&gt;, 2p&lt;sub&gt;y&lt;/sub&gt;, 2p&lt;sub&gt;z&lt;/sub&gt;</td>
<td>8</td>
</tr>
<tr>
<td>3</td>
<td>Na-Ar</td>
<td>3s, 3p&lt;sub&gt;x&lt;/sub&gt;, 3p&lt;sub&gt;y&lt;/sub&gt;, 3p&lt;sub&gt;z&lt;/sub&gt; (5, 3d orbitals are also available)</td>
<td>8 or 18 (with 3d orbitals)</td>
</tr>
<tr>
<td>4</td>
<td>K-Kr</td>
<td>4s, 3d&lt;sub&gt;x²-y²&lt;/sub&gt;, 3d&lt;sub&gt;z²&lt;/sub&gt;, 3d&lt;sub&gt;xz&lt;/sub&gt;, 3d&lt;sub&gt;yz&lt;/sub&gt;, 3d&lt;sub&gt;x&lt;/sub&gt;&lt;sub&gt;y&lt;/sub&gt;, 4p&lt;sub&gt;x&lt;/sub&gt;, 4p&lt;sub&gt;y&lt;/sub&gt;, 4p&lt;sub&gt;z&lt;/sub&gt;</td>
<td>18</td>
</tr>
<tr>
<td>5</td>
<td>Rb-Xe</td>
<td>5s, 4d&lt;sub&gt;x²-y²&lt;/sub&gt;, 4d&lt;sub&gt;z²&lt;/sub&gt;, 4d&lt;sub&gt;xz&lt;/sub&gt;, 4d&lt;sub&gt;yz&lt;/sub&gt;, 5p&lt;sub&gt;x&lt;/sub&gt;, 5p&lt;sub&gt;y&lt;/sub&gt;, 5p&lt;sub&gt;z&lt;/sub&gt;</td>
<td>18</td>
</tr>
<tr>
<td>6</td>
<td>Cs-Rn</td>
<td>6s, 5d&lt;sub&gt;x²-y²&lt;/sub&gt;, 5d&lt;sub&gt;z²&lt;/sub&gt;, 5d&lt;sub&gt;xz&lt;/sub&gt;, 5d&lt;sub&gt;yz&lt;/sub&gt;, 5d&lt;sub&gt;x&lt;/sub&gt;&lt;sub&gt;y&lt;/sub&gt;, 6p&lt;sub&gt;x&lt;/sub&gt;, 6p&lt;sub&gt;y&lt;/sub&gt;, 6p&lt;sub&gt;z&lt;/sub&gt;</td>
<td>18</td>
</tr>
</tbody>
</table>
The \(1s^1\) configuration is much less stable than the filled shell configuration, \(1s^2\). Hydrogen can share its 1 electron with another hydrogen atom. This way both hydrogen atoms will achieve the \(1s^2\) configuration. *Shared electrons are counted twice, once for each atom in the bond.*

\[
1s^1 \quad 1s^1 \quad \rightarrow \quad H - H
\]

Now carbon. This atom has an electron configuration of \([\text{He}]\) 2\(s^22p^2\). It has 4 valence orbitals (2\(s\), 2\(p_x\), 2\(p_y\), and 2\(p_z\)) each of which can hold 2 electrons for a maximum of 8 electrons.

One electron can move from the 2\(s\) orbital to one of the 2\(p\) orbitals. This requires only a small amount of energy.

There are 4 valence orbitals, each occupied by 1 electron. Each of these can combine with a hydrogen atom to form 4 bonds.

The central carbon is surrounded by 4, 2-electron bonds. Electron-electron repulsion in these electron clouds gives the molecule its tetrahedral geometry.

Oxygen has 6 valence electrons with a configuration of \([\text{He}]\) 2\(s^22p^4\).

It can complete its valence shell by forming 2 bonds with hydrogen or with another oxygen atom.

It can also transfer an electron to another oxygen. Removing an electron with a -1 charge from a neutral oxygen atom gives it a +1 charge. The oxygen atom that receives the extra electron becomes negatively charged.

Now the central oxygen atom can form 3 bonds.

**Lewis Structures**

Lewis structures are a simple way to keep track of bonding electrons, non-bonding electrons, and formal charges in molecules.
To make a Lewis structure, add all valence electrons from the component atoms of a molecule or ion. Arrange these electrons in 2-electron bonds and in non-bonding pairs so that each atom has a filled shell configuration.

You've seen how to draw the Lewis structures of some simple molecules. Let's look at a more difficult example, the compound potassium azide. This is a salt and it can be written KN₃ or [K][N₃]. By convention, the cation goes before the anion in a formula.

1. Write out the Lewis structure of each atom or ion separately.

2. Very electropositive metals usually lose electrons and form cations. (We'll worry about the charges later.)

3. Sum the number of valence electrons from the atoms in the structure. Add 1 additional electron per negative charge if the structure is an anion. Subtract 1 electron per positive charge if the structure is a cation. This total number of electrons can be used to make 2-electron bonds and lone pairs.

4. Use the formula of the molecule or ion to help you determine the arrangement of the atoms.

5. Use valence electrons to make 2-electron bonds to connect the atoms in the structure. You can make single bonds (2 electrons), 2 bonds or a double bonds (4 electrons), 3 bonds or a triple bonds (6 electrons) in some cases. Be sure that you don't exceed the maximum
electron count (filled valence shell number) for any atom.

6. Use the remaining electrons to make lone pairs of electrons on atoms. When there is an odd number of electrons, there will be a single electron on some atom (radical).

7. Does the number of electrons you have used equal the total valence count?

8. There may be more than one possible Lewis structure. If so, the one with the fewest formal charges is usually the best. A correct Lewis structure always includes the formal charges.

**Example: Lewis structure of KN₃**

Potassium is an electropositive metal. It is likely that the molecule is K⁺ N₃⁻.

Total number of electrons = 1 + (3)(5) = 16

Potassium donates its single electron to N₃.

\[
\begin{array}{c}
\text{K} \\
\text{N} \quad \text{N} \quad \text{N} \\
\end{array}
\]

Connect the atoms:

\[
\begin{array}{c}
\text{N} \quad \text{N} \quad \text{N} \\
\text{N} \\
\end{array}
\]

\(e^-\) count = 7

\(e^-\) count = 7

The \(e^-\) count is too low, let's make 2 more bonds.

\[
\begin{array}{c}
\text{N} \quad \text{N} \\
\text{N} \\
\end{array}
\]

or

\[
\begin{array}{c}
\text{N} \quad \text{N} \\
\text{N} \\
\end{array}
\]

Each nitrogen now has an electron count of 8. Which is the best Lewis structure?
Formal Charge

Formal charge can show us the electron rich and electron poor regions of a compound. It is an important part of the Lewis structure.

For each atom in the structure:

1. Sum 1/2 of all electrons in bonds to that atom and add any other non-bonding electrons.

2. Compare that number to the number of valence electrons of that atom.
   
   (a) total = number of valence electrons, formal charge is zero
   
   (b) total > number of valence electrons, the atom has a formal negative charge (-1 for every additional electron above the valence number)
   
   (c) total < number of valence electrons, the atom has a formal positive charge (+1 for every electron below the valence number)

3. Use +/- signs and numbers to indicate the formal charge.

Example: Formal Charge of KN₃

The Lewis structure above is only partial. Formal charges are missing.
First K, it has 1 e⁻ fewer than it needs to be neutral.

\[ \text{K}^+ \]

Now the first N₃ structure.
The 2 N on the ends are the same.

\[ \text{-N= +N= +N-} \]

2 e⁻ from bonds 4 e⁻ from bonds
4 other e⁻ 0 other e⁻
total = 6, total = 4
valence = 5 valence = 5
1 extra e⁻ 1 fewer e⁻

Now the second N₃ structure.
All nitrogens are different.

\[ \text{-2... +... N=N=N :} \]

1 e⁻ from bond 3 e⁻ from bonds
6 other e⁻ 2 other e⁻
total = 7 total = 5
valence = 5 valence = 5
charge = -2 charge = 0

4 e⁻ from bonds
0 other e⁻
total = 4
valence = 5
charge = +1

The first Lewis structure is better because the maximum charge is lower.
Electron Count

The electron count around an atom tells us about its reactivity. If the electron count is less than the number needed to fill the valence shell, the atom is reactive. All atoms will seek a filled valence shell.

For each atom:
Sum the electrons from bonds to that atom (2 electrons per bond) and any other electrons on the atom.

The electron count must be less than or equal to the number of electrons in the filled shell. For n=1, that is 2 electrons; for n=2, that is 8 electrons; and it is 18 for most other atoms.

Note that NO$_3^-$ is a radical. There is an unpaired electron on oxygen and that oxygen atom has fewer electrons than it needs to fill the valence shell. This is key to the chemistry of this molecule.

Molecular Shape

We use Lewis structures along with Valence Shell Electron Pair Repulsion Theory to predict the structures of molecules. The idea behind this is that electrons in filled orbitals will repel each other because they have the same charge (just as magnets with the same polarity repel).

1. All pairs of electrons, both bonding pairs and lone pairs, are important in determining the shape of a molecule.

2. Bonding pairs are smaller than lone pairs because there are 2 positively charged nuclei pulling them in.

3. Single bonds are smaller than double bonds and double bonds are smaller than triple bonds.

4. If a central atom (A) is surrounded by different atoms (B and C) in the molecule AB$_x$C$_y$, the relative sizes of B and C can affect the structure of the molecule.

The first step is to construct the best Lewis structure of the molecule. Let's look at a few examples: CH$_4$, NH$_3$, BH$_3$
The electron pairs on the central atom will be arranged in such a way as to maximize their distance to the others. Two pairs will always be 180 degrees apart, in a linear arrangement. Three pairs will be 120 degrees apart in a trigonal arrangement. Four pairs will be arranged in a tetrahedron, 109 degrees apart. When there are 5 pairs of electrons, there are two possible arrangements: trigonal bipyramidal (90 and 120 degree angles) and square pyramidal (90 degree angles). Trigonal bipyramidal is the lowest energy, but the square pyramidal structure is pretty close and is also important. When there are 6 pairs of electrons, they occupy the vertices of an octahedron (90 degree angles).
Methane and ammonia both have 4 electron pairs, arranged in a tetrahedron. Only three of those pairs are bonded to another atom in ammonia. Borane has 3 electron pairs and must be trigonal.

**Coordination Geometry**
Both bonding and non-bonding electron pairs determine the structure but we name the geometry of molecules according to the arrangement of atoms.

<table>
<thead>
<tr>
<th>Electron Pairs</th>
<th>0 lone pairs</th>
<th>1 lone pair</th>
<th>2 lone pairs</th>
<th>3 lone pairs</th>
</tr>
</thead>
<tbody>
<tr>
<td>2 e⁻ pairs</td>
<td>linear</td>
<td>linear</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3 e⁻ pairs</td>
<td>trigonal</td>
<td>bent</td>
<td>linear</td>
<td></td>
</tr>
<tr>
<td>4 e⁻ pairs</td>
<td>tetrahedral</td>
<td>trigonal pyramidal</td>
<td>bent</td>
<td>linear</td>
</tr>
<tr>
<td>5 e⁻ pairs</td>
<td>trigonal bipyramidal</td>
<td>disphenoidal</td>
<td>T-shaped</td>
<td>linear</td>
</tr>
<tr>
<td>6 e⁻ pairs</td>
<td>octahedral</td>
<td>square pyramidal</td>
<td>square planar</td>
<td>T-shaped</td>
</tr>
</tbody>
</table>

The true bond angles will usually be distorted from the idealized angles in the pictures above because all bonds and non-bonding electron pairs don’t have the same "size".

lone pairs > triple bond > double bond > single bond

Also, atoms that are bonded to a central atom make a difference. The I atoms are much larger than the H atoms in CH₂I₂ and the H-H angle is smaller than the ideal 109 deg while the I-I angle is larger.