Correlation of Trends in Measured Redox Potentials
and Computed Molecular Orbital Energies
of Derivatized Buckminsterfullerenes

In order to complete this project, you will need to refer to the three references given below; in particular, an article entitled "Redox Properties of Organofullerenes" by Suzuki et al (*J. Am. Chem. Soc.* **1994**, *116*, 1359-1363). Be advised that some of the calculations may require significant amounts of computer time; in particular, those which use density functional theory. Also, building some of them using Spartan can be a bit tricky (see below).

In the article by Suzuki et al, derivatives of buckminsterfullerene (C_{60}) were studied using cyclic voltammetry to probe how substitutions with electron-donating or electron-withdrawing groups affect the measured reduction potentials. The AM1 method was then used to calculate the energies of the molecular orbitals. The authors show that there are correlations between the calculated energies of certain frontier orbitals and the measured reduction and oxidation potentials.

AM1 is an example of a semiempirical theoretical method. It was never designed by its authors to describe the energies of molecular orbitals accurately, but rather was constructed to predict molecular geometries and heats of formation. Density functional theory calculations are considered the minimum acceptable level of theory these days. At the time this work was published, only semiempirical calculations were practical for compounds with this many atoms on ordinary personal workstations.

You will first reproduce a few of these calculations. Reproducibility is one of the most important aspects of scientific research, and often it is necessary to reproduce work from a publication in order to validate one's own methods or to challenge the results. You will also carry out additional calculations to see if the AM1 results can be improved upon by using two other semiempirical methods (PM3 and PM6) as well as density functional theory using the B3LYP functional with the 6-31G* and 6-311G* basis sets. The B3LYP method is currently the most widely used quantum-mechanical model in the field of inorganic chemistry, followed by MP2 (which can be much more numerically intensive for large systems).

You will first carry out AM1 geometry optimization calculations on unmodified C_{60}, as well as on at least three of the modified compounds. Select these appropriately in order to display a range of redox potentials similar to that considered in the Article. When building them, a good strategy is to begin with a model of buckminsterfullerene and then break and make bonds as necessary to make each derivative. Use the energies of the LUMO and the LUMO+1 for each derivative together with the data in Table 1 from the Article to reproduce the reduction potential plots in Figure 4 (E1 and E2 vs. LUMO, E3 vs. LUMO+1). Make your own version of Figure 4 (probably using a more limited data

set), fitting the data as shown. In your report, make sure to include a table of the orbital energies that you have computed and the E1/E2/E3 values you used from Table 1 of the paper.

You will then repeat the same calculations, plots and tables using the PM3, PM6, and B3LYP/6-31G* methods. The B3LYP/6-31G* calculations may take a while to complete. Finally, using the optimized B3LYP/6-31G* geometries you will carry out B3LYP/6-311G* "single point" energy calculations (Choose "Energy" within the Setup menu). These also may take a while, but significant time is saved by not re-optimizing the geometry.

In your paper, give an overview of how cyclic voltammetry was used to measure the potentials (see Reference 2 for more information). Analyze the trends in your data and the quality of your least-squares fits. How does derivatization affect the energies of the orbitals? Can you rationalize the results using atomic trends? Discuss the basis for why the correlations are generally strong. Critically analyze all four sets of results. Which model, or models, best represent the trends in the experimental data? Should other calculations be carried out in addition to the ones used in your limited study and/or the Article? If so, which ones are most important to try?

In principle, computational methods could be used to calculate redox potentials from first principles by calculating the Gibbs free energy difference between the neutral and cation for each species (for example, see References 3 and 4). If you were to carry out such an investigation, describe how you would do it. What calculations are required? Which methods (and basis sets) would you choose, and why?

References:
(1) T. Suzuki, Y. Maruyama, T. Akasaka, W. Ando, K. Kobayashi, S. Nagase, J. Am. Chem. Soc. **1994**, *116*, 1359-1363.
(2) S.N. Smirnov, "Alternative Experiment #4: Cyclic Voltammetry", http://web.nmsu.edu/~snsm/classes/chem435/Lab13/. Accessed 6/27/2013.
(3) S.J. Konezny, M.D. Doherty, O.R. Luca, R.H. Crabtree, G.L. Soloveichik, V.S. Batista, J. Phys. Chem. C **2012**, *116*, 6349-6356.
(4) J.L. Palma and V.S. Batista, "Tutorial on Ab Initio Redox Potential Calculations," http://www.chem.yale.edu/~batista/CHEM505/redoxpotentials.pdf. Accessed 6/27/2013.