Lecture 25: VSEPR

• Reading: Zumdahl 13.13

• Outline
  – Concept behind VSEPR
  – Valence Shell Electron-Pair Repulsion
  – Molecular geometries

• Both LDS and VSEPR have (backing them up) Quantum Mechanics, which tells us that electrons are paired in orbitals and bonding electrons are in molecular orbitals.
LDS and VSEPR

- The Lewis Dot Structure approach provided some insight into molecular structure in terms of bonding, but what about geometry?

- Recall from last lecture that we had two types of electron pairs: bonding and lone.

- Valence Shell Electron Pair Repulsion (VSEPR). 3D structure is determined by minimizing repulsion of electron pairs.
Steric Number

- Must consider both bonding and lone pairs in minimizing repulsion.

- Example: CH$_4$

  Lewis Structure

  VESPR Structure

  Steric Number is 4 because there are 4 objects around the C, 4 bonding pairs of electrons

  VESPR Structure (tetrahedral)
Geometry and Steric Number

- Example: NH₃ (both bonding and lone pairs).

Lewis Structure

VSEPR Structure

Steric number is still 4 (like CH₄) but on H is missing. The electrons are still arranged nearly tetrahedrally about the N but the object, defined by where the atoms are, is not tetrahedron.
Application of VSEPR

• The previous examples illustrate the strategy for applying VSEPR to predict molecular structure:

1. Construct the Lewis Dot Structure
2. Arranging bonding/lone electron pairs in space such that repulsions are minimized. Each electron pair is in an M.O.
Minimize Electron-Pair Repulsions

- Linear Structures: angle between bonds is 180°

- Example: BeF₂

Orbital showing where the bonding pair of electrons resides.

Orbital; bonding pair.

180°
Three pairs around B (steric # = 3)

- Trigonal Planar Structures: angle between bonds is 120°; arrange 3 things in a plane equally spaced from a center point. Get trigonal planar.

- Example: BF$_3$

![Diagram of BF$_3$ with 120° angles]
LPs repel more than EPs

- Pyramidal: Bond angles are <120°, and structure is nonplanar:

- Example: NH$_3$

![NH$_3$ structure](image)
Uniform Arrangement

• Tetrahedral: Any (and every) HCH angle between bonds is \( \sim 109.5^\circ \)

• Example: \( \text{CH}_4 \)

Arrange 4 things in 3-D space to be equidistant from a point. They are tetrahedrally arranged. Here the molecular structure and the bonding pairs of electrons are the same.
VSEPR Background

- Tetrahedral: angle may vary from 109.5° (exactly) due to size differences between bonding and lone pair electron densities (implies orbitals).

(a) bonding pair

(b) lone pair (Takes up more space than a bonding pair.)
Steric # 4 (two LP and two BP)

- Classic example of tetrahedral angle shift: from perfect tetrahedral (109.5°) to real water:
Steric #: 4  CH₄, NH₃, and H₂O

The molecules are not tetrahedral (only CH₄ is); however, in all cases the electrons (octet) are ~tetrahedrally arranged about the central atom.
Other shapes (PCl₅)

- Trigonal Bipyramidal, 120° in plane, and two orbitals at 90° to plane:

- Example, PCl₅:

Steric # ?

Compare with SF₄ and ClF₃
VSEPR and Octahedral Shape

- Octahedral: all angles are 90°:

- Example, $\text{SCl}_6$:
Advanced VSEPR

• Square Planar versus “See Saw”

See Saw

Square Planar

No dipole moment
Advanced VSEPR

• Driving force for last structure was to maximize the angular separation of the lone pairs.

Lone Pairs need to have more room and be further from other pairs than bonding pairs.
Advanced VSEPR Applications

- VESPR and resonance structures. Must look at VESPR structures for all resonance species to predict molecular properties.

\[
\begin{align*}
O &= O - O \\
\leftrightarrow
\end{align*}
\]

\[
\begin{align*}
O - O &= = O \\
\end{align*}
\]
• Provide the Lewis dot and VESPR structures for CF$_2$Cl$_2$. Does it have a dipole moment?

Tetrahedral
VSEPR and more molecules

\[ SO_4^- \]

\[ SF_4 \quad (cf. \ SF_6) \]

\[ PF_3 \quad (cf. \ PF_5) \]

\[ NO_2^+ \quad NO_2 \quad NO_2^- \quad O_3 \]

\[ IF_2^- \quad IF_4^- \quad IF_5 \quad IF_7 \]

Practice making LDS, arranging electrons, finding Steric #, and deciding on bond angles and molecular geometry.