Lewis Structures and Shapes of Molecules

The aim of this exercise is use the Lewis structure of a covalently bonded species to predict the three-dimensional shape of the species and to presence or absence of a dipole moment.

Lewis Structures

The concept of a molecule is an old one. In the 18th and early 19th century, we knew that compounds consisted a set of atoms present at a specific proportion of elements, but how and why the atom aggregated together was a mystery. With the introduction of the periodic table, the discovery of the electron and Bohr’s model of the atom, a model for the interactions among the atoms within a compound was developed.

In a series of papers, Lewis, Langmuir, and Kossel observed the arrangement of outermost electrons around the Inert Gases (Group 18) and the apparent lack of reactivity of the Group. This “stability” of the electron configuration of Group 18 suggested that a driving force for holding the atoms together in a molecule might be associated with:

- transferring electrons to achieve the inert gas configuration and using charges of the ions to hold the species together (ionic); or,
- sharing electrons between the atoms to achieve the inert gas configuration on each of the atoms (covalent).

This sharing of the electrons in covalent compounds – bonds – is a directional interaction of the electrons. In the simple Lewis model, electrons are distributed as pairs within a molecule or atom. (This has its origin in the Pauli principle, since each orbital can accommodate at most two electrons.)

- The electrons shared between the two atoms feel an attraction to both nuclei and are stabilized (at a lower energy) relative to the energy in the atom. This lowered energy – the covalent bond energy – is the stabilization which holds the molecule together.
- Electrons not shared are localized on a single atom. These lone pairs of electrons effectively do not contribute to the stabilization that holds the molecule together.

The sharing of electrons between two dissimilar atoms may be unequal sharing of the electron pair(s) between the atoms. This difference makes one end of the bond partially positive and the other end partially negative – polar covalent bond.

The Shape of a Molecule

This directionalization of the bonding pairs will give rise to a specific orientation of the atoms with one another in a compound – compounds have a shape. This shape can affect how a molecule interacts with its neighbors. Given that a bond is a volume of space between the two atoms occupied by electrons and a lone pair is a volume of space occupied by electrons on a single atom, the volumes of
space are occupied around the atoms will reorient in space to avoid one another. A three dimension shape will develop.

This model, named the **VSEPR** or **Valence Shell Electron Pair Repulsion** model, was first proposed by R. J. Gillespie\(^1\) in 1957 and is the most successful of the early models relating the simple Lewis dot structure to the three-dimensional shape of the molecule (molecular geometry). This model is important because it leads directly to contemporary models of the geometry of biologically interesting compounds, such as enzymes and proteins, and forms the basis of what is called “rational drug design” — the Holy Grail of the pharmaceutical industry. According to the VSEPR model\(^2\),

*The preferred arrangement of a given number of electron pairs in the valence shell of an atom is that which maximizes their distance apart.*

For electron pairs in the same shell, the arrangements in space for two, three, and four regions around the central atom are summarized in Figure 1. In the simplest picture, no distinction is made between an electron pair in a single bonding orbital or multiple bonds occupying a region of space.

### Table 1: Electronic Geometry

<table>
<thead>
<tr>
<th># groups in space</th>
<th>Lone pairs</th>
<th>Electronic Geometry</th>
<th>Molecular Shape</th>
<th>Sketch</th>
<th>Bond Angles</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>0</td>
<td>linear</td>
<td>linear</td>
<td><img src="linear.png" alt="Sketch" /></td>
<td>180°</td>
</tr>
<tr>
<td>3</td>
<td>0</td>
<td>trigonal planar</td>
<td>trigonal planar</td>
<td><img src="trigonal_planar.png" alt="Sketch" /></td>
<td>120°</td>
</tr>
<tr>
<td>4</td>
<td>0</td>
<td>tetrahedral</td>
<td>tetrahedral</td>
<td><img src="tetrahedral.png" alt="Sketch" /></td>
<td>109.5°</td>
</tr>
</tbody>
</table>

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*Molecular Geometry as a Consequence of Electronic Structure*

The presence of lone pairs around an atom makes the **molecular shape** (the spatial arrangement of the nuclei) different than the **electronic geometry** (the spatial arrangement of electron pairs) – we don’t see the location of the lone pairs, but their presence is still felt. The simple picture for predicting the electronic geometry still succeeds if we treat all groups around an atom identically: that is, lone pairs are treated as a group in the same manner as shared pairs (single bonds), and no distinction is made between single bonds and multiple bonds. A more refined picture can be obtained from this simple scheme by making the following assumptions:
1. The size of the electron cloud associated with a non-bonding or lone pair is larger and repels more strongly than a bonding pair.
   
   This is reasonable since electron pairs used for bonding are localized in the internuclear region, whereas a lone pair is in a more diffuse orbital, and thus able to interact more strongly with neighboring pairs.

2. The size of the electron cloud of a double bond is larger than that of a single bond, and a triple bond is larger than a double bond.
   
   This also seems reasonable, since two electron pairs are localized in the internuclear region in a double bond, and three pairs in a triple bond.

3. The size of the electron cloud of a bonding pair between atoms A and X decreases near atom A as the exerts a greater attraction for the shared electrons (i.e., electronegativity of atom X increases) reducing interactions with neighboring pairs.
   
   This makes sense, since as the electronegativity of atom X increases atom X withdraws the electron density from atom A.

**Polar Covalent Bonds and Electronegativity**

If two different atom share an electron pair, the two different nuclei may exert a different attraction on the pair – the concept of electronegativity. One definition of electronegativity is the tendency for an atom to attract shared electron pairs in a bond toward itself. An electronegative atom like fluorine bonded to a less electronegative central atom “withdraws” electron density from the internuclear region towards itself. This “bond polarization” creates a **polar covalent bond**, a unequal sharing of an electron pair, an asymmetric charge distribution.

These assumptions lead to the electronic geometries adopted by various species containing single bonds and lone pairs as summarized in Table II. **After we know the electronic geometry** around an atom, we can deduce what the molecular shape is, bearing in mind that lone pairs generally repel more strongly than bonding pairs. Also, note that the usual effect of lone pairs is to reduce the bond angles that include the lone pair atom.
Table 2: Electronic Geometry and Molecular Shape

<table>
<thead>
<tr>
<th>Example</th>
<th># groups in space</th>
<th>Lone pairs</th>
<th>Electronic Geometry</th>
<th>Molecular Shape</th>
<th>Sketch</th>
<th>Bond Angles</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂</td>
<td>2</td>
<td>0</td>
<td>linear</td>
<td>linear</td>
<td>B—A—B</td>
<td>180°</td>
</tr>
<tr>
<td>BCl₃</td>
<td>3</td>
<td>0</td>
<td>trigonal planar</td>
<td>trigonal planar</td>
<td>B—A—B</td>
<td>120°</td>
</tr>
<tr>
<td>SO₂</td>
<td>3</td>
<td>1</td>
<td>trigonal planar</td>
<td>V-shape or bent</td>
<td>B—A—B</td>
<td>&lt;120°</td>
</tr>
<tr>
<td>CH₄</td>
<td>4</td>
<td>0</td>
<td>tetrahedral</td>
<td>tetrahedral</td>
<td>B—A—B</td>
<td>109.5°</td>
</tr>
<tr>
<td>NH₃</td>
<td>4</td>
<td>1</td>
<td>tetrahedral</td>
<td>trigonal pyramid</td>
<td>B—A—B</td>
<td>&lt;109.5°</td>
</tr>
<tr>
<td>H₂O</td>
<td>4</td>
<td>2</td>
<td>tetrahedral</td>
<td>V-shape or bent</td>
<td>B—A—B</td>
<td>&lt;109.5°</td>
</tr>
<tr>
<td>HCl</td>
<td>4</td>
<td>3</td>
<td>tetrahedral</td>
<td>linear</td>
<td>:A—B</td>
<td>180°</td>
</tr>
</tbody>
</table>

Partial Ionic Character and Bond Dipoles

The electronegativity differences between bonded atoms leads to an unequal distribution of the electrons – the electron pair is attracted to the end occupied by the more electronegative atom. This leads to an excess of electrons (a fractional negative charge, δ⁻) on the more electronegative atom, and a deficit of electrons (a fractional positive charge, δ⁺) on the less electronegative atom. A bond that has a non-zero electronegativity difference is characterized as having partial ionic character. A bond with an electronegativity difference of zero corresponds to a 0% ionic character and is characterized as a purely covalent bond.

A molecule with partial ionic character possesses an electric dipole. The electric dipole is a vector which points along the bond from the less electronegative atom to the more electronegative atom. The magnitude of the dipole is called the dipole moment. The important aspect of this relation is this: the larger the difference in electronegativity between bonded atoms, the larger the bond dipole moment.

Molecular Dipole Moments and Bond Dipole Moments

Each polar covalent bond in a molecule contributes to the molecular dipole moment. But it is essential to remember that the electric dipole is a vector quantity – it has both a length and a direction. Therefore, the molecular dipole is the vector sum of the individual bond dipoles. It is imperative that one know the direction as well as the magnitude of each bond dipole. This is where the VSEPR
model is useful. We know the directions of each bond dipole from the bond angles predicted from the model.

For example, in carbon dioxide, each C=O bond has some ionic character, but CO2 has a linear **molecular shape**, so the two C=O bond dipoles point in opposite directions, leading to no net dipole, so CO2 is a **nonpolar** molecule – *no net direction for the electrons*

![Electronic Geometry: Linear Molecular Shape: Linear (O-C-O angle = 180) This species is nonpolar](image)

**Example:** Ammonia, NH3

For the ammonia molecule (NH₃), the electrons in each N—H bond reside closer to the nitrogen rather than the hydrogen. The shape of the molecule, a trigonal pyramid, means the sum of the three arrows don’t cancel out and the molecule has a (partial) positive and (partial) negative areas.

![Lewis structure:](image)

The presence of the dipole moment will affect how the molecule will interact with its neighbors. This is a major driving force for the folding of proteins, the solubility of compounds, and physical properties, as well.

**References**

Pre-Laboratory Exercises:

1. Draw the Lewis structures for each of the following species:
   a) Acetylene, HCCH
   b) Formaldehyde, H₂CO
   c) Methylene imine, H₂CNH
   d) Water, H₂O

2. The bond angles of these molecules have been experimentally determined as follows:

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Bond Angle</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetylene, HCCH</td>
<td>H – C – C angle = 180°</td>
</tr>
<tr>
<td>Formaldehyde, H₂CO</td>
<td>H – C – H angle = 115.8°</td>
</tr>
<tr>
<td>Methylene imine, H₂CNH</td>
<td>C – N – H angle = 116 °</td>
</tr>
<tr>
<td>Water</td>
<td>H – O – H angle = 105.2°</td>
</tr>
</tbody>
</table>

Use the tables to find the bond angles predicted by the VSEPR model. Are the predictions consistent with the observed values?