# Computational Chemistry Final Project

One of the goals of the problems sets I have assigned has been to give you a sense of the breadth of quantum chemistry.  We can predict geometries, vibrational frequencies, NMR chemical shifts, relative stabilities of families of isomers, activation energies, and reaction energies for organic, inorganic, and organometallic systems.  With contemporary methods, we can generate reasonable predictions for literally any small molecule or complex one could imagine.  This enables us to go well beyond what is known experimentally, and it can guide future experimentation.  Moreover, if we use methods of sufficient rigor, we can predict properties as accurately, or more accurately, than experimental measurements.  This is especially true for short lived and/or dangerous species.  In short, while we have not seen all that chemists do with computation nowadays, we have nonetheless seen a lot.

We will spend the last half of the semester working on projects of your own choosing.  You are free to choose any subject to which the quantum chemistry you have learned can be meaningfully applied.  (So this does exclude studying systems like enzymes, which are too large for a fully quantum mechanical treatment.)  Perhaps one of the problem sets has inspired you to explore a topic in greater detail, or the experimental research you or your classmates have done lend themselves to computational exploration.  I have some suggested topics on Page 2.

But first, here are the parameters for your project:

- You must base your work on at least one article from the primary chemical literature. The paper can be experimental or theoretical, or both (combinations are common nowadays).  You are encouraged to try to reproduce theoretical results reported in the article, but you must make new predictions as well, either by applying the same method to new systems or new methods to the same systems.  (When you write your paper and present your talk, you must use at least two other references not counting web sites.)

- Every person must base his or her work on a different article from the literature.  (You are, of course, encouraged to help one another with all aspects of the project.)  First come, first served: the first person to submit a proposal on a particular paper lays claim to it.

- At least one of your predictions must be tested against experimental data (which can be found at http://cccbdb.nist.gov, among other sources.)  However, do not be cramped by this!  While computational studies should validate their methodology against experiment, they should also make predictions that may not be verified for years to come.

- Do not worry about what specific methods you should use.  I will recommend levels of theory and basis sets appropriate to the systems you wish to study.

- You must provide at least some qualitative discussion of your computed results.  This could involve periodic trends, Lewis structures, simple molecular orbital arguments, rationalizing systematic errors in your predictions as compared to experiment, etc.  (In

other words, provide the same kinds of discussion I have tried to exemplify in lecture and in the problem sets.)  What I want you to avoid is merely tabulating numbers and calling it good!  Good computational chemistry is not just numbers!

Here are some suggested topics (somewhat biased by my personal scientific history):

- Explore how mineral acids can help stabilize the transition structures of atmospheric chemistry reactions: Robert J. Buszek, Amitabha Sinha, Joseph S. Francisco. "The Isomerization of Methoxy Radical: Intramolecular Hydrogen Atom Transfer Mediated through Acid Catalysis." *Journal of the American Chemical Society* **2011**, *13*, 2013-2015.  (Professor Francisco just completed a term as President of the American Chemical Society.)

- Test the ability of quantum chemical methods to predict the relationship between NMR chemical shifts and protonation states, using as your departure point this recent work from Professor Hoye's laboratory:  Rebecca C. Hoye, Gretchen L. Anderson, Susan G. Brown, Erica E. Schultz. "Total Synthesis of Clathculins A and B." *Journal of Organic Chemistry* **2010**, *75*, 7400-7403.

- You all love performing calculations on clusters, right?  Extend this recent study by a former scientific competitor of mine, Professor James M. Lisy of the University of Illinois at Urbana-Champaign: Oscar Rodriguez, Jr., James M. Lisy. "Infrared Spectroscopy of $Li^+(CH_4)_1Ar_n$, $n = 1-6$, Clusters." *Journal of Physical Chemistry A* **2011**, *115*, 1228-1233.

- Predict the properties and combustion enthalpies for some highly explosive molecules: Tobias Fendt, Niko Fischer, Thomas M. Klapotke, Jorg Stierstorfer.  "N-Rich Salts of 2-Methyl-5-nitraminotetrazole: Secondary Explosives with Low Sensitivities." *Inorganic Chemistry* **2011**, *50*, 1447-1458.

- Test the ability of different quantum chemical methods to predict bond dissociation energies for oxygenated free radicals, important (and often dangerous) intermediates in atmospheric and combustion chemistry: Stephen J. Blanksby, G. Barney Ellison. "Bond Dissociation Energies of Organic Molecules." *Accounts of Chemical Research* **2003**, *36*, 255-263.

Here are some key websites for searching the chemical literature (on the Macalester network):

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http://pubs.acs.org/index.html

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This site gives you access to every article published by the American Chemical Society since the 19th century! (This includes five of the six articles listed above.)  Moreover, the entire contents of every article are fully searchable.  This is a very powerful resource.

http://www.isiknowledge.com/WOS

This site lets you search virtually all of the chemical literature published since 1900. This includes many journals for which Macalester does not have a subscription.  If the article is published by a journal owned by Elsevier (such as *Chemical Physics Letters*), I can get a copy for you.  Elsewise, you can use interlibrary loan to request a copy.

## Project Timetable: What you have to do, and when!

- Tuesday, March 22: Turn in a brief proposal that (1) cites the article you have chosen, (2) summarizes this article, (3) outlines what kinds of calculations you will be doing, and (4) discusses what your scientific goals are for your project.  This should require no more than one page of writing.  You are encouraged to consult with me in person and/or by e-mail before you turn in your proposal.  Again, if you are eager to lay claim to a particular paper, turn in your proposal before March 22.

- Tuesday, April 5: Give a five-minute introduction to the class of your topic, and how your calculations are progressing.

- Tuesday, April 19: Turn in a first draft of your paper.  I do not expect you to have completed all your calculations by this date, but your draft should resemble the final paper as much as possible.  (Actually, it is normal for chemists to start writing a paper before all the data have been collected precisely to clarify what further experiments and calculations need to be done.)  My expectations for your paper are discussed below.  The more work you do at this point, the better the feedback I can offer you before you turn in the final draft of your paper.

- Tuesday, May 3: Give a 20-minute oral presentation during class.  My expectations for your talk are discussed below.

- Friday, May 6: Turn in the final draft of your paper.

## Paper Expectations

The general format is the same followed for Physical Chemistry I lab reports.  Here are the details: Your paper should contain each of the following sections, in the order given: Title, Abstract, Introduction, Procedure, Results and Discussion, Conclusions, Acknowledgment, References [and optional Appendix].

The **Title** should be specific and descriptive, but not overly long.

The **Abstract** should, in fewer than 150 words, summarize the entire work: the purpose, procedure, key results, and their significance should all be **briefly** addressed in this essential part of your paper.  The Abstract is not the place to introduce your calculations or describe the background in great detail.  Stated in another way, the paper really begins with the Introduction, not the Abstract.  Most scientists write the Abstract after they have written the rest of the paper,

since it *summarizes* the work described.  <u>Never</u> present material in the Abstract that you have not also presented somewhere in the main body of the paper.

The **Introduction** should present the scientific motivation and background for your project.  At a minimum, you should discuss the article from the chemical literature that inspired your study, as well as insights gained from two other sources, <u>not counting web sites</u>.  In this section you must also state clearly what the goals of your project were.

The **Procedure** should provide a <u>concise</u> description of the types of calculations you performed (*e.g.* locating transition structures by interpolation), what level(s) of theory you used (*e.g.* B3LYP) and what basis set(s) you used (*e.g.* 6-31G(d)).  You should cite *Gaussian 09* (see the raw output for citation information) and *WebMO*, but you do not need to cite any references for your methodology.

The **Results and Discussion** section presents the key numerical results, comparison to experimental measurements whenever possible, and your interpretation of the results.  Present your results in tables or graphs as much as possible.  I also encourage you to use Chem Draw both to show molecular structures and to construct diagrams.  Three-dimensional renderings (in color) of molecules may also be appropriate, especially for your talk.  It is appropriate here to discuss any problems you had in your calculations, and what you did to (try to) fix these problems.  As I discuss above, it is essential that you provide some qualitative discussion of your numbers.  You should draw on other references to help you interpret your data.

The **Conclusions** section should summarize what you have accomplished in your project.  Unlike the **Abstract**, the conclusion need not recapitulate every part of the paper.  This section also should contain reflections on what hypothetical future calculations would be useful or interesting.

The **Acknowledgment** section should thank every person who helped you with this project.

**References**:  You <u>must</u> cite all sources you have used except for course handouts.  Insert a superscript number the first time you cite a particular reference, and always use the same superscript number whenever you cite the same source in your report.  Instead of using footnotes, collect all citations in this final section.  Follow a modified version of the American Chemical Society's conventions:

- **Books without Editors**: Author 1, Author 2, Author 3, Author 4.  *Book Title*, number of ed.; Publisher: Place of Publication, Year; Number of Chapter(s) Cited.  For example:

  William L. Masterton, Emil J. Slowinski, Conrad L. Stanitski.  *Chemical Principles*, 5th ed.; Saunders: Philadelphia, 1980; Chapters 10-11.

- **Books with Editors**: Author 1, Author 2, Author 3, Author 4.  "Chapter Title."  In *Book Title*, number of ed.; Editor 1; Editor 2, Eds.; Publisher: Place of Publication, Year; Number of Any Specific Chapter(s) Cited.  For example:

  Jeffrey A. Norman, Mary K. Montgomery.  "RNAi and Cosuppression: Double-stranded RNA as an Agent of Sequence-Specific Genetic Silencing in Animal and Plants."  In *Molecular Biology of Double-stranded RNA*: *Concepts and Applications in Agriculture, Forestry, and Medicine.*  Stellos M. Tavantzis, Ed.; CRC Press: New York, 2001; Chapter 1.

- **Articles**: Author 1, Author 2, Author 3.  "Title of Article."  *Name of Journal* **Year**, *Volume*, Beginning – Ending Page.  For example:

  Keith T. Kuwata, Rachel I Erickson, James R. Doyle.   "Improved Interatomic Potentials for Copper and Aluminum Sputter Atom Transport Simulations."  *Nuclear Instruments and Methods in Physics Research B* **2003**, *201*, 566-570.

- **Web Sites:** Cite their URL.  Also note the last day you accessed the site.  For example:

  http://bcs.whfreeman.com/qca7e/ (accessed 2/26/2009).

An **Appendix** is not required, but it is a good place to place extra data that you should feel should be presented, but is too unwieldy to fit into the Results and Discussion section.

Finally, I have no absolute minimum or maximum length, but somewhere between 1500 and 2500 words should make the paper sufficiently detailed without being tedious.

## Talk Expectations

Prepare a formal PowerPoint presentation.  Follow the same structure that you use for your paper, except that you would not have an abstract.  Be prepared to answer questions from me and from your classmates after the talk.

<u>For your talk, I do have absolute time limits</u>.  It must be between 15 and 20 minutes, not counting time for questions.  Practicing the talk will enable you to fit it into the required length.

## Grading

Your work on this project will be graded out of 100 points, earned in the following ways:

| Max Points | Task |
|:---:|:---:|
| 10 | Proposal |
| 5 | Five-Minute Intro |
| 20 | First Draft of Paper |
| 25 | Oral Presentation |
| 40 | Final Paper |

As stated in the course syllabus, the final project is worth 35% of your overall grade.