Chemistry 1101 - Semester 1, 2007

Lecture 15: Lewis Model of Bonding
- Lewis Structures
- Representations of Molecular Structure

Lecture 16: Molecular Shapes
- (Finish off Lewis Structures first)
- Valence Shell Electron-Pair Repulsion (VSEPR) Theory

Lecture 17: Consequences of Molecular Shape

Review: Acids and their Anions
What are the Lewis structures of sulfuric acid, bisulfate, and sulfate ions (H₂SO₄, HSO₄⁻, and SO₄²⁻)?

H₂SO₄ has 32 valence electrons, leaving 20 to assign as lone pairs or multiple bonds. In this picture S already has a valence shell of 12, so we are left with the task of assigning 10 electron pairs among four O atoms.

In fact the H’s are bonded to oxygens, giving

The remaining electrons are assigned as lone pairs to fill the valence shells of oxygen.

The central S has an expanded valence shell, forming double bonds thus.

Review: Acids and their Anions
What are the Lewis structures of sulfuric acid, bisulfate, and sulfate ions (H₂SO₄, HSO₄⁻, and SO₄²⁻)?

We will start by removing a proton from H₂SO₄. The resonance structures of HSO₄⁻ are thus

so the bond order in 3 of the S-O bonds is 5/3, and the other is a single bond.

For SO₄²⁻, the resonance structures include

and the bond order of all the S-O bonds is 6/4 or 1½.
Review: How Are You Expected to Use Lewis Structures?

Lewis structures are used to describe single or higher-order bonds and lone pairs of electrons in molecules and ions.

Although they can be used with postulated molecules, the model does not describe any aspect of bond energetics, so it can’t really be used to decide whether a postulated molecule is stable or not.

E.g. We can draw a Lewis structure for PCl₃ or PCl₅, but it can’t tell us which is more stable.

E.g. NH₂⁻ has a well-defined Lewis structure, but it is not a stable species under most conditions.

In this unit we use Lewis structures to draw out plausible or reasonable structures for connectivity in molecules and ions, and to get some idea about bond order and electron delocalisation through resonance structures. Formula will be presented to you with various amounts of information to start with.

NB You are not at this stage expected to use the concept of formal charge, discussed in many texts.

VSEPR Theory

The valence shell electron-pair-repulsion (VSEPR) theory begins with the idea that electron pairs in the valence shell of an atom repel each other.

In VSEPR theory we make no distinction between bonding pairs and lone pairs. As a starting point we ignore multiple bonds.

The number of electron pairs surrounding any atom is obtained from the Lewis model of bonding.

Just as bond formation is a result of lowering energy, the shape of molecules in the VSEPR model is a result of minimizing the potential energy of interaction between electron pairs.

VSEPR tells us the geometry corresponding to the minimum potential energy.

Shape Depends on Number of Electron Pairs

The allowed shapes for a given number of electron pairs are always the same.

2 electron pairs: Linear

3 electron pairs: Trigonal

4 electron pairs: Tetrahedral

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The allowed shapes for a given number of electron pairs are always the same.

5 electron pairs:
- Trigonal Bipyramidal
- 90°
- 120°

6 electron pairs:
- Octahedral

The trigonal bipyramid has two different angles in its minimum energy geometry.

VSEPR Describes the Minimum Energy Shape

CH₄ (methane) is a canonical example of the tetrahedral molecular geometry.

If we actually calculate the energy of the CH₄ molecule as one of the H-C-H angles is increased from 90°, quantum theory shows that the minimum energy is the tetrahedral geometry.

VSEPR gives us a set of rules that empirically describe the observed results.

Number of Electron Pairs versus Number of Bonds

What are the shapes of CH₄, NH₃, and H₂O?

The Lewis structures for these molecules are

\[
\text{CH}_4: \quad \text{H} - \text{C} - \text{H} - \text{H} - \text{H}
\]

\[
\text{NH}_3: \quad \text{N} - \text{H} - \text{H} - \text{H}
\]

\[
\text{H}_2\text{O}: \quad \text{O} - \text{H} - \text{H}
\]

That is, the all have four electron pairs as single bonds and/or lone pairs. In the VSEPR structure the electron pairs are arranged tetrahedrally for all four molecules. The bond angle is very close to the tetrahedral angle for all three molecules.
The calculated electron density surface of a water molecule shows the excess electron density around the oxygen that gives it its bent shape, as VSEPR approximates.

<table>
<thead>
<tr>
<th>Number of Electron Pairs</th>
<th>versus</th>
<th>Number of Bonds</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tetrahedral (4 bonds, 0 lone pairs)</td>
<td>trigonal pyramidal (3 bonds, 1 lone pair)</td>
<td>bent (2 bonds, 2 lone pairs)</td>
</tr>
</tbody>
</table>

The calculated electron density surface of a water molecule shows the excess electron density around the oxygen that gives it its bent shape, as VSEPR approximates.

Shapes Derived from the Trigonal Bipyramid

As we replace bonds with lone pairs, the trigonal bipyramidal structure gives rise to a series of molecular shapes.

E.g. PF$_5$

The central atoms of both molecules have 5 electron pairs.

The lowest energy shape:

For SF$_4$, the lowest energy shape is the "seesaw".

The "bump" on the S that VSEPR and Lewis models describe as a lone pair is quite evident in the calculated electron density surface.

Shapes Derived from the Trigonal Bipyramid

Further reducing the number of bonding pairs gives rise to two further shapes.

E.g. ClF$_3$

The central atoms of both molecules have 5 electron pairs.

The lowest energy shape:

For XeF$_2$, the lowest energy shape is linear.

This molecule is planar but has bond angles a little below 90°, so it isn't a perfect T.

The 3 lone pairs are equatorial, leaving an F-Xe-F bond angle of 180°.
Shapes Derived from the Octahedron

The 3 molecular shapes of interest and their Lewis Structures are.

E.g. SF₆

BrF₅

XeF₄

The central atoms of these molecules have 6 electron pairs.

The 2 lone pairs get as far from each other as they can.

Consequences of Shape: Molecular Polarity

Molecules with polar bonds may have a net dipole, or the sum of all the dipolar bonds may cancel to leave no net dipole.

Molecular dipoles are important in determining intermolecular forces, and these in turn determine the properties of condensed phases - liquids, solids and liquid crystals.

E.g. Boiling points of liquids are determined by intermolecular forces.

Consider SF₆. Each S-F bond is polar. The "seesaw" shape of SF₆ has a dipole, whereas in a tetrahedral (e.g. CF₄) or square planar (e.g. XeF₄) shape the bond dipoles all cancel.

Worked Example: Molecular Polarity

Which of the molecular shapes based on octahedra has a dipole?

Only BrF₅ does not have bond dipoles that all cancel. SF₆ has pairs of equal and opposite dipolar bonds in the x, y, and z directions, and XeF₄ has pairs in the x and y directions, but BrF₅ has a distorted shape and a single Br-F bond in the z-direction that gives it a net dipole moment.

If the central atom is bonded to different atoms, then the bond dipoles will not in general cancel. E.g. IOF₅ is octahedral but polar.
Complete the table below showing Lewis structures and predicted shapes of the molecules and ions listed in the first column.

<table>
<thead>
<tr>
<th>Formula</th>
<th>Number of valence electrons</th>
<th>Lewis structure</th>
<th>Name of Molecular shape</th>
<th>Sketch of molecular shape showing lone pairs</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₃Cl</td>
<td>4</td>
<td>H-C-Cl</td>
<td>Trigonal pyramidal</td>
<td></td>
</tr>
<tr>
<td>e.g. NH₃</td>
<td>8</td>
<td>N-H-N-H</td>
<td>Triangular</td>
<td></td>
</tr>
<tr>
<td>H₂O</td>
<td>10</td>
<td>H-O-H</td>
<td>Tetrahedral</td>
<td></td>
</tr>
</tbody>
</table>

Bonding Between Carbon Atoms

We already saw that there are 3 kinds of carbon-carbon bonds in organic molecules.

1. Single bond (Alkane)
   
   ![Single bond image]
   
   Each carbon is tetrahedrally bonded to its neighbours.

2. Double bond (Alkene)
   
   ![Double bond image]
   
   Each carbon has a local trigonal geometry (~120°). The double bond only slightly affects the bond angles.

3. Triple bond (Alkyne)
   
   ![Triple bond image]
   
   A C-C triple bond is linear.

Larger Molecules and Functional Groups

The same ideas extend to the structures of large molecules containing functional groups. Once the Lewis structure and hence the number of lone pairs and bonding pairs are known, VSEPR theory can be used to draw the three-dimensional structure.

E.g. acetonitrile

![Acetonitrile image]

E.g. formaldehyde (methanal)

![Formaldehyde image]
Larger Molecules and Functional Groups

The effect of lone pairs is clearly seen in single- and double-bonded oxygens in functional groups, like aldehydes, alcohols and ketones.

E.g. ethanol, \( \text{CH}_3\text{CH}_2\text{OH} \)

E.g. acetone \( \text{CH}_3\text{COCH}_3 \) (an example of a ketone: \( R' - \text{O} - R \))

Stick notation for Organic Compounds

In extended carbon compounds the stick notation does not explicitly distinguish between tetrahedral and trigonal carbons.

E.g. in citronellol you see a zig-zag chain, but the bond angles look the same:

When we need to draw out tetrahedral carbons and show the detail of the bonding, it is done using a three-dimensional representation as follows:

Summary

You should now be able to
- Assign molecular shapes based on Lewis structures.
- Recognise four functional groups: aldehyde, alcohol, ketone and nitrile.
- Recognise three kinds of carbon-carbon bonds and know their names (alkane, alkene, alkyne) and shapes.

Next Lecture

Consequences of Molecular Shape
- Molecular Recognition
- Liquids and Liquid Crystals