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Quantum chemical exercise linking computational chemistry to general chemistry topics

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Abstract:
Students in a second semester general chemistry course used quantum chemical calculations to investigate and reinforce general chemistry concepts. Students explored the isomers of hypochlorous acid, made predictions of miscibility via dipole moments calculated from *ab-initio* means, experimentally validated/disqualified their miscibility predictions, and used molecular models to visualize intermolecular attraction forces between various compounds. Student responses in pre-/post-exercise assessments show evidence of student learning. Responses in pre-/post-exercise surveys showed an increase in student understanding of basic concepts and of the importance of quantum mechanics in common general chemistry topics.

Keywords: computational chemistry, first year undergraduate/general, hydrogen bonding, Lewis structures, molecular modeling, noncovalent interactions, physical chemistry, problem solving/decision making, quantum chemistry, theoretical chemistry

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Introduction

The inclusion of modern computational chemistry into the undergraduate curriculum is necessary to bring students to the forefront of the field of chemistry. While there is an ever-increasing number of exercises being introduced that incorporate computational chemistry, very few of these experiments are introduced to college freshmen in general chemistry courses (Cody & Wiser, 2003; Feller, Dallinger, & McKinney, 2004; Ochterski, 2014). Exercises connecting the results of computational chemistry and more traditional physical experimentation, or exploring possible avenues combining the two, are also few in number with most conducted in upper-level courses (Adams & Sonntag, 2018; Albrecht, 2014; Hein, Kopitzke, Nalli, Esselman, & Hill, 2015; Hill et al., 2014; Mazzuca, Downing, & Potter, 2019; Peterson & Pullman, 2016; Simpson & Izydorczak, 2018; Simpson, Autschbach, & Zurek, 2013). Resources for the use of DFT computational outputs to explore organic structures in the high-school curriculum have recently been reported (Zdanovskaia, Schwarz, Habib, Hill, and Esselman 2018).

One of the major difficulties in teaching molecular modeling to students in general chemistry is the lack of connection between the topic and real-world applications. Many general chemistry textbooks state that the molecular structure is important to determine properties of these compounds, but few students grasp this (Lazenby, Rupp, Brandriet, Mauger-Sonnek, and Becker 2019). Therefore, we have developed an exercise that allows students to calculate properties using quantum chemistry and connect these concepts to a physical experiment.

Herein, we describe and evaluate a dual experimental-computational exercise conducted in a second-semester general chemistry course at St. Bonaventure University. In the Supporting Information, we provide exercise materials, student handouts, grading rubrics, a pre-/post-exercise assessment, a pre-/post-exercise survey, notes for the instructor, and optimized coordinates for use by instructors.

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Experimental overview

The exercise was conducted in our second semester CHML102: General Chemistry II Laboratory course in one four-hour lab period. Five laboratory sections with approximately 12–20 students per lab section conducted the experiment. This experiment was conducted after the topics of molecular orbital theory and intermolecular attraction forces were covered in lecture. At St. Bonaventure the laboratory course is a separate 1-credit hour course (CHML 102) from the 3-credit hour lecture course (CHEM 102). The material corresponding to this exercise overlapped with the lecture material, with the first introduction of the material being conducted in the lecture course.

The open-sourced General Atomic and Molecular Electronic Structure System (GAMESS) (Schmidt et al., 1993) quantum chemical software package was utilized in this experiment. In conjuction with GAMESS, the web-based WebMO (Schmidt & Polik, 2013) software package was used. WebMO provides a simple graphical user interface (GUI) that allows students to construct/edit molecular models and submit calculations to an external computer cluster. A free version of WebMO is available, however we elected to use the proprietary Enterprise Version in order to use the queueing system implemented on our computer cluster. The Beowulf computer cluster utilized in the experiment was equipped with four Dell PowerEdge R300 servers. These servers were equipped with quad-core processors and 16 GB of RAM. Student wait times for the most computationally expensive calculations were on the order of seconds.

The exercise was comprised of three parts:

- Part A: Students were asked to determine the lowest energy structure for hypochlorous acid (HClO) using the WebMO graphical user interface, GAMESS, and Hartree-Fock (HF) Theory. Students worked individually in this section.
- Part B: Students were asked to draw the Lewis structures of various compounds and determine the dipole moment of these compounds from their HF optimized structures. From this computed information, students were asked to predict the miscibility of the solvents based on the adage “like-dissolves-like” and then experimentally determine these miscibilities. Students come to the conclusion that this general rule is not always followed. Students worked in pairs in this section.
- Part C: Students were asked to determine the binding energy (BE) to gauge the strength of different intermolecular attraction forces using the WebMO graphical user interface, GAMESS, and the post HF method second-order Møller-Plesset model (MP2). MP2 is more computationally expensive than HF but is required for this section as HF completely ignores electron correlation, which is necessary to describe dispersion interactions (Grimme, Hansen, Brandenburg, & Bannwarth, 2016). Students worked individually in this section.

Atomic coordinates of optimized structures are included in the Supporting Information (SI). Vibrational frequency calculations were conducted to confirm that each structure was a minimum on the potential energy surface.

The effectiveness of this exercise was assessed by administering an assessment of student learning of the content and a survey that evaluated student perceptions of the quantum chemistry topics. The students completed the same written assessment and survey before (pre), immediately after (post), and five weeks after (long-term) the exercise. The assessment responses were graded as either correct or incorrect with no partial credit given. The survey responses were an ordinal scale in increments of one ranging from one (strongly disagree) to ten (strongly agree). To determine statistically significant trends in these non-parametric and ordinal data from the survey, the Wilcoxon signed rank test was utilized. All statistics were determined using the stats package in R version 3.6.0 “Planting of A Tree” (2019-04-26).

Hazards

The computer-based portions of the experiment (Parts A & C) have no associated hazards. Goggles and gloves should be worn throughout Part B while using these solvents which have the following associated hazards. When using acetone, avoid breathing vapors, mist, or gas. Ensure adequate ventilation. Acetone is a highly flammable liquid and vapor, therefore, it should be kept away from all ignition sources. It is also toxic if swallowed and should not be consumed. Methanol is a highly flammable liquid and vapor therefore it should be kept away from all ignition sources. It is also toxic if swallowed and should not be consumed. Ethanol is a highly flammable liquid and vapor, therefore, it should be kept away from all ignition sources. 1-propanol is a highly flammable liquid and vapor, therefore, it should be kept away from all ignition sources. It may cause drowsiness or dizziness. Ensure adequate ventilation. 2-propanol is a highly flammable liquid and vapor, therefore, it should be kept away from all ignition sources. It may cause drowsiness or dizziness. Ensure adequate ventilation. Ethylene glycol is harmful if swallowed.

Avoid breathing vapors, mist, or gas of tetramethylsilane (TMS). Ensure adequate ventilation. TMS is extremely flammable and all sources of ignition should be removed and should be stored in a cool, well-ventilated place. Ethyl acetate is a highly flammable liquid and vapor, therefore, it should be kept away from all ignition sources. It may cause drowsiness or dizziness. Ensure adequate ventilation. Cyclohexane is a highly flammable liquid and vapor, therefore, it should be kept away from all ignition sources. It may cause drowsiness or dizziness. Ensure adequate ventilation.

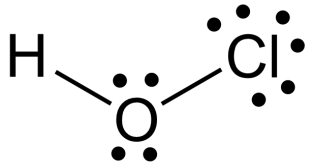
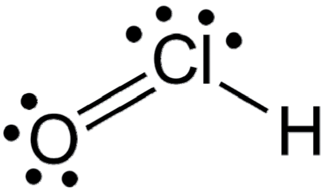
Results and discussion

Experimental results

Part A – which is the correct Lewis structure?

In this section, students conducted geometry optimizations on two of the possible isomers of hypochlorous acid. From the results of these outputs (see Table 1), students determined which of the plausible isomers was the minimum in energy and therefore more likely structure of the acid in the gas phase. The goals of this section were: (1) to familiarize students with using WebMO/GAMESS, (2) to familiarize students with retrieving results from the outputs of the calculations, (3) to provide students with an exercise in unit conversions from Hartree (au) to kJ/mol, (4) to provide students with an exercise in “meaningful” digits that are the result of quantum chemical calculations, (Hoffmann, Schleyer, & Schaefer, 2008) (5) for students to understand what is meant by the term relative energy (E_{rel}), and (6) demonstrating that the rules for choosing the best Lewis structure agree with the computational result. Success in Part A relates directly with student issues using the program throughout the experiment. It is suggested that the students to review with the instructor which isomer is lower in energy.

Table 1: Determining the correct lewis structure.

Structure	Energy, kJ/mol	$E_{rel,}$ kJ/mol
	−1404228	0
	−1403942	286

The major student errors in this section stemmed from understanding that the lower in energy system was the system with the most negative energy. Some students would consider the magnitude of the energy rather than the actual value of the energy. For example, students would incorrectly assume the energy of structure 2 in Table 1 to be lower in energy due to the fact that the magnitude of the energy of structure 2 is smaller than the magnitude of structure 1. However, the energy of structure 1 is more negative making it lower in energy than structure 2.

The relative energy (E_{rel}) was calculated by:

$$E_{rel} = E_{isomer} - E_{min} \tag{1}$$

where E_{min} is the energy for the lowest-energy structure and E_{isomer} is the energy of the isomer in question. According to our post-assessment, the majority of students determined the correct structure to be lowest in energy.

Part B – miscibility

In this section, students reported the dipole moments (see Table 2) resulting from quantum chemical calculations. The students used this information to predict the miscibility of solvents based on the adage "like-dissolves-like" and confirm/deny the validity of this saying. Students were not asked to consider different thermodynamic properties such as enthalpy (H), entropy (S), or Gibbs Free Energy (G) of mixing as the lecture portion of the course corresponding to these topics occurs later in the semester. These topics are highlighted later on in lecture to formally explain miscibility. Students then tested their predictions by physically mixing these solvents in small quantities (<1 mL) using glass dropper bottles and test tubes. Goals for this section were: (1) for students to draw connections between theory and experiment, (2) for students to see a potential and practical use in computational chemistry, (3) to provide students with an exercise in drawing Lewis structures, (4) to provide students with an exercise in optimizing geometries using GAMESS and retrieving dipole moments of these molecules from the calculation's output, (5) for students to visually determine miscibility of a variety of different compounds, (6) for students to develop general rules for miscibility using the results of their combined theoretical and experimental results, (7) determine the validity of "like-dissolves-like" based on dipole-moments without considering thermodynamic properties such as enthalpy of mixing, entropy of mixing, or Gibbs free energy of mixing.

Table 2: Dipole moment of Part B compounds using HF/6-31G(d).

Compound	Dipole moment (Debye)
Water	2.199
Acetone	3.119
Methanol	1.867
Ethanol	1.738
1-Propanol	1.799
2-Propanol	1.709
Ethylene glycol	2.342
Tetramethylsilane (TMS)	0.000
Ethyl acetate	1.963
Cyclohexane	0.000

One difficulty in this section was that students would incorrectly draw the Lewis structure of the molecule and therefore enter the wrong structure into WebMO/GAMESS. This error resulted in incorrect predictions of the dipole moments and miscibilities. Another student difficulty was drawing $SiMe_4$ or TMS flat in the molecular viewer of WebMO. The consequence of this was that GAMESS would optimize the structure incorrectly or would be unable to optimize the structure due to symmetry constraints of the pre-optimizer in WebMO. To minimize this issue, the instructor should reiterate to use the pre-optimization protocol mentioned in the student handout and ask students to draw the best possible 3-dimensional representation of the molecule in WebMO.

The majority of students determined that the general rule of "like-dissolves-like" based upon the argument of similar dipole moments to not be valid. They did determine that molecules with drastically different dipole moments would not be miscible. Generally, students discerned that molecules with similar dipole moments were miscible with exceptions. For example, students noted that while ethylene glycol had a similar dipole moment to methanol and ethyl acetate, yet the compounds were immiscible. The majority of students indicated something was missing from their consideration of miscibility. This point is reiterated in the lecture sections of the course when discussing the thermodynamics of mixing.

Part C – intermolecular attraction forces

In this section, students used computational software packages to predict the strength of different intermolecular attraction forces by calculating the BE of two molecules listed in Table 3. The collection of these two molecules is referred to as a dimer, while the individual molecules are referred to as monomers. The chosen molecules highlight dipole-dipole, dispersion, and hydrogen bonding interactions. The goals for this section were: (1) to provide students with a visualization of adjacent molecules interacting via intermolecular attraction forces and (2) for students to understand/estimate the strength of these intermolecular attraction forces.

Table 3: Determining the binding energy (be) for compounds investigated in Part C using MP2/6-31G(d).

Compound	Dimer energy, kJ/mol	Monomer energy, kJ/mol	Binding energy, kJ/mol
Water	−400140	−200055	−31
Molecular Hydrogen	−6008	−3004	0
Hydrogen Sulfide	−2094045	−1047019	−7
Methane	−211787	−105893	−1
Hydrogen Fluoride	−526090	−263028	−34
Ammonia	−295936	−147958	−20
Hydrogen Chloride	−2416478	−1208235	−8

Students determined that dimers with hydrogen bonds had the largest BE while systems with only dispersion forces had the lowest BE.

In this section, students were asked to switch the level of theory from HF to MP2. The reason for this is that HF theory fails to accurately describe correlation energy, which is necessary to describe dispersion forces (Grimme et al., 2016) However, MP2, a post-HF method, can be used to approximate the correlation energy.

The BE is calculated by:

$$\mathrm{BE} = \mathrm{E}_{\mathrm{dimer}} - 2 \cdot \mathrm{E}_{\mathrm{monomer}} \tag{2}$$

where $\mathrm{E}_{\mathrm{dimer}}$ is the MP2 energy of the optimized dimer and $\mathrm{E}_{\mathrm{monomer}}$ is the MP2 energy of an optimized monomer. The more negative the BE, the more energetically favorable the interaction is by the way that BE has been defined herein.

Assessment of student understanding

The students completed the same written assessment and survey before (pre), immediately after (post), and five weeks after (long-term) the exercise. The assessment questions can be seen in Table 4 with the average responses listed in Table 5. The assessment responses were graded as correct or incorrect with no partially correct answer.

Table 4: Pre-/post-assessment questions.

Question #	Question
1	Explain the term miscibility
2	Draw two plausible structures of hypochlorous acid (HClO)
3	Using your answer from question 2, explain which structure is the lowest in energy
4	Draw the Lewis structure of cyclohexane (C_6H_{12})
5	Approximate the dipole moment of cyclohexane in Debye
6	Will water (H_2O) and acetone (CH_3COCH_3) mix?
7	Draw a low-in-energy HF dimer
8	Rank the following intermolecular attraction forces in terms of increasing strength: Dipole-dipole, Dispersion, Hydrogen bonds
9	Explain one way quantum mechanical calculations can be used to help guide experiment

Table 5: Assessment results showing the percentage of students who answered each question correctly.

	1	2	3	4	5	6	7	8	9
Pre (n = 57)	58%	7%	21%	35%	19%	51%	7%	49%	18%
Post (n = 57)	86%	58%	56%	81%	47%	86%	68%	81%	51%
Long-term (n = 50)	58%	34%	44%	70%	35%	60%	66%	82%	52%

In the pre- and post-assessments, 57 students participated and in the long-term assessment, 50 students participated. The questions for the assessment are contained in Table 4.

Students improved on every question in both the post-assessment and the long-term assessment compared to the pre-assessment, increasing on average by 36 and 25 percentage points, respectively. The results of the assessments are listed in Table 5. Before this laboratory exercise, students showed some understanding of miscibility, with over 50% of students correctly defining the term miscibility and identifying that acetone and water will mix. Students had a very limited understanding of many topics related to quantum chemistry. For questions related to Lewis structures, low-energy structures, dipole moments, intermolecular forces, and quantum mechanical calculations, less than 50% of students answered correctly. Less than 10% of students correctly answered the questions to identify potential structures of a molecule and to predict the dimer structure with the lowest energy. In the post-assessment, the majority of students answered eight out of the ten questions correctly. Long-term assessment of this material showed improvement from the pre-assessment, but not as high as the post-assessment, for all of the assessment questions besides question 1.

The student survey responses ranged from one (strongly disagree) to ten (strongly agree) in increments of one. The questions contained in the survey are listed in Table 6. In both the post and long-term survey, students responded more positively on every question. As seen in Table 7, all trends comparing the post or long-term survey results to the pre survey were found to have a significant increase ($p < 0.05$) using the Wilcoxon signed ranked test except for one long-term survey response indicating if students were interested in quantum chemistry. The assessment, survey, and full results are presented in the Supporting Information.

Table 6: Student survey questions.

Question #	Question
1	I understand the importance of quantum chemistry
2	I think quantum chemistry is important
3	I understand how quantum chemistry can be related to chemical experiments
4	I am interested in quantum chemistry
5	I feel like I understand what intermolecular attraction forces are
6	I can visualize intermolecular attraction forces
7	I can visualize 3D representations of Lewis structures
8	I feel like I understand the relative strengths of intermolecular attraction forces
9	I understand what is meant by "low-in-energy structure"

Table 7: Survey results showing the change in average response compared to the pre survey (n = 57).

	1	2	3	4	5	6	7	8	9
Post (n = 57)	1.8 (p = 4.7E-8)	1.0 (p = 3.5E-5)	2.5 (p = 2.9E-8)	0.8 (2.4E-3)	1.1 (p = 7.4E-6)	1.7 (p = 7.7E-7)	1.04 (p = 3.6E-6)	1.5(p = 1.4E-5)	2.5(p = 2.4E-8)
Long-term (n = 50)	1.8 (p = 1.8E-6)	1.1 (p = 3.4E-5)	2.0 (p = 1.5E-6)	0.4[a] (p = 2.1E-1)	1.8 (p = 4.7E-6)	2.3 (p = 4.0E-7)	1.00 (p = 1.1E-2)	2.0(p = 5.3E-7)	2.2(p = 7.4E-6)

The significance of the difference was determined using the Wilcoxon signed-rank test and the p-value is listed and indicated ([a]) if above 0.05. The questions for the survey are contained in Table 6.

In addition to providing an effective tool for learning about topics incorporating quantum and computational chemistry, this exercise successfully introduced their importance and applicability to the general chemistry laboratory curriculum. Prior to this exercise, the majority of students said they disagreed or were neutral that they understood the importance of quantum chemistry, understood how it related to physical experiments, and were interested in quantum chemistry. In the post and long-term surveys, the majority of students agreed that they thought quantum chemistry is important (74%), understand how it relates to physical experiments (80%), and understand the importance of quantum chemistry (68%). Though the majority of students did not find quantum chemistry interesting, the students' understanding of the importance of quantum chemistry demonstrates the success of this exercise.

Summary

We have created an introductory computational chemistry and experimental exercise for an undergraduate general chemistry laboratory. This exercise uses computational methods to explore and visualize Lewis structures, miscibility, and intermolecular attraction forces. Additionally, this exercise draws a connection between results of molecular modeling with a physical experiment. Our pre-/post-assessments show that the students' ability to correctly answer questions relating to Lewis structures, dipole moments, miscibility, and intermolecular attraction forces increased upon completion of the exercise.

Associated Content

Supporting information

The Supporting Information is available on the Publications website which include:
- Notes for Instructors (DOCX)
- Grading Rubric (PDF)
- Student Handout (DOCX)
- PRE-/POST-Assessment (DOCX)
- Student Survey (DOCX)
- Coordinates (DOCX)

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