Molecular Modeling with Spartan

In class we learned how to use the Valence-Shell Electron-Pair Repulsion (VSEPR) model to predict a molecule's or an ion's geometry by arranging its electron domains in a way that minimizes repulsion between pairs of electrons. While this provides a general sense of the geometry around a central atom, it cannot provide more quantitative information about the molecule or ion, such as bond lengths, bond angles, and bond energies.

To provide a more detailed picture of bonding, we can use more computationally rigorous mathematical models. For example, we can use classical mechanics and Coulomb's law to maximize attractive interactions and to minimize repulsive interactions, and we can use quantum mechanics and the wave equation to calculate bond lengths and bond angles. In this lab you will use the molecular modeling program Spartan to optimize the structure of some inorganic molecules and polyatomic ions, and then evaluate your results against the simple VSEPR model and the known periodic trends for the elements.

Three Important Cautions. First, a computational lab changes what and how you record information in your lab notebook. Reproducing the result of a calculation requires that you begin with the same structure and that you use the same settings; it is essential, therefore, that you maintain a record of the structures and settings you use for each molecular or ion you are studying.

Second, the computers in the Computational Chemistry Lab are configured to delete all locally saved files on each restart. If you wish to save your work you must use a USB drive or cloud storage.

Third, Spartan occasionally becomes stuck during a computation. If this happen, you will need to reboot your computer and restart the calculation.

Pre-lab Assignment. Read through the lab paying particular attention to the instructions for using Spartan. We will review the software using the ions PF_6^- and NO_3^- as examples, so come to lab having drawn Lewis structures for each ion and having predicted each ion's geometry using VSEPR.

Procedure. After you receive training on the use of Spartan, you can work at any time convenient for you (the computer lab is open during the day and during some evenings). Work with your assigned partner to complete the molecular modeling exercises described below and, as a team, prepare a single report of your work. You may choose to divide up the work in any way you wish provided that each partner uses Spartan.

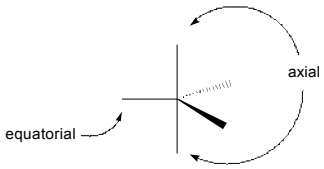
Molecular Modeling Exercises

Begin each exercise by drawing appropriate Lewis structures and using VSEPR to predict the geometry around the central atom.

Exercise 1. The ion and molecules NH_4^+, NH_3, $N(CH_3)_3$, and H_2O have the same number of electron domains around the central atom (nitrogen or oxygen) but differ in the number of bonding domains and in the substituents (including lone-pairs of electrons) bound to the central atom. Use Spartan to optimize their structures. Measure the bond angles in each structure (N or O in the middle) and organize them from largest-to-smallest. What do your results imply about the relative size of a lone pair of electrons compared to –H and $–CH_3$? Explain your reasoning.

Exercise 2. The molecules NF_3, PF_3, AsF_3, SbF_3 and BiF_3 have the same number of electron domains and the same geometry around the central atom, but differ in the identity of their central atom. Use Spartan to optimize their structures and measure the F–X–F bond angles and the F–X bond

distances, where X is the central atom. Organize each set of results from largest-to-smallest and then describe and explain the trends you see in this data, as well as any subtleties or discontinuities in these trends, in terms of the relative size of the central atom.



Exercise 3. As shown to the right, a trigonal bipyramidal geometry has two unique positions around the central atom: two axial positions and three equatorial positions. One consequence of this is that we can draw two structures for a molecule, such as SF_4, that has four bonding substituents and a single lone-pair of electrons, placing the lone-pair in either an axial position or an equatorial position. Use Spartan to optimize each structure; however, *skip the step where you first minimize the energy using the minimization tool on the toolbar*. Identify the geometry that Spartan finds most stable and explain why this is the more stable structure.

Exercise 4. Chemists often study a series of related compounds to gain insight into the relationship between structure and physical properties. For example, the compounds listed here have the general formula PF_3R, where the identify of R is different: PF_4^+ (R = F); PF_3 (R = lone pair); PF_3O (R = O, double bonded to phosphorous); and PF_3S (R = S, double bonded to phosphorous). Use Spartan to optimize the structure for each compound. Identify one bond angle **or** one bond length that is present in all four compounds and use it to rank R in order of increasing size. As part of your response, be sure to explain your reason for choosing this bond angle or bond length.

Exercise 5. The oxo anions of chlorine are ClO^-, ClO_2^-, ClO_3^- and ClO_4^-. All four ions have a tetrahedral electron domain geometry. Use Spartan to optimize each of these ions. Rank the ions from largest-to-smallest Cl–O bond order (based on bond length) and explain the trend in your results by considering possible resonance structures.

Exercise 6. Use Spartan to optimize the structure for NO_2^+, NO_2, and NO_2^-. Because NO_2 has an unpaired electron, when you set up your calculation you must let Spartan know that its ground electronic state is a **doublet** (this is just a fancy way of saying that NO_2 has an unpaired electron) rather than a **singlet**. Compare the O–N–O bond angles in each molecule and propose a plausible explanation for your results.

Final Report

You and your partner will turn in a single report. Although you may have worked on separate exercises, each of you is responsible for understanding the results for all six exercises, so be sure to ask questions of each other for those problems on which you did not work.

For each exercise, begin by drawing a three-dimensional representation of the relevant molecules and/or ions. Annotate these drawings by including all bond lengths and bond angles ***relevant*** to the exercise; please do not include unnecessary bond lengths and bond angles. Finally, for each exercise, include a well-written paragraph that addresses the question raised or issue explored in the exercise. Your report may be typed or handwritten; for the latter, please be sure it is legible.