Chem 612- Fall, 2008
Take-Home Final Examination

Your answers to these problems are due in my electronic or physical mailbox in the Chemistry Department by 5:15 pm on Wednesday, December 17th. Please use word processing. If you have questions about any problems, see me in my office or contact me by email. You may not consult with any other individual or with any printed or electronic source, except the following: your notes and homework, the materials posted on the course website, the two texts used for this course, any sources cited in the questions below (which you may access through the Healey Library, if desired), the reprinted article distributed for this test and any references cited in that article.

1. (52 points) The following series of questions focuses on the paper "A Topological Study of the Geometry of AF₆E Molecules: Weak and Inactive Lone Pairs" by J. Pilmé, E. A. Robinson, and R. J. Gillespie. This paper makes use of another computational method for analyzing the electron density, called the electron localization function (ELF). ELF is explained briefly in the paper, but you may also want to access a general review article by Gillespie and Robinson, which gives a slightly more detailed overview of the technique (cf. p. 404). You should also review Chapter 9 in the Gillespie and Popelier text for more background on VSEPR, LCP, and AIM analysis of hypervalent structures.

   a. (6 points) All known main group examples of AX₇ molecules have a pentagonal bipyramidal structure (D₅h). Describe the kinds of positions and their characteristic relative lengths in main group AX₇ molecules with this geometry. In cases with mixed ligands (e.g., (CH₃O)_2TeF₅⁻) the bulky or less electronegative ligands preferentially occupy certain of these positions. Which positions do bulky ligands occupy and why? Compare and contrast this observed behavior with the occupancy of mixed ligands in tbp AX₅ molecules.

   b. (6 points) Although a pentagonal bipyramidal domain geometry might suggest a pentagonal pyramidal (C₅v) structure for AX₆E molecules, this is never observed. Why not?

   c. (6 points) Most known AX₆E molecules have an octahedral structure (O₆h), but a few (e.g., SeF₆²⁻, TeF₆²⁻, IF₆⁻, XeF₆) have a distorted octahedral structure (C₃v). What properties of A and X seem to favor one structure over the other?

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1J. Pilmé, E. A. Robinson, and R. J. Gillespie, Inorg. Chem., 2006, 45, 6198. Copies will be distributed in class, but you may prefer to access this through the Healey Library, because some of the key illustrations are in color.

d. (6 points) In the molecules with the distorted structure (SeF$_6^{2-}$, TeF$_6^{2-}$, IF$_6^-$, XeF$_6$), A–F bonds 1, 2, and 5 are longer than A–F bonds 3, 4, and 6 (cf. Fig. 1 in reference 1). What accounts for this? Why are these structures described as fluxional?

e. (6 points) The $C_3v$ distortion is described as a pseudo-Jahn-Teller effect. What is the Jahn-Teller Theorem and why is this a pseudo-Jahn-Teller distortion, rather than a genuine Jahn-Teller effect?

f. (6 points) The extent of the deformation from $O_h$ to $C_{3v}$, as reflected in $\angle$F$_1$–A–F$_2$, increases in the order BrF$_6^-$ < SeF$_6^{2-}$ < TeF$_6^{2-}$ < IF$_6^-$ < XeF$_6$. Why does this trend occur? How is it reflected in the ELF domains calculated in reference 1?

g. (8 points) As noted in reference 1, in the ELF analysis of the $O_h$ structure the only basins that are observed are the V(F) basin for each fluorine and the large-core basin C(A) of the central atom. In the $C_3v$ structure, a supplementary valence-shell monosynaptic basin V(A) is localized between F$_1$, F$_2$, and F$_5$. No disynaptic basins are observed. For all the $C_3v$ structures, the core population excess $\Delta$ is very small or generally slightly negative. How do these results relate to the VSEPR/LCP models of $O_h$ and $C_{3v}$ structures of these AX$_6$E molecules?

h. (8 points) SF$_6$ is an $O_h$ AX$_6$ molecule. Contour plots of $\rho$ and $L = -\nabla^2 \rho$ are shown in Figure 9.20 on page 250 of the Gillespie and Popelier text. Discuss what these plots show about the nature of the sulfur and fluorine atoms and about the bonding between them in SF$_6$. If you had similar plots for SeF$_6$ and SeF$_6^{2-}$ how might they be similar to and different from the plots for SF$_6$.

2. (32 points) The two known examples of AX$_5$E$_2$ molecules are XeF$_5^-$ and IF$_5^{2-}$. As shown in reference 1, Figure 4, the ELF domains of XeF$_5^-$ include two nonbonding basins V(Xe), one above and one below the equatorial plane, consistent with the predicted domain structure of VSEPR theory for an AX$_5$E$_2$ molecule. In the original paper reporting the discovery of XeF$_5^-$, Christe et al.$^3$ calculated the MO scheme, using 5s and 5p orbitals on Xe, and 2p orbitals on the fluorine atoms. The three 2p orbitals on each fluorine were taken to be engaged in sigma bonding through 2p$_x$, out-of-plane pi bonding through 2p$_z$, and in-plane pi bonding through 2p$_y$. As is typical of non-transition metal hypervalent structures, d-orbitals on the central Xe are only minimally involved in MO formation and may be ignored.

a. (6 points) Determine the symmetry of the five sigma SALCs of XeF$_5^-$ formed from 2p$_z$ orbitals on the fluorine atoms.

b. (1 points) Determine the symmetries of the 5s and 5p AOs on the central Xe atom in XeF$_5^-$.  

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c. (10 points) Using projection operator techniques, derive normalized wave functions for the σ-SALCs of XeF$_5^−$. In setting up the problem, label the five $p_z$ orbitals that point toward the central Xe atom as $p_1$, $p_2$, $p_3$, $p_4$, $p_5$. The following relationships will be useful:

Let $\omega = 2\pi/5 = 72^\circ$ and $2\omega = 4\pi/5 = 144^\circ$

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\begin{align*}
\epsilon + \epsilon^* &= 2 \cos \omega = 2 (0.3090) \\
\epsilon - \epsilon^* &= -2i \sin \omega = -2i (0.9511) \\
\epsilon^2 + \epsilon^{2*} &= 2 \cos 2\omega = 2 (-0.8090) \\
\epsilon^2 - \epsilon^{2*} &= -2i \sin 2\omega = -2i (0.5878)
\end{align*}
\]

You will need to use the numerical values to carry out the normalizations. But write the final normalized functions in terms of the trigonometric functions of $\omega$ (e.g., $\pm \cos \omega$, $\pm \sin \omega$, $\pm \cos 2\omega$, $\pm \sin 2\omega$), rather than their numerical equivalents, for those equations in which they occur.

d. (10 points) As noted above, the complete MO scheme derived by Christe et al. involves both sigma and pi interactions. Nonetheless, a simplified sigma-only scheme gives a satisfactory first approximation to the bonding in XeF$_5^−$. Develop a sigma-only MO scheme, using the symmetry results you obtained in parts a and b of this problem. Clearly label all levels by MO type ($\sigma$, $\sigma^*$, $\sigma^n$) and Mulliken symbol. Show the filling of the scheme with electrons from Xe 5s and 5p and the five F 2px orbitals. For purposes of electron counting, either consider XeF$_5^−$ as a neutral Xe atom, five neutral F atoms, and a negative charge; or equivalently as a Xe$^{4+}$ ion surrounded by five F$^−$ ions. As an aid to determining the ordering of the upper MOs, realize that there are no unpaired electrons.

e. (5 points) Draw sketches of the two highest occupied MOs in your scheme (i.e., the HOMO and NHOMO). Are the orbitals you have drawn consistent with the ELF contours shown in reference 1? Discuss.\(^4\)

3. (10 points) Using equations 7.2–7.6 in *Molecular Symmetry and Group Theory*, construct the reducible representation for a free-ion F term in $D_{3h}$ arising from an $nd^6$ configuration, and by reducing it into its component irreducible representations show the terms into which an F term is split in either a trigonal planar or trigonal bipyramidal crystal field. (Do not attempt to determine the energy ordering of the terms.)

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\(^4\)The actual HOMO and NHOMO in the full scheme with pi-bonding (reference 3) are quite different. Do not use these. Only use the implied MOs from your sigma-only scheme.
4. (6 points) ML₅ transition metal complexes are generally either trigonal bipyramidal or square pyramidal. There are no known examples of pentagonal planar transition metal complexes. Nonetheless, if such a structure were discovered, what would be the CFT splitting pattern of d orbitals on M? Label your scheme by orbital type and Mulliken symbol. Why is a pentagonal planar transition metal complex unlikely to be found?