

Written Report due Sunday, May 10, 5 PM

Oral Exams: May 11-13 by appointment

In additions to the exams and homework, I would like each of you to work on a computational project of your own devising. This project will entail the following:

- Identifying an *open* problem of interest *from the research literature*
- Developing a hypothesis regarding your problem
- Developing a computational strategy for testing your hypothesis
- Carrying out the necessary computations
- Reporting your work in a written document
- Defending your work and document in an oral exam

Because time is limited, a number of practical constraints will be observed.

Timing. I would like to meet with each of you between April 15-17 to discuss your problem, hypothesis, and computational strategy. Bring a copy of the research article on which your study is to be based. The two purposes of this meeting are to give you a chance to describe your project idea to me, and to give me a chance to keep you from working on a potentially impractical project. If you would like to meet earlier than these dates, that's fine. If you are have two ideas and aren't sure how to choose between them, that's fine too. I can help you choose.

Content. Your project should use the modeling skills that we have been practicing, i.e., the ability to calculate conformational preferences, reaction energies, and/or activation energies, to analyze structural motifs, to analyze frontier MOs and charge distributions. Your project should not require much beyond these skills.

Notice that this skill set can be applied readily to selectivity and reactivity problems, especially problems like, "why did only (or more of) this product form?", "why is this reactant more reactive than that one?", and, "why is this reactant conformer more reactive (or preferred) over others?" Notice too that all of these problems entail *comparisons*. Molecular models are always approximations, but if you use them to compare two closely related items, the approximations may not matter.

Computational practicality. The project should not demand modeling tools beyond HF/3-21G and even these calculations should not be too time-consuming.¹ Given these considerations, avoid projects involving the following:

- Species that contain a transition metal or main-group atom larger than Cl
- Excited state species
- Very large systems^{2,3}
- Reactions involving polar bond changes (nucleophilic addition/substitution, electrophilic addition, etc.). These are likely to show large solvent and ion pairing effects.
- Other systems likely to show large solvent effects

Significance. While it is essential to be practical, it is also important to have a project with real bite to it. Do not investigate anything that has already been the subject of a modeling study. You should investigate an “open” question, but don’t confuse “open” with “original”. If the authors of your research paper speculate about a particular problem, *but don’t investigate it computationally*, you can consider it open for study.

Step #1 - identify the problem. You may base your study on a paper that you have already read for this class or for your junior qualifying exam. *Organic Letters* is a good source of material because the papers are short. Pericyclic reactions lend themselves nicely to computational studies, but avoid metal-catalyzed reactions and photoreactions (see list of projects to *avoid* above).

Step #2 - clarify your thinking. Can you state your problem? (Write it down and show it to someone. Can they understand the project from what you have written?). What are your (or the authors’) ideas regarding the problem? Which molecules, and which properties of these molecules, will be definitive for resolving the problem? What additional concerns, such as conformational flexibility, assistance from catalysts, and so on, might need to be addressed? How do you propose to address these concerns? What kind of *supporting analysis* might be useful?

¹ I’m expecting you to perform most or all of the calculations during the last week or two of the semester and write your report during reading week.

² “Large” depends on the nature of the problem. For example, the calculation of reaction energies is much easier than the calculation of activation energies, so you can calculate reaction energies for larger molecules.

³ It is possible to convert a large system into a smaller one by “truncating” spectator groups. For example, one can often use a methyl group in place of a large complicated alkyl group. If you are unsure about what kinds of structural replacements might be acceptable, check with me.

Steps #3, #4, #5. After you meet with me and we agree on a computational strategy, you should perform the necessary calculations, analyze the results as thoroughly as you can, relate them to whatever experimental and theoretical literature is available, and write them up. *I encourage you to check back with me at any point in this process.*

Organize your report like a typical *journal* article.⁴ It must stand on its own. Dr. Jill Random must be able to pick it up, read it with total comprehension of the problem that interested you, what had been observed and thought previously by others, what work was performed by you, what observations you made, and how you interpreted your findings. Include a title, abstract, introduction, methods, results and discussion, labeled figures and tables, and references. Attach a copy of the research paper that your project is based on.

The results and discussion section should include a *supporting analysis*. By this I mean *additional* data that helps you *interpret* your models and boosts your *confidence* in them. For example, if you think a molecule is destabilized by, say, steric repulsion, describe structural evidence for this in the molecule's geometry. If you think a molecule is stabilized by conjugation, describe structural evidence (geometry or charge distribution) for this.

Don't skimp on this analysis. Remember one basic fact of life: bench chemists don't trust models. While they *may* agree that computer models are the best models we can make, and are better than any chemist's mental image or drawing, they won't hesitate to point out that models are always approximations and are inherently untrustworthy. This is where your supporting analysis comes in. If you can tie together several features of your models (energy + geometry + electron distribution + orbitals) that all point to a particular result, the internal consistency may overwhelm the greatest skeptic. At the very least, you can get your readers to believe that your results are something more than a cosmic computer joke.

How long should your report be? It is too short if it fails as a scientific document, i.e., if individual sections do not perform their intended functions. It is too long if it begins to suck up too much time. I expect the full assignment (find problem, perform calculations, write report) to be challenging, but not onerous. I don't expect it to dominate your schedule unless you procrastinate.

⁴ Please refer to the online article, **Journal articles – described** (Miscellaneous section of web site), that contains important statements about journal article writing from the ACS Style Guide.