Lecture 17: VSEPR & polarity 2

Read:  BLB 9.3
HW:  BLB 9.33,35,38
     Sup 9:8–11

• molecular geometry
• molecular polarity

Exam #2: Monday, March 2 @ 6:30; review previous material, so you UNDERSTAND what we’ve done and what we are doing now, and start preparing now! Last day to sign up for conflict exam is Wed, Feb. 25.

Final Exam: Monday, May 4 @ 12:20; MUST register on elion for a final exam conflict or overload by March 8. See http://www.registrar.psu.edu/exams/exam_overload.cfm
http://www.psu.edu/dus/handbook/exam.html#conflict

Need help?? Get help!! TAs in CRC (211 Whitmore) and Supplemental Instruction (SI)—hours on Chem 110 website; Sheets office hours: Mon 12:30-2; Tue 10:30-12 in 324 (or 326 Chem Bldg)
Calculating a dipole moment

• **dipole moment** \( (\mu) \): an observable measure of the overall polarity of a molecule
  
  \[
  \text{H–F} \quad \Delta\text{EN} = 4.0 - 2.1 = 1.9
  \]

• \( \mu \) is a vector: it has magnitude & direction; debye (\( D \)) = 3.33 \times 10^{-30} \text{ C m}

• for a **diatomic molecule**: \( \mu = Qr \)

• \( r \) is separation distance

• \( Q \) is charge; \(-Q\) and \(+Q\) are equal in magnitude for diatomic molecule; units of \( Q \Rightarrow 1.6 \times 10^{-19} \text{ C} = \text{charge of an e}^- \)

• for two charges (+1 and −1) separated by 1 Å, \( \mu = 4.8 \text{ D} \)

• in **polyatomic molecules**, \( \mu \) depends on:
  1. bond polarities
  2. molecular geometries
Dipole trends in HX

<table>
<thead>
<tr>
<th>HX</th>
<th>bond length ([r] (\text{Å}))</th>
<th>(\Delta EN)</th>
<th>(\mu (D)) (expt.)</th>
<th>(\mu (D)) (ionic)*</th>
<th>% ionic</th>
</tr>
</thead>
<tbody>
<tr>
<td>HF</td>
<td>0.92</td>
<td>1.9</td>
<td>1.82</td>
<td>4.42</td>
<td>41%</td>
</tr>
<tr>
<td>HCl</td>
<td>1.27</td>
<td>0.9</td>
<td>1.08</td>
<td>6.10</td>
<td>18%</td>
</tr>
<tr>
<td>HBr</td>
<td>1.41</td>
<td>0.7</td>
<td>0.82</td>
<td>6.77</td>
<td>12%</td>
</tr>
<tr>
<td>HI</td>
<td>1.61</td>
<td>0.4</td>
<td>0.44</td>
<td>7.74</td>
<td>6%</td>
</tr>
</tbody>
</table>

* if full charge separation occurs; \(\mu = 4.80 \ r \ D\) (where \(r\) is bond length); see prev page

\(X\) = halogen; \(\mu\) (expt.) = experimentally observed \(\mu\); 
% ionic = \(\mu\) (expt)/\(\mu\) (ionic) \times 100

• consider HCl: full charge separation (ionic): 
  \(\mu = 6.10 \ D\)

**but** HCl molecule has an actual \(\mu = 1.08 \ D\)

thus, the charge separation in HCl is only 
(1.08 D / 6.10 D) = 0.18 of the full charge

therefore, it’s polar covalent 
\(\text{H—X} \quad \delta^+ \quad \delta^-\)
Oxidation numbers, formal charges & partial charges

- **oxidation number**: a charge an atom would have if its bonds were *completely ionic*: i.e., assign $e^-$ to the more electronegative atom (Chap 4 ~Lecture 34; FYI right now…); **electronegativity is overemphasized**

  *Oxidation number—FYI only for now…*

  1. atoms in elemental form: 0
  2. monoatomic ions: charge on the ion
  3. nonmetals are usually negative
     - O is $-2$, except in peroxides where it is $-1$
     - H is +1 when bonded to nonmetals, and $-1$ when bonded to metals
     - F is $-1$, other halogens $-1$ in binary compounds, but positive in oxyanions
  4. sum must equal the charge on the species

- **formal charge**: a charge an atom *would* have *if* all bonding $e^-$ were *shared equally*; $\text{FC} = \text{VE} - \text{LSE}$ (review Chap 8); **electronegativity is deemphasized**

- **partial charge**: “*real*” charges on atoms in molecules; *most accurate* way of representing charges; **electronegativity is explicit**
Oxidation numbers, formal charges & partial charges (cont.)

• consider HCl:

<table>
<thead>
<tr>
<th>oxidation numbers</th>
<th>formal charges</th>
<th>partial charges (real)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H–Cl</td>
<td>H–Cl</td>
<td>H–Cl</td>
</tr>
</tbody>
</table>

polar covalent
\[ \mu = 0.18 \]

• consider HCl: **full** charge separation (ionic):
  \[ \mu = 6.10 \text{ D} \]

*but* HCl molecule has an **actual** \[ \mu = 1.08 \text{ D} \]
thus, the charge separation in HCl is only
\[ (1.08/6.10) = 0.18 \text{ of the full charge} \]

• dipole moment is one measure of the **actual charges** on atoms in a molecule
Molecular geometry & dipole moment

Do not memorize this table; think things out! NOTE: this table is presented in terms of molecular formula not in terms of ED geometry as we’ve seen before. Draw the generic structures & think about them to verify! NOTE: X is the same atom on all positions; A is the central atom

<table>
<thead>
<tr>
<th>formula</th>
<th>molecular geometry</th>
<th>dipole moment</th>
</tr>
</thead>
<tbody>
<tr>
<td>AX</td>
<td>linear</td>
<td>? HCl</td>
</tr>
<tr>
<td>AX₂</td>
<td>linear</td>
<td>0 CO₂</td>
</tr>
<tr>
<td></td>
<td>bent</td>
<td>? H₂O</td>
</tr>
<tr>
<td>AX₃</td>
<td>trigonal planar</td>
<td>0 BF₃</td>
</tr>
<tr>
<td></td>
<td>trigonal pyramidal</td>
<td>? NH₃</td>
</tr>
<tr>
<td></td>
<td>T-shaped</td>
<td>?</td>
</tr>
<tr>
<td>AX₄</td>
<td>tetrahedral</td>
<td>0 CH₄</td>
</tr>
<tr>
<td></td>
<td>square planar</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>seesaw</td>
<td>?</td>
</tr>
<tr>
<td>AX₅</td>
<td>trigonal bipyramidal</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>square pyramidal</td>
<td>?</td>
</tr>
<tr>
<td>AX₆</td>
<td>octahedral</td>
<td>0</td>
</tr>
</tbody>
</table>
Dipole moments of *cis* & *trans* isomers

• which molecule is polar and why???

```
cis       trans
Cl---Cl    Cl---H
C=C       C=C
H---H     H---Cl
```

• this is an example of a geometric isomer; atoms are connected in the same order & with same bonds **BUT** spatial orientation is different; this is NOT the same as structural isomers (see Lecture 13)

**electronegativity:** H = 2.1  C = 2.5  Cl = 3.0

**bonds:**

\[
\begin{align*}
\text{C—H} & : \Delta EN = 2.5 - 2.1 = 0.4 \\
\text{C—Cl} & : \Delta EN = 3.0 - 2.5 = 0.5
\end{align*}
\]

**what about symmetry of the molecule?**

**NET dipole?**
Example:

CO₂ is not polar  
(Lect 16, p 13)

Is SO₂ polar?

CF₄ is not polar  
(Lect 16, p 13)

Is SF₄ polar?
Yet another example:
Rank by increasing polarity

A. Cl
   Cl
B. Cl
   Cl

C. Cl
   F
D. F
   F

E. F
   F
F. F
   F
• **Lewis structures**: accounts for e\(^-\) pairs involved in bonding & lone pairs (non-bonding)

• **VSEPR**: accounts for ED & molecular geometry

• SO, *how are bonds made anyway? & where are the electrons???
Molecular orbitals

• e\textsuperscript{−} distribution in atoms: \textit{atomic} orbitals (s, p, d ...); orbitals give us the \textit{probability} of finding an electron (review Chap 6)

• \textit{two models describe e\textsuperscript{−} distribution in molecules}:

• \textit{valence bond theory}: valence orbitals on one atom \textit{with} valence orbitals on another atom, resulting in a \textit{covalent bond} (what we’re talking about now)

• \textit{molecular orbital theory}: a better model that uses wave theory, BUT not covered in Chem 110 😞 [will see in organic chemistry]
Covalent bonding

• **covalent bonding:** overlap or combining of two singly occupied *atomic orbitals* to form a new doubly occupied *molecular orbital*, allowing for sharing of electrons by the two nuclei; e\(^-\) of opposite spin share the common space between nuclei.

• **two forces operating:**
  ⇒ increased overlap of atomic orbitals (better sharing)
  
  ⇒ closer distance between nuclei increases e\(^-\) density between nuclei thereby lowering energy (see next page)

balance of forces ⇒ bond length (0.74 Å for H\(_2\))

\[ E \propto \frac{Q_1 Q_2}{d} \]

recall:
Energy & bond breaking or formation

When a bond forms, the system loses energy (or enthalpy). $\Delta E$ (or $\Delta H$) < 0, this is exothermic, or energetically favorable.

And, it takes energy to break a bond. $\Delta E$ (or $\Delta H$) > 0, this is endothermic, or energetically unfavorable.

This is true whether we are talking about covalent bonds or intermolecular forces (Chap 11).

Taken from: Olmsted & Williams, Chemistry 4th Ed. Wiley, 2006
Two bond types

1. $\sigma$ (sigma) bond: results from overlap of orbitals; e$^-$ density is symmetric about the internuclear axis

examples:

where $sp^x$ and $sp^y$ are hybrid orbitals (more in Lecture 18)
Two bond types (cont.)

2. $\pi$ bond: results from overlap of orbitals; $e^-$ density is above & below the internuclear axis

**example:** two p-orbitals

So... a covalent bond ($\sigma$, $\pi$) results from orbital overlap; understanding Lewis structures, electron domain geometry & molecular geometry is CRITICAL!!!
Before next class:

**Read:**  BLB 9.4–9.5
**HW:**  BLB 9.43,47
Sup 9:12–16; Sup Organic:5–6

**Know:**
- molecular orbitals
- orbital hybridization
- sigma ($\sigma$) bond
- pi ($\pi$) bond
- localized vs delocalized pi bonds & resonance

**Answers:**
p. 8: $\text{SO}_2$ is polar; $\text{SF}_4$ is polar
p. 9: $A = F < B < C < D < E$