CHM 3411, Dr. Chatfield, Spring 2018

Problem Set 2

Due Friday, Jan 26

Suggested "warmups" (not to turn in): Discussion questions 7C.1-3 and 8A1-3; Exercises [all (b)] 7C.1-7

This problem set explores some of the fundamental principles of quantum mechanics. Problem 1 explores the Born interpretation of the wavefunction; problem 2 gives you practice normalizing a wavefunction; problem 3 explores the ideas of eigenfunction and eigenvalue; problem 4 has you construct quantum mechanical operators for observables; problems 5 and 6 are Spartan problems that will be introduced in class.

1. P7B.4

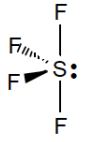
2. P7B.1, parts i, ii, and iii only. Note that in iii, you will need to integrate in 3 dimensions.

3. P7C.4

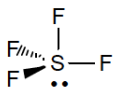
4. P7C.2

5. For this problem, you will need to use Spartan.

Background: The problem concerns VSEPR (**V**alence **S**tate **E**lectron **P**air **R**epulsion) theory, which uses two simple rules to assign geometry (remember from General Chemistry). First, the geometry about an atom follows by insisting that electron pairs (bonds or lone pairs) are as far apart as possible. Second, it is more important to separate two lone pairs than it is to separate a lone pair from a bond than it is to separate two bonds. Taken together, these two rules properly account for the observed "see-saw" structure of sulfur tetrafluoride, SF_4. Sulfur atom surrounded by five electron pairs (four bonds and a lone pair) assumes a trigonal bipyramidal geometry, and the lone pair prefers an *equatorial* position. What VSEPR theory does not tell us is whether this is the only structure of SF_4, in particular, whether a trigonal pyramid structure (which obeys the first rule but violates the second) might also be an energy minimum.



"see saw"



trigonal pyramid

Spartan calculations: Use the HF/6-31G* model to obtain geometries for both forms of SF_4. For the"see saw" structure, the simplest thing is to go to Inorganic and choose the trigonal bipyramid motif with S as the central atom. Add the 4 Fs and delete the remaining dangling bond (you figure out which one). You can construct the trigonal pyramid structure by deleting a different dangling bond. Do not worry about the lone pairs (Spartan takes care of them). In each case, do an "Equilibrium Geometry" calculation. Check the bond lengths and bond angles before and after doing the "Equilibrium Geometry" calculation to see if they change (sometimes it is no obvious from visual inspection).

Answer these questions: (a) Are both structures depicted above ("see saw" and "trigonal pyramid") stable structures (energy minima) or is there only one kind of structure after the "Equilibrium Geometry" calculations are done? (b) If there is only one structure, is it the observed structure? If there are two structures, is the observed structure favored? (c) If there are two structures, is the higher-energy structure likely to be observed at room temperature? (Assume that it must make up at least 5% of the mixture to be detected.)

To answer question (c), you will need the following relationship. For a binary mixture of A and B, with B representing the higher-energy isomer, the fraction of B is:

$$\frac{n_B}{n_A + n_B} = \frac{e^{-\Delta E/kT}}{1 + e^{-\Delta E/kT}}$$

where n_x is moles of x, E is the energy difference between the isomers, k is Boltzmann's constant, and T is in Kelvin. Assume a temperature of 298 K (room temperature). Be sure energy units match!