

Department of Chemistry
University of Massachusetts Amherst
Graduate Core Course I (891G): Physical/Organic Chemistry

Team Project #1

Due Friday 30 September 2011

Computational Chemistry

1. *Objective*: To perform a computational chemistry study on a question of your choice. You will write this up as a brief report (no longer than 4 pages, not counting references) in the form of a *Chemical Communications* article (see class website for two relevant examples of *Chem Comm* articles). In contrast to *Chem Comm* articles which lack sections, your report will have the following sections:

- Title and Authors
- Abstract
- Introduction (including relevant figures)
- Methods
- Results and Discussion (including relevant figures, tables, etc.)
- Conclusions
- References

As mentioned above, all content (except for References) must fit within 4 pages (1 inch margins, single spaced, 11 pt Times font).

2. *Approaches*: (for more info see: http://en.wikipedia.org/wiki/Computational_chemistry)

Question: First your team must develop a question to answer. For this class, your question should involve some aspect of Organic Chemistry. Your team should begin by considering broad themes such as molecular structure, molecular stability, reaction yield, reaction mechanism, etc.; then formulate a broad question related to your theme.

Molecules: Once your team has agreed on a broad question, your team must iteratively refine the question, making it successively more specific, until you can write down a collection of actual molecules to consider for the purpose of studying some trend. Only after you have a list of actual molecules to study is your question specific enough.

Properties: Once you have a list of molecules, you have to compute some properties. The properties you choose will be based on the specifics of your question. Properties may include: molecular electronic energy, molecular structure (bond lengths, angles, torsions, etc.), vibrational frequencies, electronic distribution (dipole moment, partial charges), HOMO-LUMO energy difference, etc. Only after you have a set of properties to compute can you even think about starting some calculations.

WebMO/Gaussian Calculations: The actual calculations you will perform will involve (approximately) solving the molecular electronic Schrödinger Equation using a program called Gaussian03, and using a “front end” called WebMO. WebMO is a web-based program (duh!) that helps you build a molecule (or molecules), set up input files, run calculations, and interpret results. The real computational “engine” though is Gaussian03, which solves the Schrödinger

Equation using various approximations such as “Hartree-Fock theory” (HF, mean field theory), density functional theory (DFT, usually better than Hartree-Fock with little to no extra expense), semi-empirical theory (very cheap calculation with unpredictable accuracy), etc. In general, these various “Levels of Theory” provide different treatments of electron-electron repulsions. Gaussian03 also contains a “force field” calculation (UFF) which for some problems (intermolecular forces, floppy molecules) can be a good way to generate useful starting geometries for subsequent refinement using higher levels of theory (e.g. HF or DFT).

Building Molecules/System Size: The TAs will show you how to build molecules during Recitation. If your molecules are pretty standard and not too big, you can build it using WebMO. If they are very complex with non-standard configurations, you may have to generate coordinates elsewhere and incorporate them into WebMO. Keep in mind that electronic structure calculations are ****very**** expensive, and you will have a limited amount of computer time to finish your work (4 hours/person or 16 hours total for a team with 4 people). For this reason, you should limit your system sizes to containing no more than 15 2nd row elements or 8 3rd row elements (we don’t count terminal hydrogens because they only have 1 electron). If you want to study something involving transition metals, then you can take 1 transition metal with 10 2nd row elements, or 1 transition metal with 5 3rd row elements. Bottom line: keep your systems as small as possible to keep the calculations tractable!

Setting Up Calculations: Here you need to make some choices about the charge of your molecule, the spin state (usually singlet but not always, especially for radicals), level of theory (HF, DFT, etc.), basis set (more on that below). In general, when it comes to choosing Level of Theory/Basis Set, you have two choices:

- Pick “model chemistry”: this means you choose a particular Level of Theory/Basis set (e.g., B3LYP/6-311G(d,p)) and stick with it for all your calculations, thus making sure that when comparing energies for different molecules, you compare “apples to apples.”
- Converge results: this means you use successively better Levels of Theory and Basis Sets until your property (best if it is an *energy difference*) stops changing, meaning you’ve found the correct result! This is very difficult, and only should be attempted for the simplest systems (with the fewest electrons). ***No matter what you do, you should always start with the simplest possible calculations, and work up to successively more demanding calculations; you should never do the other way around (think about why).***

Basis Set: This allows molecular orbitals to take many shapes, become extended (aka diffuse) in space, and allows many possible ways for the electron wavefunction to oscillate in space. Remember to begin with “cheaper” basis sets and work up to more expensive basis sets if you plan to converge your properties.

Interpreting Results: After your calculations are complete, you will have much molecular data to analyze. The electronic energies you will obtain are “total ionization energies,” i.e., the energy to completely ionize the molecule. Very rarely is this the process we seek to understand. But also remember that by computing energy differences (e.g., LUMO-HOMO, product-reactant, transition state-reactant, etc.) we can obtain quantities relevant to our questions.

You should think very hard about how all your numbers relate to your original question (don’t be afraid to ask for help here), and in general, whether computational chemistry helped to answer your question (sometimes yes, sometimes no, depending on the question).