LECTURE NOTES FOR GENERAL CHEMISTRY
CHAPTER 10
BONDING THEORY AND MOLECULAR STRUCTURE

THE VALENCE SHELL ELECTRON PAIR REPULSION METHOD (VSEPR) IS BASED ON THE IDEA THAT PAIRS OF ELECTRONS IN BONDED ATOMS REPEL EACH OTHER.

A MOLECULE IS IN ITS MOST STABLE GEOMETRY WHEN ITS ELECTRON PAIRS ARE AS FAR APART AS POSSIBLE.

ELECTRON GROUPS THAT EXERT REPULSION UPON ONE ANOTHER INCLUDE:
- SINGLE UNPAIRED ELECTRONS \( \cdot \cdot \cdot \)
- LONE PAIRS \( \cdot \cdot \cdot \cdot \)
- ONE BONDED PAIR \( \cdot \cdot \cdot \cdot \)
- TWO BONDED PAIRS \( \cdot \cdot \cdot \cdot \)
- THREE BONDED PAIRS \( \cdot \cdot \cdot \cdot \)

ONCE ELECTRON GROUPS MAXIMIZE DISTANCE FROM ONE ANOTHER, SIMPLE LOGIC DICTATES THE MOLECULAR GEOMETRY

2 GROUPS → LINEAR
3 GROUPS → TRIGONAL PLANAR
4 GROUPS → TETRAHEDRAL
5 GROUPS → TRIGONAL BIPYRAMIDAL
6 GROUPS → OCTAHEdRAL

IN THE VSEPR NOTATION, \( A \) STANDS FOR THE CENTRAL ATOM
\( X \) STANDS FOR TERMINAL ATOMS
\( E \) STANDS FOR LONE PAIRS

NUMERICAL SUBSCRIPTS INDICATE HOW MANY OF EACH

EXAMPLE \( H_2O \):
\( AX_2E \) 4 GROUPS → TETRAHEDRAL
\( CH_4 \):
\( AX_4 \) 4 GROUPS → TETRAHEDRAL

VSEPR METHOD
1) DRAW A LEWIS STRUCTURE
2) COUNT THE ELECTRON GROUPS (EITHER BONDS OR LONE PAIRS)
3) ESTABLISH ELECTRON GROUP GEOMETRY
4) ESTABLISH MOLECULAR GEOMETRY (NEGLIGENCE LONE PAIRS)
Examples: Nitrate ion \( \text{NO}_3^- \)

1) Lewis structure

\( \text{O}^\cdot \text{N}^\cdot \text{O}^- \)

All 24 assigned, but N has no octet.

So, move lone pair to bonding pair.

\( \cdot \text{O}^- \cdot \text{N}^\cdot \cdot \cdot \)

2) Count electron groups → 3 or \( \text{AX}_3 \)

3) Electron group geometry → 3 groups → trigonal planar

4) Molecular geometry → 3 groups → trigonal planar

Structures with lone pairs:

\( \text{NH}_3 \) Ammonia

Total 5 + 3 → 8 electrons \( \text{AX}_3\text{E} \)

\( \text{H}^\cdot \text{N}^- \text{H}^\cdot \text{H} \)

4 groups → tetrahedral

Molecular geometry is trigonal pyramidal

\( \text{H}_2\text{O} \)

Total 6 + 2 = 8 electrons \( \text{AX}_2\text{E}_2 \)

\( \text{H}^\cdot \text{O}^- \text{H}^\cdot \text{H} \)

4 groups → tetrahedral

Molecular geometry is angular

Now that we can use molecular geometry, we can show the difference between polar bonds and polar molecules. Recall that a polar bond is one between atoms of different electronegativities.

\( \text{C} - \text{Cl}^+ \text{C}^- \) or \( \text{C} = \text{O} \)
If a molecule is highly symmetrical, it will be nonpolar even if it contains polar bonds.

\[ \text{O} = \text{C} = \text{O} \quad \text{dipoles cancel} \quad \mu = 0 \]

The classic example is carbon tetrachloride \( \text{CCl}_4 \).

The classic example of an asymmetric, polar molecule is \( \text{H}_2\text{O} \).

\[ \text{H} \quad \text{O} \quad \text{H} \quad \text{overall dipole} = 1.8 \mu \]

Valence bond theory

A covalent bond is formed by the pairing of 2 electrons with opposing spins in the region of overlap of atomic orbitals between 2 atoms. The overlap of 2 atomic orbitals results in a molecular orbital, which is a region of high electron density between 2 nuclei.

Some highlights

- In a compound, most electrons remain in the same orbital locations they occupied in the unbonded atoms.
- Bonding electrons are "localized" in the region of atomic orbital overlap.

Hybrid orbitals

To account for the observed structures and geometries of most molecules, we introduce hybrid orbitals.

Hybrid orbitals are theoretically made by "blending" atomic orbitals together. An \( sp^3 \) hybrid orbital blends 1s plus 3p to make 4 \( sp^3 \) hybrid orbitals.

In carbon (\( 2s^22p^2 \)) \[ \begin{array}{c}
\begin{array}{c}
2s \\
2p
\end{array}
\end{array} \quad \text{hybridize} \quad \begin{array}{c}
\begin{array}{c}
\uparrow \downarrow \uparrow \downarrow
\end{array}
\end{array} \quad 4 \text{ } sp^3 \text{ hybrid orbitals} \]
HYBRID ORBITALS
- Often used for only the central atom
- The number of hybrid orbitals formed is equal to the number of atomic orbitals combined
- For bonding, hybrid orbitals may overlap with other hybrid orbitals or with atomic orbitals
- Molecular geometry is determined by the shapes and orientations of the hybrid orbitals

\[
\begin{align*}
SP & \rightarrow \text{linear} \\
SP^2 & \rightarrow \text{trigonal planar} \\
SP^3 & \rightarrow \text{tetrahedral} \\
SP^3d & \rightarrow \text{trigonal bipyramidal} \\
SP^3d^2 & \rightarrow \text{octahedral}
\end{align*}
\]

THE \( SP^3 \) HYBRID
- 4 equal orbitals \( \rightarrow \) tetrahedral
- Almost all of carbon chemistry is \( SP^3 \) (smaller amounts of \( SP^2, SP \))
- Also seen in \( AX_3E \) (\( NH_3 \)) \( AX_2E_2 \) (\( H_2O \))

THE \( SP^2 \) HYBRID
- Most useful in double bonds \( C=O, C=O, \text{etc} \)

THE \( SP \) HYBRID
- Triple bonds \( C≡C, C≡O, \text{etc} \)

HYBRID ORBITALS WITH O SHELLS
\( SP^3d \) - trigonal bipyramidal
\( SP^3d^2 \) - octahedral

As in \( SF_6 \)
\[
\begin{array}{c}
3s^2 \\
3p^4 \\
3d \\
\end{array}
\]

Hybridize

\[
\begin{array}{c}
\uparrow \uparrow \uparrow \uparrow \uparrow \uparrow \uparrow \\
\text{six equivalent orbitals}
\end{array}
\]

\[
\begin{array}{c}
\uparrow \uparrow \\
\text{remaining 0 orbitals}
\end{array}
\]

HYBRID ORBITALS AND DOUBLE BONDS
Especially in carbon, double bonds are formed from \( SP^2 \) hybrids

\[
\begin{array}{c}
\uparrow \uparrow \uparrow \uparrow \uparrow \uparrow \\
\text{A carbon with this hybridization can form 3}
\end{array}
\]

Each carbon has a p orbital overlap of p orbitals makes a \( \pi \) bond

\[
\begin{array}{c}
\uparrow \uparrow \\
\text{H.C=C-H}
\end{array}
\]

These are called \( \sigma \) sigma bonds
THE FINAL PIECE OF THE PUZZLE IS MOLECULAR ORBITALS
FORMED BY A LINEAR COMBINATION OF ATOMIC ORBITALS (LCAO)
THE NUMBER OF MOLECULAR ORBITALS IS THE SUM OF THE NUMBER
OF ATOMIC ORBITALS COMBINED

\[ \begin{array}{c}
\text{2 H Atoms} \quad \sigma^* \text{ Anti Bonding Molecular Orbital} \\
\text{ } \quad \sigma \text{ Bonding Molecular Orbital}
\end{array} \]

- Electrons seek the lowest MO available
- A maximum of 2 electrons in each MO (Pauli Exclusion)
- Electrons enter molecular orbitals of identical energies singly with parallel spins before they pair up (Hund’s Rule)

2\text{nd} PERIOD ELEMENTS

4 Atomic Orbitals \((1s, 3p) \rightarrow 8\) Molecular Orbitals

See Figure 10.3 p.447

4 Bonding, 4 Anti Bonding

For these orbitals and the diatomic molecules of the 2\text{nd} PERIOD
IT PREDICTS THE NEW TRIPLE BOND AND UNPAIRED ELECTRONS IN \(\text{O}_2\)

SKILLS

USE THE USEPR METHOD

UNDERSTAND MOLECULAR DIPOLE MOMENTS

USE VALENCE BOND THEORY FOR HYBRID ORBITALS

BE ABLE TO USE MOLECULAR ORBITAL THEORY

SPECIALLY FOR DIATOMICS OF 2\text{nd} PERIOD

NOT COVERED

GEOMETRIC ISOMERISM p.440-442

BONDING IN BENZENE p.448-451