Chem 105       Monday,  1 Nov  2010

Drawing Lewis Formulas
Formal charge
Resonance
Connection “map”

Molecular formula (list of elements and charge)

Lewis formula

 approximate geometry

Computation: “Geometry Optimization”

(nearly) exact geometry and polarity

Single crystal X-ray diffraction

The exact geometry
NB: Molecular formula is just a LIST. It does NOT necessarily indicate bond connections!

1. Count total no. valence electrons (+ or – according to charge)

2. Connect atoms with single bonds (2 e- per bond) per “map” information.

3. Starting with outer atoms, add remaining valence e- in pairs to make up octets.

4. For ions, put bracket around formula and total charge on top, right.

Chlorite ion ClO$_2^-$ (Cl is central)

$7 + 2(6) + 1 = 20$ valence e-

Now there are $20 - 2(2) = 16$ e- left

(still 4 e- left)

Each atom has an octet.
Formaldehyde CH\textsubscript{2}O (C is central)

1. Count total no. valence electrons (+ or – according to charge)

2. Connect atoms with single bonds (2 e\textsuperscript{-} per bond) per “map” information.

3. Starting with outer atoms, add \textbf{remaining valence} e\textsuperscript{-} in pairs to make up octets.

4. If a central atom is shy of octet, create a multiple bond by \textbf{moving in} an e\textsuperscript{-} pair. Repeat as necessary.

4 + 2(1) + 6 = 12

12 – 3(2) = 6
How many valence electrons are in carbon dioxide?

1. 8
2. 10
3. 12
4. 16
5. 20
Counting valence electrons

$\text{CO}_2$: $1(4) + 2(6) = 16$
board

Chlorate ion $\text{ClO}_3^-$

Slide has FCs
Formal charge on atom = Group# - \left( \frac{\text{# bonding } e^-}{2} + \text{# nonbonding } e^- \right)

Sum of formal charges = total charge on molecule (=0) or ion.

Chlorate ion

Formal charge = 6 – 6 – 1 = -1

Formal charge = 7 – 2 – 3 = +2

Sum of charges = -1 - 1 - 1 + 2 = -1
How does **Formal Charge** relate to **Oxidation Number**?

**Chlorate ion**

```
ClO₃⁻
```

- **Formal charge** (FC) electrons in bonds shared **equally**:

```
\begin{align*}
\text{O} & : \text{O} & \text{Cl} & : \text{O} \\
\text{O} & : \text{O} & \text{Cl} & : \text{O}
\end{align*}
```

- **Oxidation #** puts both bond e⁻ onto **more electronegative atom**:

```
\begin{align*}
\text{O} & : \text{O} & \text{Cl} & : \text{O} \\
\text{O} & : \text{O} & \text{Cl} & : \text{O}
\end{align*}
```

**ClO₃⁻**

```
+5  -2
ClO₃⁻
```

“Oxidation #” puts both bond e⁻ onto **more electronegative atom**.
Which is “correct”, formal charge or oxidation #?

**Formal charge** numbers are closer to computed values (see below). **Oxidation numbers** are useful for analyzing and classifying chemical reactions involving electron transfer.

Electrostatic potential 3D Mapped Isosurface qualitatively reflects formal charges
Resonance

Bonds in Lewis structures are limited to “two-atom electron sharing”.

However, some molecules or ions share bonding electrons over 3 or more atoms.

In these cases we use multiple Lewis structures linked by the “resonance symbol” $\leftrightarrow$ to describe the valence electron distribution.

Example: thiocyanate ion $\text{SCN}^{-}$

Not the same as the chemical equilibrium arrows.
Thiocyanate ion  SCN⁻

Related to thiocyanic acid HSCN, which is a strong acid.

In smokers, SCN⁻ ion is produced by metabolism of HCN present in tobacco smoke.

CN⁻ ion is metabolized by the enzyme rhodanase. SCN⁻ is detectable in saliva by infrared (vibrational) spectroscopy.
How many valence electrons in the $\text{SCN}^-$ ion?

1. 16
2. 14
3. 15
4. 13
5. 12
6. 11
Counting valence electrons

$$\text{SCN}^- \quad 6 \quad + \quad 4 \quad + \quad 5 \quad + \quad 1 = 16$$

Add one electron for - charge.

(Add two electrons for 2- charge.)
Thiocyanate ion  SCN⁻

Start with “connection map” in this case assume the bonding reflects the order in the formula

Subtract the number of bonding electrons already added from the total.  \(16 - 2(2) = 12\)

Now, add those electrons to the outer atoms to give them octets.

If the center atom does not have an octet, create additional shared pairs.
This says that in thiocyanate ion, the bonding is not EITHER ONE of these: rather it is a HYBRID of both.

The ion does NOT SWITCH BACK and FORTH between these structures – not even really, really fast!

Nor are there “some of one, some of the other”: the real ions are ALL EXACTLY ALIKE.

You can show this computationally by computing the energy and electron distribution starting with any of these formulas – get the same result! This is the approach taken in Expt 10 with the HCO$_3^-$ and similar ions.
HyperChem Intro: Use the **Drawing Tool** to place atoms and draw bonds
HyperChem Intro. Before you can compute, you must **BUILD** the structure. This puts in the basic **atomic orbitals** for the different atoms as a starting point for the calculation.
HyperChem Intro. Use **SETUP, SEM-EMPIRICAL menu** to define how Schrödinger Equation will be computed.

**Semi-empirical** method uses the Schrödinger Equation with pre-calculated wavefunctions for standard atom types.

Semi-empirical is faster, but less accurate, than **“ab initio”**. The latter makes fewer assumptions about the wavefunctions of the atoms.
Hyperchem calculates exactly the same energy content, partial charges, bond distances, and electrostatic potential 3D-mapped isosurface almost regardless of how the original ion is drawn! This is because the Schrödinger equation takes into account only the number of nuclei and total number of electrons.

The calculated distribution of charge in the thiocyanate ion. This indicates that there is only one thiocyanate ion structure, which is a hybrid of both Lewis structures that can be drawn.

“lines” are not necessary for correct quantum calculation.

(NB: Hyperchem is installed on the computers in NSF 170. You may use these any time the room is open. There is a student version of HC available for $89 from www.hyper.com)
What about the 3-atom bond mentioned above, which is indicated by the existence of resonance forms?

Electrons in molecules and multi-atom ions exist in molecular orbitals that are completely analogous to the atomic orbitals we discussed for atoms. Their shapes and energies are obtained by approximate solutions to the Schrödinger Equation, just like with atoms. These are not s, p, d etc, but they are mathematical combinations thereof.

Double bonds like C=N or C=S contain electrons in an orbital that spans the gap directly between atoms (a “σ-bond”), plus one located off to the sides of atoms. This is called a “π-bond”. Thiocyanate contains two giant π-bonds that extend across the whole ion. They are perpendicular to each other:
The end