

Final Project  
Due Sunday, May 11, 5 PM  
Oral Exams: May 12-14 by appointment

You will spend the rest of the semester working 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 must be enforced.

First, I would like to meet with each of you no later than Friday, April 25 to discuss your problem, hypothesis, and computational strategy. Bring a copy of the research article on which your study is to be based. The purposes of this meeting are 1) to give you a chance to clarify your thinking by describing it to me, and 2) to give me a chance to keep you from working on a potentially impractical project. I will have office hours from 10-11 AM and from 3-4 PM on Friday, but you are welcome to meet with me before then.

Second, the project should use modeling skills that you have already developed, 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.

These skills can be applied without great difficulty to at least two types of problems: product selectivity and reactant conformation. The first problem asks, “why did only (or more of) this product form?” The second asks, “why did is this conformer preferred? (Option: why is this conformer most reactive?) Another kind of problem you might examine: relative reactivity. Why is this compound more reactive than that one? 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.

Third, the project should lend itself to study by relatively approximate modeling tools such as HF/3-21G. Also, the computations should not be too time-consuming. With these factors in mind, I strongly recommend *against* projects involving the following:

- Species that contain a transition metal or main-group atom larger than Cl
- Excited state species
- Very large systems<sup>1,2</sup>
- 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

Fourth, while it is essential to have a practical project, it is also important to have a project with enough bite to it. Do not investigate anything that has already been the subject of a modeling study. The problem should be an “open” one. (Note: an “open” problem doesn’t have to be an “original” problem. 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.)

**The first step is to identify the problem you want to investigate.** You may you’re 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. Also,

**The second step is to clarify your thinking.** 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 and assistance from catalysts or solvent, might need to be addressed? How do you propose to address these concerns? What kind of supporting analysis might be useful?

The supporting analysis consists of *additional* data derived from your models (or possibly the experimental literature) that help you *interpret* your models and boost your *confidence* in your models. Do not skimp on this analysis.

The importance of a supporting analysis can be appreciated by remembering one basic fact of life: bench chemists don’t trust models. This view is simultaneously lamentable

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<sup>1</sup> “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.

<sup>2</sup> 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.

and laudatory. Computer models are the best models we can use. They are better than any chemist's mental image. They are better than any drawing. But models are approximations. We can't really trust them. This is where your supporting analysis comes in. If you can identify and describe several features of your models (energy + geometry + electron distribution + orbitals) that all point to a particular result, the internal consistency may build confidence in that prediction. At the very least, you can get your readers to believe that your results are something more than a cosmic computer joke.

**The final step is to write a report.** 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.

Your paper is not a homework exercise. It is not an email, or a response to something that I wrote or said. It must stand on its own as a scientific research report, i.e., Joe or Jill Random must be able to pick it up, (and assuming J.R. is a chemist) 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.

Write your report in *journal style*. Include a title, abstract, introduction, methods, results and discussion, and references. Attach a copy of the research paper that is the foundation for your project.

I haven't specified the report's length. I would say it is too short if it fails as a scientific document, i.e., if the individual sections do not perform their intended functions. By the same token, I would say a report (or project) is too long if it begins to suck up too much of your time. Given the time frame, I expect this assignment (finding a problem + performing the calculations + writing the report) to be challenging, but not onerous. I don't expect it to dominate your schedule unless you neglect it.

The American Chemical Society has produced a *Style Guide* that explains the purpose of a title, abstract, and so on. I have placed excerpts on line in the Miscellaneous section of the course web site. Please refer to it whenever you have questions about what goes where.