NSF Highlights

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Integrating Computational Chemistry into the Physical Chemistry Laboratory Curriculum: A Wet Lab/Dry Lab Approach

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Computational chemistry has become an essential tool in many areas of chemistry. Yet real and perceived barriers have slowed its widespread inclusion in the undergraduate chemistry curriculum. Barriers include cost, hesitation to add a new topic to a full curriculum, and concern about the breadth of the topic. At Grand Valley State University (GVSU), the first barrier was significantly lowered by the awarding in 1998 of an NSF ILI-IP grant[1] for the purchase of 10 Silicon Graphics workstations[2] and software.[3–5] The software and hardware allowed our students to perform a wide range of computational and molecular modeling tasks. With this equipment in hand we sought to learn how to use computational chemistry in a pedagogically effective manner in the undergraduate chemistry curriculum.

We concentrated our efforts in the physical chemistry laboratory, where we designed a set of computational ("dry") laboratories that are closely coupled to traditional ("wet") physical chemistry laboratories. This coupling of laboratories allows students to experience an experiment from a macroscopic, empirical point of view as well as on a more abstract, theoretical level that rigorously considers molecular-level events. The coupled wet/dry laboratory approach has students use the computational tools as they are most often used in the real world—to explore and support experimental results. Finally, this approach mitigates the problem of adding to a full curriculum because computational chemistry is used in such a way that it supports and enhances the traditional curriculum.

This article will describe our new physical/computational chemistry course, assessment of course efficacy, and changes we instituted to make the course structure more effective.

Course Structure

Physical chemistry laboratory at GVSU is a two-semester sequence, generally taken concurrently with the two-semester physical chemistry lecture course. The new physical/computational chemistry course sequence, inaugurated in 1998–1999, consists of four hours of laboratory per week. Several experiments have both a traditional physical chemistry bench component (the wet lab) and a computational chemistry component (the dry lab). Students work on either the wet or dry laboratory for one week, then do the complementary portion during the second week. There are also some investigations in which the wet and dry portions are uncoupled. In the first semester all students are required to take both the computational portion and the traditional laboratory portion of the course, attending lab for four hours per week. In the second semester the computational portion of the course is optional, so approximately 50% of the students attend only the traditional wet laboratory for four hours every other week. The wet/dry experiments are designed to fuse computational chemistry into physical chemistry in a manner that allows students to learn the software, visualize complex mathematics, and explore the strengths and weaknesses of computational versus experimental methods. Table 1 contains brief descriptions and comments on some of the coupled wet/dry experiments that we have used. Descriptions of all of the experiments done during both semesters are available in this issue of *JCE Online*.[W] One experiment, Thermodynamics of Cyclodextrin-Indole Inclusion Complexes *(1)*, is run as a culminating "mini-research" project that allows students to critically analyze and compare data from wet and dry experiments at a time when they have had enough experience in both methods to make meaningful comparisons.

The course is co-taught by two faculty members, one teaching the wet laboratory portion and the other the dry laboratory portion. These two faculty members work together to ensure that the links between the two parts of the investigations are explicit. It is a writing-intensive course and requires formal written laboratory reports that are expected to address the computational and the bench laboratory components of each experiment.

Calculations are performed on Silicon Graphics workstations with Cerius2 by Molecular Simulations Inc.[3] as the user interface. Each student is able to work at his/her own workstation. Cerius2 includes MOPAC 6.0.[4] Gaussian 94[5] was purchased separately. The Cerius2 interface supports MOPAC, Gaussian, and molecular mechanics and dynamics, so students need learn only one user interface.

Assessment

How does one best use computational chemistry to teach undergraduates? Henderleiter performed an in-depth assessment of the new physical/computational chemistry course in order to help answer the question in the context of our course. She interviewed students in the course several times throughout the year and made classroom observations of the laboratories. The interviews and observations, coupled with instructor and student comments and course evaluations, led to improvements in course structure.

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Changes in Course Structure

One change involved the order in which lecture and laboratory topics were presented. When the physical/computational chemistry course was instituted in 1998, thermodynamics and kinetics were taught first semester and quantum mechanics and spectroscopy were taught second semester. However, many of the coupled wet/dry laboratories in the first semester relied on quantum mechanical methods, causing an obvious teaching dilemma. Students were forced to use the quantum mechanical programs in a "black box" kind of way. The following year, the topic order was changed so that quantum mechanics and spectroscopy are now taught before thermodynamics in both the lecture and laboratory curricula. This change has offered additional pedagogical benefits. It is now easier to invoke elementary statistical mechan-

ics as the basis for traditional (macroscopic) thermodynamics. In fact, one of the dry laboratory exercises (a molecular dynamics simulation of a box of argon atoms) helps tremendously to make the link between statistical, atomic-level events (quantum mechanics, statistical mechanics) and macroscopic observables (thermodynamics) clear and intuitively accessible to the students.

The second major change involved a restructuring of the laboratory meeting times. The course was originally designed to meet for four hours per week, with wet and dry laboratory exercises alternating weeks. However, it was found that working with the computers for four hours every other week was insufficient for students to remember keystrokes and processes needed to solve problems. To address this concern the laboratory meeting schedule has been modified. The wet laboratory still meets every other week

Table 1. Examples of Coupled Wet/Dry Experiments

Bench Laboratory	Computational Laboratory	Comments
Absorption of conjugated dyes (4)	Conjugated dye HOMO–LUMO energy gaps (2, 3)	Compare computed λ_{max} values to bench laboratory results. Semi-empirical calculations predict trend in λ_{max}, but not absolute magnitude. Explore meaning of $L_{effective}$ of conjugated π system. Compare particle-in-box model with semi-empirical MO model. Visualize molecular orbitals.
Infrared spectra of HCl/DCl (4)	Vibrational normal modes (2, 3)	Very comparable bond lengths and vibrational frequencies. Animation of normal modes for more complex molecules is also included.
Absorption/emission spectra of molecular iodine (4)	Diatomic potential energy curves (2, 3)	I_2 potential energy curve calculated via Hartree–Fock (LANL2DZ basis set) predicts bond length and strength in the ground state but does a poor job in excited state. Calculate Franck–Condon factors using potential energy curves based on literature parameters.
Kinetics and mechanism for the halogenation of acetone (5)	Transition state searching (2, 3)	The computationally predicted rate constant is poor, but the exercise helps conceptual understanding of transition state. Transition state is tracked to products and reactants.
Bomb calorimetry and heats of combustion (4)	Combustion of formaldehyde (2, 3)	Heats of combustion improve with better ab initio methods, though error is 10%.
Thermodynamics of cyclodextrin–indole (1)	Binding free energy of cyclodextrin–indole (2, 3)	Computationally determined absolute binding Gibbs energies are poor, but relative binding Gibbs energies are comparable to experimental results. Visualizing binding geometry very effectively helps students understand steric interactions, hydrogen bonding, and the effect of solvent environments.

for four hours. The dry laboratory now meets for three hours every other week, opposite the wet laboratory. The students return to the computational chemistry laboratory on their "off" (wet laboratory) week to complete a one-hour assignment. This assignment closely duplicates the previous material in terms of methods and molecules used.

Several of the computational experiments allow the students to work with "realistic" 3-dimensional images of molecular orbitals, normal modes, and molecular transition states.

Henderleiter continues to assess the effects of the 3-dimensional images on students' conceptual understanding of abstract concepts such as wave functions and reaction mechanisms. However, it is clear that these images open up an avenue for these students to think more deeply about the physical meaning of the abstract mathematical concepts they study in lecture.

Results

Our students experience computational chemistry integrated tightly with bench chemistry in the physical chemistry laboratory sequence. Several students have done computational research or smaller computational projects for other professors as a result of this experience. The coverage of computational methods in lecture has been expanded due to the students' familiarity with it from laboratory. Some student comments have indicated that computational laboratory helped them with lecture concepts, although other students indicate that the links need to be made even more explicit. An effective course structure and sequence has been developed for incorporating computational chemistry into the curriculum. We plan to use what we have learned about "what works" in the physical chemistry laboratory course as we incorporate computational chemistry into other areas of our curriculum.

ᵂSupplemental Material

Supplemental material describing the wet and computational laboratory exercises in more detail is available in this issue of *JCE Online*.

Notes

2. Silicon Graphics O2, IRIX OS from SGI, 1600 Amphitheatre Parkway, Mountain View, CA 94043; *http://www.sgi.com* (accessed Mar 2004).

3. *Cerius2 User Guide*, Versions 3.9–4.2. Molecular Simulations Inc.: San Diego, CA, 1997. (Molecular Simulations, Inc. was renamed Accelrys, Inc.; they continue to publish Cerius2.)

4. Stewart, J. J. P. *MOPAC93*; Fujitsu Ltd.: Tokyo, 1993. MOPAC6 and MOPAC7 are public domain programs developed and maintained by J. J. P. Stewart and distributed by the Quantum Chemistry Program Exchange, Bloomington, IN.

5. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Jamieson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T. A.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Peng, C. Y.; Ayala, P. A.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. *Gaussian94*; Gaussian, Inc.: Pittsburgh PA, 1995.

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2. Foresman, J. B.; Frisch, Æ. *Exploring Chemistry with Electronic Structure Methods;* Gaussian: Pittsburgh, PA, 1996.

3. Hehre, W. J.; Shusterman, A. J.; Nelson, J. E. *The Molecular Modeling Workbook for Organic Chemistry*; Wavefunction Inc.: Irvine, CA, 1998.

4. Schoemaker, D. P.; Garland, C. W.; Nibler, J. W. *Experiments in Physical Chemistry*, 6th ed.; McGraw-Hill: New York, 1996.

5. Sime, R. J. *Physical Chemistry Methods, Techniques, and Experiments;* Saunders: Philadelphia, 1990.

In the NSF Highlights column, recipients of NSF CCLI grants share their project plans and preliminary findings. Mary E. Karpen, Julie Henderleiter, and Stephanie A. Schaertel are in the Department of Chemistry, Grand Valley State University, Allendale, MI 49501-9403; schaerts@gvsu.edu.