Lecture 24: Lewis Dot Structures

• Reading: Zumdahl 13.9-13.12
• Outline
  – Lewis Dot Structures (LDS)
  – Localized Electron (LE) Bonding Picture
  – Resonance
  – Those annoying exceptions
• Problems (Chapter 13, Zumdahl 5th Ed)
• 47, 48, 50, 59, 62, 63, 67, 68
Localized Electron (LE) Models

- Consider our energy diagram for $\text{H}_2$ bonding:
Localized Model Limitations

• It is important to keep in mind that the models we are discussing are just that…..models.

• We are operating under the assumption that when forming bonds, atoms “share” electrons using atomic orbitals. (Electrons do pair up in orbitals.)

• Electrons involved in bonding: “bonding pairs”. Electrons not involved in bonding: “lone pairs”.

Lewis Dot Structures (LDS)

• Developed by G. N. Lewis to serve as a way to describe bonding in polyatomic systems.

• Central idea: the most stable arrangement of electrons is one in which all atoms have a “noble” gas configuration.

• Example: NaCl versus Na\(^+\)Cl\(^-\)

\[
\begin{align*}
\text{Na: } & [\text{Ne}]3s^1 \\
\text{Cl: } & [\text{Ne}]3s^23p^5 \\
\text{Na}^+: & [\text{Ne}] \\
\text{Cl}^-: & [\text{Ne}]3s^23p^6 = [\text{Ar}]
\end{align*}
\]
LDS Mechanics

- Atoms are represented by atomic symbols surrounded by valence electrons.
- Core Electrons are not shown but they are there on the atom.
- Electron pairs between atoms indicate bond formation.

A Lone Pair \( (lp) \) on one F of \( F_2 \)

Bonding Pair
LDS Mechanics

• Three steps for “basic” Lewis structures:

1. Sum the valence electrons for all atoms to determine total number of electrons.

2. Use pairs of electrons to form a bond between each pair of atoms (bonding pairs).

3. Arrange remaining electrons around atoms (lone pairs) to satisfy the “octet rule” (“duet” rule for hydrogen).
LDS Mechanics

- An example: \( \text{Cl}_2\text{O} \)

\[
\begin{array}{ccc}
\cdot & \cdot & \cdot \\
\cdot & \cdot & \cdot \\
\cdot & \cdot & \cdot \\
\end{array}
\]

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

20 e\(^{-}\)

\[
\begin{array}{ccc}
\cdot & \cdot & \cdot \\
\cdot & \cdot & \cdot \\
\cdot & \cdot & \cdot \\
\end{array}
\]

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

16 e\(^{-}\) left

The octet:
4 pairs of electrons.

Find lone pairs and bonding pairs
LDS for Methane, Z13.47

- An example: CH₄

\[
\text{H} \cdot \text{H} \cdot \text{H} \cdot \text{H} \cdot \cdot \text{C} \cdot \quad 8 \text{ e}^- \\
\text{H} \quad \text{H} \quad \text{C} \quad \text{H} \\
\text{H} \quad \text{H} \quad \text{C} \quad \text{H}
\]

\[
\text{H} \quad \text{C} \quad \text{H} \\
\text{H} \quad \text{H} \quad \text{H} \\
\text{H}
\]

Done! Check to be sure C has 8e around it, and each H has 2e.
Carbon always like 4 bonds.
Compare with NH₄⁺ (isoelectronic)
LDS for CO$_2$ (Z13.47)

- An example: CO$_2$

\[
\begin{array}{c}
\bullet \quad \bullet \\
O \quad O \quad C
\end{array}
\]

16 e$^-$

\[
\begin{array}{c}
\circ \quad \circ \\
O \quad C \quad O
\end{array}
\]

12 e$^-$ left

Octet Violation on C

\[
\begin{array}{c}
\circ \quad \circ \\
O \quad C \quad O
\end{array}
\]

0 e$^-$ left

CO double bond;
C has 8; Each O has 8;
2 lp on each O.
LDS for ions

- An example: $\text{NO}^+$ (remove an electron)

\[
\begin{array}{c}
\cdot N \quad \cdot O \\
\cdot \cdot \cdot \cdot \cdot \\
\end{array} \quad \rightarrow \quad \begin{array}{c}
\cdot N \\
\cdot \cdot \cdot \cdot \cdot \\
\cdot O \quad + \\
\cdot \cdot \cdot \cdot \cdot \\
\end{array}
\]

10 e⁻

\[
\begin{array}{c}
\cdot N \quad \cdot O \\
\cdot \cdot \cdot \cdot \cdot \\
\cdot \cdot \cdot \cdot \cdot \\
\end{array} \quad \rightarrow \quad \begin{array}{c}
\cdot N \\
\cdot \cdot \cdot \cdot \cdot \\
\cdot O \quad + \\
\cdot \cdot \cdot \cdot \cdot \\
\end{array}
\]

8 e⁻ left

\[
\begin{array}{c}
\cdot N \quad \cdot \cdot \cdot O \cdot \cdot \\
\cdot \cdot \cdot \cdot \cdot \\
\cdot \cdot \cdot \cdot \cdot \\
\end{array} \quad \rightarrow \quad \left[ \begin{array}{cc}
\cdot N \equiv \cdot O \\
\cdot \cdot \cdot \cdot \cdot \\
\cdot \cdot \cdot \cdot \cdot \\
\end{array} \right]^{+}
\]

Compare with $\text{N}_2$, isoelectronic, same number of atoms

Compare with HCN, also isoelectronic, $Z_{13.47,49}$.
LDS Practice (Z13.47,50)

• Compare NH₃, PH₃, PCl₃ (very similar)

• Compare CH₄ and CHCl₃, CF₂Cl₂.

• Compare OCO, SCO, OCN⁻, SCN⁻, N₃⁻
Resonance Structures

• We have assumed up to this point that there is one correct Lewis structure.

• There are systems for which more than one Lewis structure is possible:
  – Different atomic linkages: Structural Isomers
  – Same atomic linkages, different bonding: Resonance
Resonance Structures

The classic example: $O_3$: It is not linear, but it is not a triangle either, there is a central $O$ which is different from the other two.

Both structures are correct!
Resonance Structures

• In this example, \( \text{O}_3 \) has two resonance structures:

\[
\begin{align*}
\text{O} = \text{O} - \text{O} & \quad \Leftrightarrow \quad \text{O} - \text{O} = \text{O} \\
\end{align*}
\]

• Conceptually, we think of the bonding being an average of these two structures.

• Electrons are delocalized among the oxygen atoms such that on average the bond strength is equivalent to 1.5 O-O bonds.
Structural Isomers

• What if different sets of atomic linkages can be used to construct correct LDSs:

  \[ \begin{align*}
  &\text{Cl} \cdot \text{O} \cdot \text{Cl} \quad \text{Cl} \cdot \text{Cl} \cdot \text{O} \\
  &\text{Cl} \cdot \text{O} \cdot \text{Cl} \\
  &\text{Cl} \cdot \text{Cl} \cdot \text{O}
  \end{align*} \]

• Both are correct, but which is “more” correct?
• We use the “Formal Charge” to settle the issue.
Formal Charge (F.C.)

• Formal Charge: (Consider each atom individually)
  – Find the number of valence electrons on the free atom (FA)
  – Find the number of valence electrons assigned to the atom in the molecule (dividing bonding electron pairs by 2).
  – Difference is known as the “formal charge”.

• (Contrast with Oxidation Number—this is not the same)

```
#Ve-FA  7   6   7   7   7   6
#Ve-   7   6   7   7   6   7
Formal 0   0   0   0 +1  -1
Charge

• Structure with smaller F. C. is more correct.
```
A Formal Charge Example

• Example: CO$_2$

\[
\begin{array}{c}
\text{O} \equiv \text{C} \equiv \text{O} \\
\text{O} \equiv \text{O} \equiv \text{C} \\
\text{O} \equiv \text{O} \equiv \text{C} \\
\end{array}
\]

\[
\begin{array}{ccc}
e^{-} & 6 & 4 & 6 \\
e^{-} & 6 & 6 & 4 \\
e^{-} & 6 & 6 & 4 \\
FC & 0 & 0 & 0 \\
FC & 0 & +2 & -2 \\
FC & -1 & +2 & -1 \\
\end{array}
\]

More Correct
Beyond the Octet Rule

• There are numerous exceptions to the octet rule.

• We’ll deal with three classes of violation here:
  – Sub-octet systems
  – Valence shell expansion
  – Odd-electron systems
Beyond Octet Rule, e.g. BF$_3$, sub-octet

- Some atoms (Be and B in particular) undergo bonding, but will form stable molecules that do not fulfill the octet rule.

- Notice no formal charges for left hand structure (which does not satisfy “octet rule”), so it is more realistic model.

- Experiments demonstrate that the B-F bond strength is consistent with single bonds only.
Expanding the Octet

• Third-row-up element ("Period 3") atoms can take more than 8 valence electrons.

• Two different explanations (theories) for expansion:
  – the energetic proximity of the d orbitals allows for the participation of these orbitals in bonding.
  – Hyperconjugation is an alternative theory to bonding.

• Example: ClF$_3$ (a 28 e\(^{-}\) system)

  F obey octet rule

  Cl has 10e\(^{-}\), an expanded octet

  2 lone pairs, 3 bonding pairs
Beyond the Octet Rule

• Finally, one can encounter odd electron systems (radicals) where full pairs will not (cannot) exist.

• Example: Chlorine Dioxide.

Unpaired (lone) electron

[Diagram of Chlorine Dioxide molecule]
SO$_4^{2-}$ and Conflicting Criteria

- Two possible ways to consider the sulfate ion’s LDS:
- S (Ox=+6), and 4 O (Ox=-2) make the very stable anion. But what is its structure?
- (Next section) either choice for LDS leads to same geometry.
- Analyze the two possibilities in terms of octet rule, expanded octet, and resonance structures.

\[ \begin{array}{c}
\ddot{O} \\
\dddot{O} - S - \dddot{O} \\
\dddot{O} \\
\end{array} \quad \begin{array}{c}
\dddot{O} \\
\dddot{O} = S = \dddot{O} \\
\dddot{O} \\
\end{array} \]

The first one satisfies the octet rule. But all 4 Os have FC= -1, and only a single bond; FC(S)=+2; The second one expands S octet (but so do P and Cl) and only two Os have -1 FC, and two Os have double bonds. There are 6 resonance structures. So second is favored (but the issue is not settled).
Resonance and bond length (Z13.63)

- $CO_3^{2-}$ has 3 CO bonds that are equal and have a bond length between a single and double bond. Show the resonance structures and explain this length.
- This is one of three resonances, so we expect a bond length that is about that of a 1.33 bond. Experimentally the bond length is between the single and double bond lengths of CO.

\[
\begin{bmatrix}
:O: \\
\| \\
:O&-C&-O:
\end{bmatrix}^{2-}
\]

A linear interpolation of the experimental bond lengths gives a bond order of 1.35, in excellent agreement with the resonance theory.
Summary

• Remember the following:

  – C, N, O, and F almost always obey the octet rule.
  – B and Be are often sub-octet
  – Second row (Period 2) elements never exceed the octet rule
  – Third Row elements and beyond can use valence shell expansion to exceed the octet rule.

• In the end, you have to practice…..a lot!