**Chem 612 – Fall, 2008**
Assignment 4 Solutions

1. Draw sketches of the expected shapes of the following molecules: PF_4Br, SF_2Cl_2, IF_2Cl.

   In AX_5, AX_4E, and AX_3E_2 molecules that have ligands with different electronegativities, the less electronegative ligands preferentially occupy the equatorial positions and the more electronegative ligands preferentially occupy the axial positions.
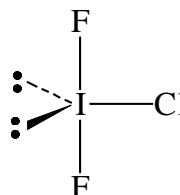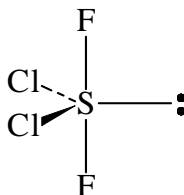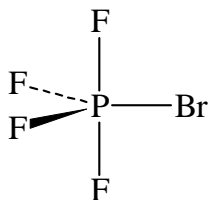
2. In AX_5E molecules, the four basal bonds are generally longer than the axial bond. For example, in ClF_5 the basal bonds are 167 pm and the axial bond is 157 pm. In terms of VSEPR theory, why is this tendency in the bond lengths observed?

   Repulsions with the lone pair cause the four basal (also called equatorial) positions to move up toward the apex relative to the central atom. This closes the X_{basal}–A–X_{axial} angle to less than 90°, and it also forces the four basal ligands away from the central A atom, thereby increasing the A–X_{basal} bond length.

3. Consider the bond angle data given below for some AX_2E_2 molecules.

Molecule	Angle (°)	Molecule	Angle (°)
OF_2	103.3	OCl_2	110.9
SF_2	98.2	SCl_2	102.8
SeF_2	94	$SeCl_2$	99.6

a. In all cases, except OCl_2, the bond angle is less than the tetrahedral angle of 109.5°, as expected from lone-pair – bond-pair repulsions. In terms of VSEPR theory, why is the angle in OCl_2 greater than the tetrahedral angle?

   Chlorine is less electronegative than oxygen. Therefore, the chlorine ligands do not effectively localize the central oxygen electrons into four tetrahedrally oriented domains, and ligand-ligand repulsions are more responsible for the bond angle.

b. The data are consistent with the generalization that in molecules with lone pairs bond angles decrease with increasing electronegativity of X or decreasing electronegativity of A. In terms of VSEPR modeling, why is that expected?

When ligands are more electronegative than the central atom, they draw bonding electron density away from the central atom. The space occupied by the bonding domains is lessened, and the ligands can approach each other more closely. Lone pair domains occupy a greater space and thereby push the ligand domains together. For the same central atom, the greater the ligand electronegativity the smaller the bond angle will be. Thus, the fluorine compounds in the table have smaller bond angles than their chlorine analogues. For the same ligand, as the electronegativity of the central atom decreases the electron-withdrawing effect of the ligands is increased, and the bond angles become smaller. Thus, for either the fluorine or chlorine compounds, the angles lessen through the series $O > S > Se$.

c. In general terms, how does LCP theory rationalize the bond angle data for these molecules?

LCP theory approaches the bond angles as a consequence of characteristic ligand radii specific to the central atom. Because chlorine is bigger than fluorine, two chlorine ligands maintain a larger separation and therefore a larger bond angle with each central atom. For either fluorine or chlorine ligands, the central atom size increases through the series $O < S < Se$. Although the effective ligand radius becomes bigger through the series as the electronegativitiy of the central atom decreases, the increased size of the central atom allows the ligands to approach more closely through the series, resulting in decreasing bond angles.

4. The ligand radius for a given element is not fixed, but rather depends upon the central atom to which it is bonded. For a given ligand, what is the trend in ligand radius with varying central atom? Why does this trend occur?

Ligand radii for a given ligand become bigger with decreasing electronegativity of the central atom. (See data in Gillespie and Popelier's Table 5.6, p. 121.) With decreasing central-atom electronegativity, the ligand is able to withdraw more electron density to itself, resulting in a larger ligand size.

5. Answer the following questions concerning OF_2 and HOF, two OX_2E_2 molecules. Show the set-up for your calculations in each case. Your answers to parts a and b should be given to 3 significant figures. Do not rely on the numbers shown in class for these molecules.

a. The O-F bond length in OF_2 is 140.9 pm and the bond angle is 103.3°. Calculate the F···F distance in OF_2 and from it the fluorine ligand radius with oxygen.

From the special case of the Law of Cosines for an isosceles triangle (or from an alternative trigonometric analysis), we can calculate the F···F distance from
$$d_C = \sqrt{2d_A^2(1 - \cos\gamma)} = 2d_A\sin(\gamma/2)$$
By either expression, $d_{F \cdots F} = 221.1_{54}$ pm $= 221.2$ pm, from which the ligand radius is 110.6 pm. To three significant figures, this is 111 pm.

b. In HOF the H–O bond distance is 96.4 pm and the F-O bond distance is 144.2 pm. The bond angle is 97.2°. With these data calculate the H⋯F distance. Assuming that the fluorine ligand radius is the value you calculated in part a, calculate the hydrogen ligand radius with oxygen in HOF.

From the general Law of Cosines, the H⋯F distance can be calculated as
$$d_C = \sqrt{d_A^2 + d_B^2 - 2d_A d_B \cos\gamma}$$
from which $d_{H⋯F}$ = 183.2 pm. Assuming the ligand radius with oxygen is 110.6 pm, as calculated in part a, the ligand radius of H with O is r_H = 183.2 pm – 110.6 pm = 72.6 pm.

c. Based on H_2O, Robinson and Gillespie give a value of 76 pm for the value of the hydrogen ligand radius with oxygen. [E. A. Robinson and R. J. Gillespie, *Inorg. Chem.* **2004**, 43, 2318.] Compare your calculated value to this value, and offer an explanation for the difference.

The value calculated in part b is somewhat smaller. With very electronegative ligand F in competition with H for the electron density on the central O, the H ligand obtains less electron density than it does in H_2O. This would make the H ligand somewhat smaller than it is in H_2O.

6. Consider the following data for A–F distances (pm), taken from E. A. Robinson, G. L. Heard, R. J. Gillespie, *J. Mol. Struct.* **1999,** *485-486*, 305-319:

BeF_3^-	149	BeF_4^{2-}	155.4
BF_3	130.7	BF_4^-	138.2
CF_3^+	124.4	CF_4	131.9

As these data show, bond length increases with coordination number (CN) for a given central atom with a specific ligand (here, fluorine). How have the shorter lengths of the CN3 species been rationalized in the past? How does LCP theory predict this trend? Calculate the F⋯F distance for each of these molecules. Are the results consistent with the concept of a relatively fixed ligand radius for fluorine bonded to a particular central element? Discuss.

In the past, the shorter distances in the AF_3 trigonal planar species have been rationalized as the result of back-bonding from filled $2p_z$ orbitals on the pendant fluorine atoms to the formally vacant (unhybridized) $2p_z$ orbital on the central atom (Be, B, C). This mode of bonding is not available if the central atom is sp^3 hybridized. The LCP model sees the shorter distances as the geometrical consequence of maintaining a relatively fixed ligand non-bonding radius between close-packed fluorine atoms around the central atom. Using the Law of Cosines and the data given in the table above, we can calculate the F⋯F distances and fluorine ligand radii as half these distances, obtaining the following results.

AX_3	$d_{F\cdots F}$	r_F	AX_4	$d_{F\cdots F}$	r_F
BeF_3^-	258	129	BeF_4^{2-}	253.8	126.9
BF_3	226.4	113.2	BF_4^-	225.7	112.9
CF_3^+	215.5	107.7	CF_4	215.4	107.7

The apparent fluorine ligand radius for a particular central element is nearly the same for both CN3 and CN4. The longer A–F distances in the CN4 cases are therefore a consequence of close packing of the ligands at a smaller angle (109.5º) compared to the CN3 cases (120º). The LCP model obviates the need to postulate back-bonding to rationalize the bond length increase with coordination number.