Chemistry 212, Problem Set #3: Geometric Structure and Localized Bonding Models

Due in class, Wednesday, 4 February 2009

1. For each of the following chemical species: (i) write acceptable Lewis structures (including major resonance contributors and indicating formal charges); (ii) designate oxidation states for all atoms; and (iii) draw the stereochemical structures predicted by VSEPR arguments, noting deviations from ideal bond angles and predicting the direction of molecular dipoles.

   a. $ClOF_3$ b. $[OTeF_5]^-$

   c. $XeCl_4$ d. $H_2C{=}SF_4$ (indicate CH_2 orientation)

   e. BF_3 f. N_2O_5

2. Polynitrogen species, $[N_n]^z$ ($n > 2$, z = charge), "are of significant interest as high energy density materials (HEDM) for propulsion or explosive applications." The $[N_5]^+[AsF_6]^-$ salt, prepared in 1999, contains the first new polynitrogen species reported in over a century. The compound is described as a "highly energetic, strongly oxidizing material that can detonate violently. It should be handled only on a very small scale while using appropriate safety precautions (face shields, leather gloves, and protective clothing)."

   a. Write acceptable Lewis structures (including major resonance contributors and formal charges) for the cation. What stereochemistry is predicted by the VSEPR model? Are all N–N bonds the same length? Explain.

   b. Only one other polynitrogen molecule is known. What is its trivial name? Give its Lewis structure and geometry. Are all N–N bonds the same length? Where might you find this molecule in daily life and in what application?

   c. Theoretical chemists have explored the possible existence of other polynitrogen species, including neutral molecules of composition N_4. Write Lewis structures for two different molecules with this composition. Why are they predicted to be unstable?

   d. There is only one stable polyoxygen species. What is its name, Lewis structure, and geometry? What is the significance of this species?

3. White phosphorus, P_4, is a reactive, molecular allotrope of phosphorus.

   a. White phosphorus has no multiple bonds. Draw the Lewis-VSEPR structure for this molecule.

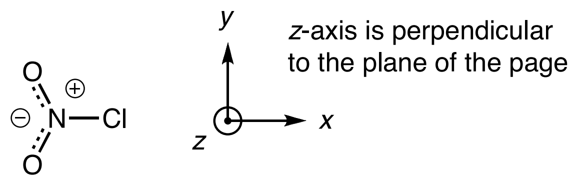
   b. What are the percentage *s* and *p* orbital contributions for hybrid orbitals that are constructed to maximize overlap between the P–P bonds?

   c. The hybrids in (b) are problematic. Why?

   d. Assuming that phosphorus and hydrogens are of comparable electronegativity (hence, comparable electron-donating/withdrawing capacity), do you expect the phosphorus centers in white phosphorus to be more or less basic than the phosphorus center in PH_3? Explain.

4. Consider the trigonal planar NO_2Cl molecule oriented against the coordinate system shown at right:

$\angle$O–N–O = 130°
$\angle$O–N–Cl = 115°



   a. Using the bond angles provided in the figure and the general properties of hybrid orbitals, construct normalized hybrid orbitals for nitrogen that describe the σ-framework in this system.

   b. Demonstrate that the hybrid orbitals derived in part (a) are orthogonal to one another.

   c. Plot one of the oxygen-directed hybrids as a cross-section on the *x-y* plane.

   d. Using two different theoretical models, predict how the structure of NO_2F will differ relative to the structure of NO_2Cl.