Student-led Computational Inorganic Chemistry Research in a Classroom Setting

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ABSTRACT

Advanced computational inorganic methods were introduced as course-based undergraduate research experiences (CUREs) through use of the National Science Foundation's Extreme Science and Engineering Discovery Environment (NSF XSEDE). The ORCA ab initio quantum chemistry program allowed students to conduct independent research projects following in-class lectures and tutorials. Students wrote publication-style papers and conducted peer review of classmates' papers to learn about the full scientific process.

Keywords

Computational chemistry, CURE, inorganic chemistry

1. INTRODUCTION

Undergraduate Research Experiences (UREs) have been shown to be beneficial for learning and retention [1], and science persistence rates for those who participate in UREs are 14-17% higher than for those who do not [2-4]. For small teaching institutions there are oftentimes not enough research positions for all students who are interested in UREs, so there is a need to provide other opportunities for students to have similar experiences. Course-based UREs (CUREs) have been proposed as an alternative, allowing research modules to be incorporated into a class to provide research experience to all students in the course [5]. Five specific components of a well-designed CURE include 1) Use of scientific practices, 2) Discovery, 3) Broadly relevant or important work, 4) Collaboration, and 5) Iteration. For a CURE to achieve similar benefits to learning and understanding as a URE, it should include student-led research modules and appropriate mentoring. A lack of mentoring and the short time-scale of coursework are the most common pitfalls in successful implementation of CUREs [1].

In the chemistry curriculum CUREs are oftentimes difficult to implement in a lecture-based course because laboratory experiments require specialized equipment, space, and have additional safety concerns. Computational chemistry offers a unique alternative because the safety concerns are mitigated, and computers can easily be implemented in a standard lecture class. Additionally, if computational chemistry modules are posted on the web, students can access content and conduct research from anywhere with an internet connection. Despite these advantages, there are few publically available computational chemistry CUREs. A semester-long course using WebMO is available [6], and two individual modules for organic and general chemistry have been published by Hope College. [7] Several modules focus on the introductory concept of valence shell electron pair repulsion (VSEPR) theory, so more advanced computational chemistry applications are of interest. Herein, a state-of-the-art quantum chemical computational CURE for an advanced undergraduate and Master's course is described.

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2. STRATEGY

2.1 Course structure

A newly developed CURE module was implemented in the course, Advances in Inorganic Chemistry (CHM 571 and 572), at Cal Poly Pomona (CPP) in Spring 2016 (6 students) and Fall 2017 (17 students). The course met twice a week for 1.5 hours during a 10-week quarter in a classroom with an individual PC computer workstation for each student. The general format of the course included a lecture the first day each week, and hands-on computational tutorials during the second class period. **Table 1** depicts the weekly schedule for the course. Although the course is offered as part of the Master's curriculum at CPP, advanced undergraduates also take the course and most students had not taken an inorganic chemistry course before.

Table 1: Weekly Schedule for Advances in Inorganic Chemistry, Fall 2017

Week	Type	Topic
1a	Lecture	Electron counting
1b	Lecture	Group theory
2a	Lecture	Molecular orbital theory
2b	Lecture	Density functional theory
3a	Lecture	Input files/geometry optimization
3b	Lab	Input files/geometry optimization
4a	Lab	Analysis of results
4b	Lecture	Crystallography
5a	Lecture	Infrared & Raman spectroscopy
5b	Lab	Vibrational frequency calcs.
6a	Lecture	Electron paramagnetic resonance (EPR) and magnetism
6b	Lab	EPR calculations
7a	Lecture	Moessbauer
7b	Lab	Moessbauer calcualtions
8a	Lecture	X-ray absorption spectroscopy (XAS) and time-dependent density functional theory (TD-DFT)
8b	Lab	TD-DFT and XAS calculations
9a	Lecture	X-ray emission spectroscopy (XES)
9b	Lab	XES calculations
10a	Lab	In-class peer review
10b	Lecture	Responding to peer review

The first two weeks comprised of a brief introduction to organometallic and inorganic chemistry to ensure that all students had a basic understanding of metals, d-orbitals, counting electrons, and symmetry. The computational component began in the fourth class meeting with a lecture introduction to density functional theory. For the rest of the quarter, a lecture was generally given the first day of the week to introduce a new spectroscopy and the computational method for calculating spectra.

2.2 Implementation of computational modules

2.2.1 Computational resources

Prior to the start of the course, 50,000 SUs of computational resources on the Gordon compute cluster and 500 GB of storage were requested and received from the National Science Foundation's Extreme Science and Engineering Discovery Environment (NSF XSEDE). On the first day of class, students were instructed to create user accounts as homework using a self-guided tutorial. The classroom contained 30 PC workstations for students to use. All students had personal laptops for conducting research projects from home, however students could also use the classroom computers outside of class.

2.2.2 Programs used

All programs used in the course are free for academic use. The ORCA ab initio quantum chemistry program [8] was used for all computational modules in this course. Additional support programs included WinSCP (PC) and Cyberduck (Mac) for file transferring, Avogadro for molecular visualization and centering, and Chimera [9] for visualization of orbitals. Excel was also used for plotting calculated spectra.

2.2.3 Tutorials

Step-by-step tutorials were developed as text documents with screen shot images to guide students through all of the computational techniques listed in the lab sections of **Table 1**. During class, students worked through the tutorials and the instructor was available to help. The tutorials were posted through the class Blackboard site to ensure that students could remotely access the tutorials as needed.

2.3 Independent research projects

2.3.1. Independent projects

Independent research projects were designed to incorporate all 5 areas of a well-designed CURE. In particular, a goal was to teach students the full scientific process including project proposal, project implementation, paper writing and peer-review. By week 3 of the course, students were required to submit a project proposal for a project that they would complete during the course of the 10-week quarter. In total, there were 7 project components (I-VII) that students turned in. This framework fulfilled CURE area 1) Use of scientific practices.

2.3.2 Proposal

The proposal (component I) included searching the inorganic and organometallic chemistry literature for complexes containing first row transition metals that had been crystallographically characterized. The complex should also have experimental data available for one of the types of spectroscopy addressed in class, but have no computational studies. Students each proposed four complexes, of which the instructor chose one for the student to study. Having the instructor choose the ultimate complex for study avoided problems resulting from systems that would be too complicated. Many students also had difficulty assessing whether or not calculations had been previously published, so the instructor could omit those. This project proposal fulfilled CURE area 2) Discovery.

2.3.3. Independent research

The independent research each student conducted included conducting a geometry optimization, generating a d-orbital splitting diagram (Fig. 1), and calculating one spectrum (Fig. 2). From the geometry optimization, students compared their calculated to experimental bond distances and angles to assess the validity of their computational model. The spectrum they calculated was compared to the experimental data. When students finished the in-class tutorials teaching a new computational method, they had time to work on their independent projects. The rest of the project was completed as homework. Although only a geometry optimization and one spectroscopic calculation were required for the final project, most students practiced each new method on their research complex. The research component fulfilled CURE areas 1) Use of scientific practices, 2) Discovery, and 3) Broadly relevant or important work.

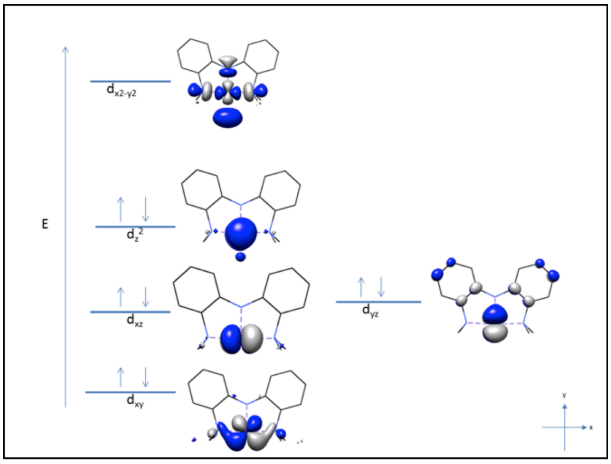

Figure 1: Qualitative *d*-orbital splitting diagram from a geometry optimization generated by a student in the course for ($^{Me}N_2N$)Ni-H [10].

2.3.4. Publication writing

In order to facilitate reasonable progress in the research project and writing, a series of due dates were set for specific project components I-VII. Students were also told that they could turn in assignments early for additional feedback. In week 5, students submitted a geometry optimization check (component II) with their input files and an expected d-orbital splitting diagram. This ensured that errors in coding could be addressed early on. In week 7 the paper introduction and results section (component III) for the geometry optimization were due. This included a comparison of experimental and calculated bond distances and angles, and a d-orbital splitting diagram. In week 8, the methods section and analysis of spectroscopic properties (component IV) were due. In week 9, a final draft (component V) was given to a peer reviewer. In week 10 the peer review (component VI) was due, and in finals week the final project (component VII) was due. This fulfilled CURE area 5) Iteration.

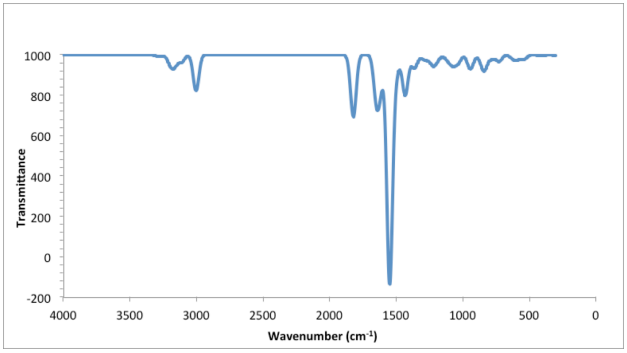

Figure 2: Calculated infrared spectrum for ($^{Me}N_2N$)Ni-H, generated by a student in the course.

2.3.5. Peer review

The final component of the project was to learn about the peer review process by conducting an in-class peer review. The instructor distributed student papers to other students in the course, making sure to omit names and assign papers to classmates who were not sitting near each other. The instructor gave a brief introduction to peer review and utilized a published paper with posted reviewer comments for students to see what real reviewer responses look like [11]. Most students did not actually know what peer review really meant, and how formalized of a process it was. At the end of the class period, students had the chance to ask the instructor clarifications about the paper. Students had one day to write their formal peer reviews so the instructor could return the reviews to the student authors. The following class period, students received their peer review comments and could ask the instructor for advice. The peer review fulfilled CURE area 4) Collaboration, although this CURE area was also achieved throughout the course because students oftentimes worked together on the tutorials.

3. ASSESSMENT

3.1 Assessment strategy

3.1.1. Course assessment

Students performance in the course was assessed through homework, in-class quizzes and the final research project. Since students had varying degrees of chemistry experience and most had not taken inorganic chemistry, the course was designed to be project-based.

3.1.2. Homework

There were eleven homework assignments to give students practice in basic inorganic chemistry. The areas of focus were electron counting and group theory. The group theory assignments were based on completion of self-guided programs using Alan Vincent's book, Molecular Symmetry and Group Theory: A Programmed Introduction to Chemical Applications.

3.1.3. Quizzes

Five in-class quizzes were distributed throughout the quarter. The first three tested basic inorganic chemistry concepts including electron counting and group theory. Because the group theory homework could only be assessed based on completion due to the nature of the programs, quizzes tested the students' understanding of group theory. The last two quizzes tested knowledge of the ORCA input and output files, respectively. The averages for quizzes were typically between 76 – 80% (n = 17).

3.2 Final project assessment

The final project comprised of 40% of the final grade. Of this, the grade distribution for each of the components was 40% for components I-V, 20% for component VI, and 40% for component VII. Components I-V were graded based on effort and completion to ensure that students were learning. This gave students the opportunity to work on their writing and receive detailed feedback from the instructor without worrying about whether the answer was "right" or not. In particular, since research does not always have a defined answer, this was a valuable approach for students to learn and gave them ownership and taught independence. Component VI, the peer review, was a significant component of the grade to ensure that students took the process seriously and wrote thoughtful reviews. Component VI was graded on completion, level of thought and thoroughness. The final project component VII was graded based on quality of research and writing. Most students made vast improvements in their writing over the course of the quarter and submitted research projects that were of very high quality. The average grade for this component was 91% (n = 17).

3.3 Course assessment

3.3.1. Evaluation of success

Students were highly engaged in the course and were very positive in both informal and formal evaluations. Formal university evaluations resulted in scores of "very good" and "good" (the highest possible) for all thirteen categories that were questioned in both years the course was taught. In particular, questions included "instructor presents material in an interesting manner," and what is your overall rating of the instructor in this course?" Informal interactions with students during office hours gave the impression that students had to work a lot, but they felt like they were learning so much that the time was worth it. Students reported being very excited to conduct their own research projects and do work that no one in the world had done before. They also remarked upon their own improvements in writing, and were excited by their progress. Perhaps the most indicative indicator of success of the course was that one out of six students in the first year of the course continued to use ORCA and XSEDE for his own computational research, taught his whole group how to use these, and applied for XSEDE resources with his PI. In the second year of the course, two out of seventeen students joined the instructor's research group and began computational research projects, and one additional student in a synthetic research laboratory used ORCA to calculate the compounds he was making.

3.3.2. Lessons learned

Students were very interested in conducting original research projects and doing calculations that had never been done before. As such, most students were highly motivated to learn and do a good job. It was impressive that students were able to learn such advanced computational techniques over a short period of time (10 weeks) and write such high quality research papers.

What was perhaps most surprising was the limited computer literacy of many students. In the first year of the course only one

student (n = 6) had used the command line, and in the second year none had (n = 17). As such, on the first computational lab day of class, a significant amount of time needed to be spent on basic command line and linux commands. Several students were also not familiar with computer file structures and did not know how to locate the C drive or search for files. Future iterations of the course will include additional command line tutorials to be completed as homework. With regards to writing, at least half of the students were not comfortable with basic formatting using Microsoft Word, including adding footnotes or references and figures. In the future, students will be directed to additional tutorials to learn formatting. The second year the course was taught, there was a TA who had taken the course in the previous year and was of significant help during the computational lab tutorials.

3.3.3. Reproducibility and recommendations for implementation

The course has been taught twice at CPP and student responses to the course were highly reproducible and favorable. The overall structure of the course and research project is a model that could be applied for a wide range of topics. Although computational inorganic chemistry is highly specialized, the general structure of the research project could be implemented for any type of computational project. For example, the research project proposal and writing components were implemented as a literature review project in an advanced Metals in Biology course in Spring 2017. A TA or student helper with command line experience is strongly recommended for classes with more than 10 students.

3.3.4. Relevance to workforce training

This course taught computational inorganic chemistry methods that are used by active research groups throughout the world and are at the forefront of the field. A course of this type is entirely unique and teaches students computational methods that they would normally only learn through a Ph.D. research program. Additionally, this gave students a research experience and confidence in using free software for conducting calculations of chemical systems, which they could apply to a variety of future careers. The strong focus on writing will benefit students in any future endeavor.

4. CONCLUSIONS

Computational inorganic chemistry techniques using density functional theory were taught in a 10-week lecture course through the use of a CURE. The course was taught in a lecture and tutorial lab format, and students conducted original self-designed research projects. The research projects included a proposal, a paper and a formal peer review process, allowing students to experience the full scientific process. Overall, student responses to the course were highly favorable, and several students continued to use the computational programs, methods and XSEDE resources after completion of the course.

5. ACKNOWLEDGMENTS

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