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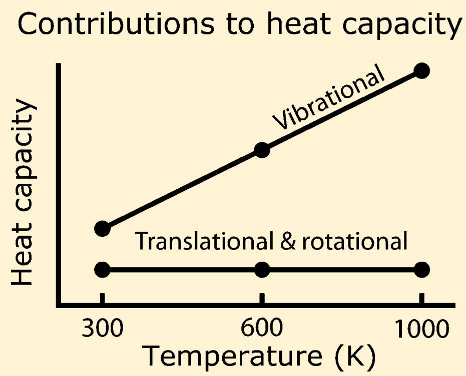
Integrating Computational Chemistry into a Course in Classical Thermodynamics

Sheridan R. Martini and Cynthia J. Hartzell*

Department of Chemistry and Biochemistry, Northern Arizona University, Flagstaff, Arizona 86011, United States

Ⓢ *Supporting Information*

ABSTRACT: Computational chemistry is commonly addressed in the quantum mechanics course of undergraduate physical chemistry curricula. Since quantum mechanics traditionally follows the thermodynamics course, there is a lack of curricula relating computational chemistry to thermodynamics. A method integrating molecular modeling software into a semester long thermodynamics course is proposed in this paper. With the introduction to a computational chemistry program earlier in their undergraduate curriculum, students are given more opportunity to appreciate the vast applications and benefits of the science. The structure of the out-of-class assignments has been modified over the course of three semesters in order to improve correlation with lecture material and focus the goals of each lesson.



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The undergraduate physical chemistry curriculum at Northern Arizona University comprises a two-semester sequence of lecture courses taught at the upper-division level plus a comprehensive lab taught during the second semester of this sequence. The first-semester course covers thermodynamics and kinetics. The second-semester course covers quantum mechanics and spectroscopy, plus a brief foray into statistical mechanics. The two-credit laboratory course consists of experiments based in thermodynamics, quantum mechanics and spectroscopy. Computational chemistry tutorials and assignments have been incorporated into the quantum mechanics course and the laboratory course, on a limited basis, for the last 14 years. Acquisition of a computational software site-license four years ago significantly increased student access. With the goal of enriching the thermodynamics curriculum, an out-of-lecture exercise correlating with topics in thermodynamics was created to parallel the successful integration of computational chemistry exercises into quantum chemistry curriculum reported by Johnson and Engel.[1] Specifically, these authors reported that students did not find learning the software to be difficult and nearly half the students found the computational problems useful.

The series of assignments introduces students to the scientific modeling software Gaussian ’09 and to functionalities of Excel that support data analysis. The exercises guide students through a graphical display of the temperature-dependence of heat capacity, providing a pedagogical counterpoint to homework calculations requiring integration of multi-term, temperature-dependent heat capacities. The assignments also provide a visual comparison of the translational, rotational and vibrational contributions to the heat capacity. This material is introduced in the second chapter of the classical-thermodynamics text currently in use at NAU.[2] Graphical analysis of the data improves student proficiency with Excel, a critical skill for students in any scientific field.

The use of a computational program to model basic concepts of statistical thermodynamics is advantageous for students who are not mathematically inclined. Although math prerequisites are enforced, each student varies in his or her depth of understanding; especially when facing the application of mathematical concepts to a chemical system. As long ago as 1929, physical chemists lamented, “Inadequate preparation in mathematics now constitutes the greatest problem in the teaching of physical chemistry.”[3] More significantly a problem in quantum chemistry, but still relevant to thermodynamics, the discussion of chemical theory is minimized during lecture because time must be spent reviewing mathematical techniques.[4] Students who often struggle with computation spend their time in the lecture course navigating the mathematical relationships instead of learning the concepts. However, by incorporating computational software into the course, students who struggle with the mathematics are able to visualize theoretical relationships without having to overcome the barrier of calculation.

■ CURRICULUM OVERVIEW

Integration of computational chemistry was achieved through the creation of a three assignment series as outlined in Figure 1. The exercises were constructed based on the premise that students had no prior experience with the software program, Gaussian ’09. The initial structure was designed to prevent

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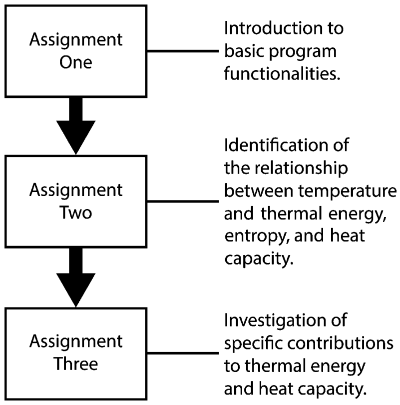

Figure 1. Outline of Gaussian assignment series correlating each lesson with its overall purpose.

complications resulting from variability within the student population as well as limited resources.

The thermodynamics lecture can be filled by up to 50 students, who are pursuing degrees varying from chemistry to engineering. Engineers taking the class often excel at data analysis, while chemists sometimes lack understanding of basic analytical program functionalities. Thus, a technique of step-by-step, how-to explanation was implemented to best accommodate a range of technical abilities. However, once a lesson was taught via step-by-step instruction, it was never outlined again. Consecutive assignments required implementation of previously taught techniques so as to progressively build a technical foundation.

Physical chemistry is a rigorous course, which yields little extra lecture time to provide explanation of the assignment series. Additionally, the capacity of the chemistry computer lab is not comparable to the number of students enrolled in the thermodynamics course. As a result of minimal in-class instruction time and limited in-class access to licensed computers, the curricula are intended as self-teaching, out-of-class lessons. Students at NAU access the program, at their convenience, in on-campus computer labs that are open daily.

■ ACCLIMATING STUDENTS TO SOFTWARE

The first assignment in the series is dedicated to providing students with an introduction to program functionalities. Students are required to familiarize themselves with the different task windows, to identify relevant icons on the builder tool bar, and to practice constructing familiar molecules. Since program navigation is difficult, only icons necessary for future assignments are explored.

Step-by-step instructions are provided for the construction of each molecule, including what molecular fragment to use and what window to position it in. Following creation of a molecule, the builder window reports molecular properties to the user that describe the constructed molecule. These molecular properties are recorded on the assignment sheets. Points may then be assigned based on the accuracy of the molecular properties of the constructed molecule. An improperly built molecule will be obvious as a different number of atoms or electrons could result from a misplaced bond.

■ DATA COLLECTION

In the second assignment, students track the effect of temperature change on the physical properties of a given molecule. The relevant data is collected from the computation output file. Students record this data and transfer it to an Excel document for analysis.

To ensure intellectual honesty, students are randomly assigned one of 10 molecules. Students must refer to Assignment 1 for instructions on how to build the molecule but, to ensure proper construction, were provided a picture of the molecule and the molecular properties to match with the output. Then, in a step-by-step format, Assignment 2 directs students to input predetermined calculation parameters. With each new calculation, students must locate the computed values in the data output. The quantities of thermal energy, heat capacity and entropy are evaluated at three temperatures, 298, 600, and 1000 K. Students also track the change in the number of active vibrational modes as temperature increases.

The use of small molecules allows calculations to be carried out by *ab initio* methods. Since semiempirical calculations will be used in later calculations, students benefit by gaining exposure to multiple computational methods. It is important to note that program errors can be incurred during these calculations if the file name contains special characters other than letters and numbers.

To enhance the computational investigation of the effect of temperature on energy, students observe select vibrational modes of their assigned molecule. When recollecting these vibrational motions, students routinely speak of dancing molecules and seem more engaged with the assignment topics.

■ ANALYSIS RELEVANT TO LECTURE MATERIAL

Students are then tasked with analyzing the collected data; this is initiated in Assignment 2 and concluded in Assignment 3. Once the data is organized in an Excel document, the total values of thermal energy, heat capacity, and entropy are plotted on a single graph as seen in Figure 2. Students are asked to

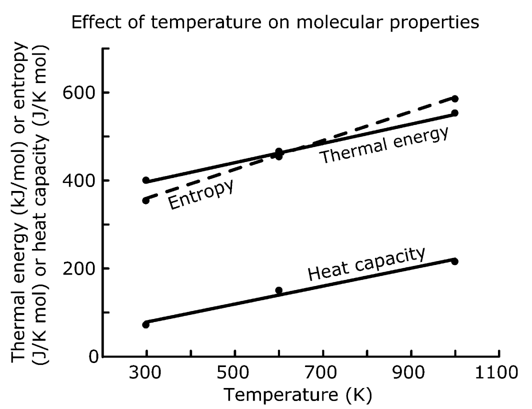

Figure 2. A representative Excel plot displays the effect of temperature on thermal energy, heat capacity and entropy for benzyl alcohol.

discuss and explain the effect of temperature on the number of active vibrational modes and on the various thermodynamic quantities displayed in their Excel plot. Specific questions are detailed in the assignments available in Supporting Information.

Assignment 3 continues with the trend of data analysis; however, the focus is shifted from comparing the effect of temperature on overall quantities to the translational, rotational and vibrational contributions to energy and to heat capacity. Plots of the contributions to thermal energy show students the variation of each with temperature. A graphical comparison with the contributions to heat capacity reveals the variation of

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the vibrational heat capacity with temperature while the rotational and translational contributions remain constant across the temperature range 298−1000 K. A representative plot of the contributions to heat capacity for benzyl alcohol is shown in Figure 3.

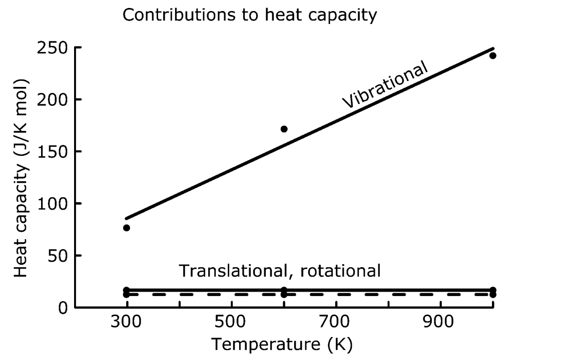

Figure 3. A representative Excel plot compares the effect of temperature on translational, rotational and vibrational contributions to heat capacity for benzyl alcohol. The translational and rotational lines are offset slightly for clarity.

Although more thoroughly covered in quantum mechanics, the vibrational, rotational, and translational energies are explored to introduce students to the impact of these degrees of freedom within a molecule. As the temperature is increased, students will observe a linear increase in the translational and rotational energies as predicted in the high-temperature limit. In contrast, calculated translational and rotational contributions to heat capacity are constant at 12.47 J/(K mol), in agreement with the $C_{v,m}$ value of $3R/2$ predicted by the equipartition theorem. A brief in-class discussion can facilitate observation of trends by comparing the heat capacities of different sized molecules. Larger molecules, which have more vibrational degrees of freedom, are capable of possessing a heat capacity of a greater magnitude than smaller molecules. Analysis of the plot in Figure 3 should aid students in recognizing that the differences in heat capacity arise from the availability of vibrational modes.

MODIFICATIONS TO FOCUS STUDENT LEARNING

Although the curriculum was successfully integrated throughout a semester of thermodynamics, the assignments were modified in a subsequent semester to improve correlation with lecture material by focusing on heat capacity. Chemistry students are first introduced to the concept of heat capacity in general chemistry courses. Approximately 76% of surveyed instructors reported the concept of heat capacity as important-to-cover in the thermochemistry lecture material during a general chemistry lecture course.[5] Limited instruction in the topic can impact a student's success in thermodynamics because a significant amount of course material is defined in relation to heat capacity. Since the comprehension of heat capacity is fundamental to investigating the temperature-dependence of energy, Assignment 2 was restructured to specifically address heat capacity. Indeed, Assignments 1 and 2 could be successfully incorporated into a general chemistry course.

In the future, addition of a fourth assignment to the series will require students to calculate the enthalpy of reaction using Gaussian. This will act as an expansion of student understanding of heat capacity and will improve correlation with lecture material. The assignments can additionally be modified to require calculations at more than three temperatures to investigate nonlinearity of the temperature-dependence of heat capacity. A truly linear response is only expected for translational and rotational energies, as mentioned above.

These assignments will always be a work-in-progress. There will always be new questions that the students can address by analyzing the results of such calculations. The initial goal was develop a series of exercises that students could complete on their own without hidden pitfalls. Based on the quality of the results that students handed in, that goal has been met. Based on the response to exam questions comparing predicted temperature-dependence of heat capacities for atoms and molecules, the majority of students did complete the course with a grasp of the contributions.

CONCLUSION

Incorporation of the assignment series into traditional coursework enables students to develop a foundation for conceptual understanding within physical chemistry despite possible mathematical limitations. Additionally, exposure to degrees of freedom and computational chemistry segues between thermodynamics and quantum mechanics. Use of this computational assignment also exposes students to functionalities of Excel that can be applied to any coursework for which data analysis is required.

The assignment series presented in this article is designed as out-of-class work for an institution with licensed access to a computational chemistry program. Although the lessons are optimized for physical chemistry curriculum setup as first semester thermodynamics and second semester quantum mechanics, implementation can be modified for distribution as needed.

ASSOCIATED CONTENT

Supporting Information

The original student assignment handouts. This material is available via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

* E-mail: Cynthia.Hartzell@nau.edu.

Notes

The authors declare no competing financial interest.

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