

Introducing the Practical Aspects of Computational Chemistry to Undergraduate Chemistry Students

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Educating early undergraduate level students in theoretical and computational chemistry can be a daunting task. In most cases students do not have a solid background (if any) in differential equations and even linear algebra may not be a prerequisite at some institutions before entering a second-year physical chemistry class. A proper background in ab initio quantum chemical techniques as well as computational implementation usually does not come until the fourth and final year or, in some cases, graduate school. Consequently, students are often left underexposed to computational chemistry and are unfamiliar with the value and limitations of the discipline. This is unfortunate, as the field has grown to become an important tool to chemists of all disciplines and can provide valuable experience to students at any level.

Efforts in the literature to address this issue have been appearing for over a decade with varying degrees of success. One of the earliest accounts was a review by DeKock et al. (1) that provides an excellent introduction to the pedagogical issues that arise when teaching quantum theory to students near the beginning of their undergraduate careers. Since that time there have been over a dozen reports of educational exercises and strategies published for this very task. Most describe computational activities for students at various levels, including the calculation of ionization potentials (2), potential energy surfaces (3–5), UV spectra (6), molecular structure (7), and much more (8–10). Others describe details of course offerings that have been developed at various institutions (11–13), again for students at different levels. Computational exercises for students will inevitably be problematic owing to the existence of the “black box” effect, meaning that students know nothing (or very little) about how the computational algorithm arrives at the final answer. The above exercises are no exception. Full course offerings are valuable tools for students that allow for a more complete understanding of important concepts yet can be difficult and slow to implement in a university environment.

The need for a means to introduce early undergraduate students (particularly physical chemistry students in their second year of study) to computational chemistry has been recognized and a laboratory exercise has been developed for that purpose. Great care has been taken to alleviate the “black box” effect while placing no burden on the lecturer to adjust or add to existing course content. Our requirements for the exercise were that it highlight the practical aspects of performing quantum chemical calculations (including the compromise between accuracy and computational time as well as the limitations of a non-correlated approach to certain molecular properties) while incorporating existing classroom material. Also, the use of research-grade software was desirable so that the student could gain valuable and useful experience that could be easily carried forward to future endeavors (e.g., a summer research or honors project). Finally, it was necessary that the

exercise be implemented in a relatively short period of time (i.e., 3 to 4 hours).

In this article we describe the details of the aforementioned laboratory exercise. Students perform many relatively small-sized calculations that emphasize standard classroom material such as the rigid rotor approximation and the harmonic oscillator while using Gaussian 03 (14), standard research-grade software, giving the students valuable exposure. While this experiment was performed and is described for use with Gaussian 03, there is nothing preventing it from being used with any other quantum chemistry programs.

Project Details

Each student is assigned a set of three diatomic molecules found in Table 1. The first step of the exercise involves calculating the rotational constant, B , for each of these molecules via a Hartree–Fock (HF) 6–31G optimization. A novel treatment of this optimization is that the students make no use of the resulting optimized geometry and instead calculate the optimum bond length, r_e , by hand from the rotational constant via the rigid rotor approximation for a diatomic molecule

$$r_e = \sqrt{\frac{h}{8\pi^2 B} \frac{m_A + m_B}{m_A m_B}} \quad (1)$$

where m_A and m_B are the masses of atom A and B, respectively. This helps to lessen the dependence of the student on the software package and avoid the “black box” effect. It also helps to strengthen the understanding of the rigid rotor.

The students then perform a series of single point calculations above and below r_e to generate a potential energy surface (PES). Using r_e , the students then perform a frequency calculation. The resulting fundamental frequency, ν_0 , is used to calculate the force constant of the bond, k , via the follow-

Table 1. The Nine Series of Molecules Assigned to the Students

Series	Molecules		
1	LiF	LiCl	LiBr
2	NaBr	NaCl	NaF
3	KF	KCl	KBr
4	F ₂	Cl ₂	Br ₂
5	HF	LiF	NaF
6	KBr	NaBr	LiBr
7	N ₂	F ₂	O ₂
8	HF	HCl	HBr
9	CO	NO	O ₂

ing equation:

$$v_0 = \frac{1}{2\pi} \sqrt{k \frac{m_A + m_B}{m_A m_B}} \quad (2)$$

This is analogous to the bond length calculation in that although r_e was readily obtainable from the output, it was calculated by hand. An additional PES is then generated using the harmonic approximation via the Hooke's law relation

$$E_p = \frac{k(r - r_e)^2}{2} \quad (3)$$

where E_p is the harmonic oscillator potential at an internuclear distance of r . Students plot both the HF/6-31G and the harmonic approximation surfaces together to generate a diagram such as that in Figure 1.

To demonstrate the shortcomings of a non-correlated method, students then calculate the bond dissociation energy (BDE) of their diatomics by homolytic cleavage using the standard formula

$$\text{BDE}(A-B) = E(A\cdot) + E(B\cdot) - E(A-B) \quad (4)$$

where $E(A\cdot)$ and $E(B\cdot)$ are the HF/6-31G energies of the A and B radicals, respectively, and $E(A-B)$ is the energy of the complete molecule.

Finally, the students repeat the first step for their third molecule using the 3-21G basis set and then the 6-311G++(p,d) basis set, keeping track of the computational time. This will afford them the opportunity to compare bond lengths calculated with various basis sets of increasing complexity to experimental values and also to observe that the increased complexity (and increased accuracy) comes at a cost of increased computation time.

Learning Outcomes

The steps of this exercise are summarized in Figure 2. By performing many of the calculations themselves (i.e., by hand) the students remain engaged in the lab rather than simply passively waiting for results from Gaussian. Students become more confident in their understanding of both the rigid rotor model and the harmonic oscillator model; two key concepts. They generate a qualitative and quantitative appreciation for the limitations of a harmonic potential as a diatomic bond is compressed or stretched significantly.

By comparing the bond lengths and BDEs generated for their molecules with the literature the students gain an important appreciation of the value and limitations of the HF method as invariably their BDEs will be in significant error while their geometries will be consistently good. Also, by using additional basis sets, students will observe that increased accuracy comes at a computational cost, *vide supra*.

As an important caveat, it must be stated that the specific basis sets and molecules presented here have been chosen to highlight the desired effects. Therefore they should be strictly adhered to in the implementation of the lab.

Hazards

This laboratory exercise involves no significant hazards.

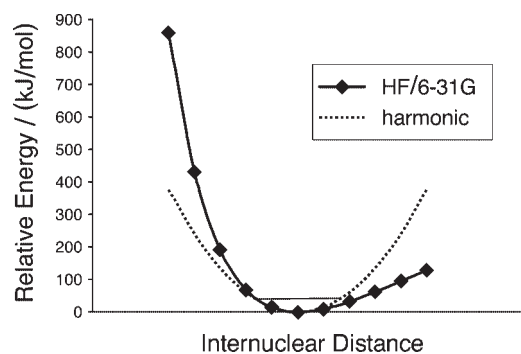


Figure 1. Potential energy diagram for the diatomic HCl. The solid line represents the HF/6-31G level while the dashed line represents the harmonic oscillator potential.

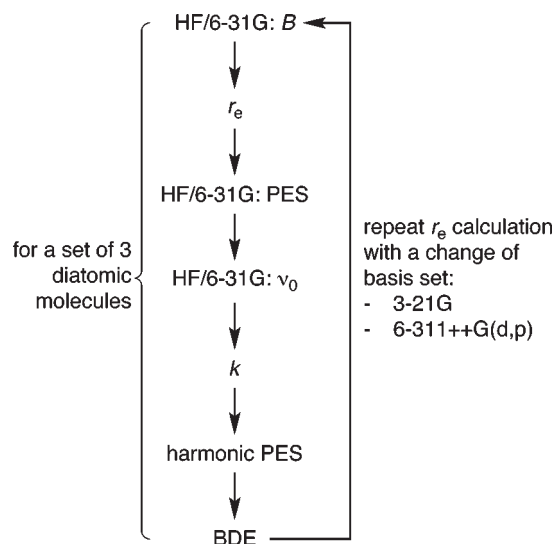


Figure 2. Flow chart summarizing the steps involved in this laboratory project.

Assessment

Student reaction to this exercise was generally positive. Prelab and postlab surveys were used to gauge the necessity and the value of the project. Results of these surveys are summarized in Tables 2 and 3. It is clear that at this level students are without proper instruction in theoretical or computational chemistry, yet have plenty of experience with computers and thus have all the tools they need to complete this exercise (Table 2). After completing the lab the students generally enjoyed the experience and left with a stronger understanding of standard concepts such as the rigid rotor and harmonic approximations (Table 3).

Conclusions

The current work demonstrates a laboratory exercise aimed at physical chemistry students in their second year of study designed to highlight the practical aspects of computational chemistry. The exercise uses existing course content such as the rigid rotor and harmonic oscillator approxima-

Table 2. Answers to Selected Questions on the Prelab Survey

Question	Average Response
How familiar are you with using computers for calculations and plotting data with programs such as Microsoft Excel?	4.6 ± 0.6
How would you rate your current background in computational or theoretical chemistry?	1.8 ± 0.8
How familiar are you with the Gaussian 03 software package?	1.1 ± 0.3

Note: Answers were on a scale from 1 to 5, 1 indicating the student was not at all familiar and 5 indicating the student was very familiar. The average response value is given with the standard deviation.

Table 3. Answers to Selected Questions on the Postlab Survey

Question	Average Response
I enjoyed this laboratory exercise.	4.0 ± 0.8
The lab handout provided adequate information for me to finish the exercise.	4.4 ± 0.7
The lecture material provided adequate background for my understanding of the exercise.	3.0 ± 1.0
This exercise was helpful in strengthening my understanding of the rigid rotor model.	4.0 ± 1.0
This exercise was helpful in strengthening my understanding of the harmonic oscillator model.	3.8 ± 0.9

Note: Answers were on a scale from 1 to 5, 1 indicating the student completely disagreed and 5 indicating the student completely agreed. The average response value is given with the standard deviation.

tions so that students already have the required mathematical background and no additional material needs to be incorporated into the lecture portion of the course. It has been implemented in a three-hour laboratory period but is easily expanded to four hours if necessary. The exercise also allows many students to participate using their own individual set of molecules, which provides variety and promotes intellectual honesty.

Requiring that various molecular properties be calculated by hand enables students to begin to transcend the “black box” effect (although not completely) and gain a greater appreciation for the data they generate. Also, the exercise is designed so that the students perform many small-sized calculations of various kinds as opposed to fewer more computationally intensive calculations. This affords the students with the opportunity to develop a more intimate knowledge of the user interface of the research-grade software (Gaussian 03).

Finally, via the analysis of their data and by comparison with the literature students learn valuable practical aspects of computational chemistry such as the increase in computational cost that accompanies an increase in accuracy and the effects of using a non-correlated method on certain molecular properties.

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Supplemental Material

The laboratory handout and data sheet provided to students are available for download in this issue of *JCE Online*.

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