The Effective Use of Technology in a Graduate Molecular Modeling Class

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Abstract - The methodology for the use of computational software in a graduate-level molecular modeling class is outlined. In many engineering curricula it is difficult to cover all of the fundamental concepts that are required to provide all students with an optimum base for the solution development of new problems and applications. However, by replacing the learning and understanding of fundamental concepts with starting parameters and a list of equations to use as tools, you are limiting the capabilities and potential accomplishments of the students. This trap is easy to fall into since it is nearly impossible to cover all the fundamentals in addition to the applications. Because of this, a chemist or physicist may be able to develop new ideas more readily since their training through education has taught them to derive the equations they are using. Engineers are typically admired for their ingenuity and their creativity, but with a curriculum that does not require them to derive and to consistently ask ‘why’ and ‘from where,’ engineers will soon lose these merits of which they are so well known.

Index Terms –molecular modeling, ab initio

INTRODUCTION

Within a graduate-level molecular modeling class, computational chemistry software was used as a tool to bridge the gap that exists between fundamental concepts in chemistry to applications within the field of chemical engineering. In the case of reactor design problems in which rate expressions must be known, activation energies and rate constants are typically provided as input parameters for a particular design equation. Since more sophisticated methods for approximating rate constants are not taught in traditional chemical engineering courses, the development of a rate expression was chosen as one of the main objectives of this molecular modeling course. The calculation of a rate expression involves many tasks, including the development of a quantum mechanical-based potential energy surface (PES) and the understanding of reaction kinetic tools such as transition state theory. Similar methodologies have emerged recently in the literature for assimilation into graduate chemistry coursework [1,2]. However, the current methodology is unique due to its incorporation into a chemical engineering department curriculum, where it serves to couple fundamental chemical principles to applications in chemical engineering through a combination of ab initio theory and reaction kinetics.

The course was offered for the first time in the Chemical Engineering Department at Worcester Polytechnic Institute during the Fall 2005 semester. A 6-week assignment termed, “Learning through a Reaction Example,” served as the main driving force throughout the course and was reflected both in terms of lecture material as well as student exercises. The course methodology carried out to accomplish the goal of bridging the gap between fundamental principles in chemistry to applications in chemical engineering is self-contained in that it can be adopted by any instructor wishing to achieve this goal through offering a similar class within his/her department.

The course was divided into the following sections:

• Principles by which ab initio-based methods and basis sets are comprised; background of key features and concepts of quantum mechanics (QM), i.e., exact solutions to the Schrödinger wave equation (SWE), methods used in solving approximations to the SWE, e.g., variational methods and perturbation theory, classical problems from QM, e.g., particle in a 1-D box, harmonic oscillator, and the hydrogen atom. These topics comprised 4 weeks of the course, culminating with a closed-book in-class exam.

• “Learning through a Reaction Example” was assigned, which included five weekly assignments and a take-home exam that required the students to compile the individual components into the form of scientific papers, which were then submitted for publication as a series of two manuscripts. Details of this assignment are discussed within this article. This aspect of the course involved a combination of lecture and interactive learning through computational in-class lab exercises, i.e., using the Gaussian98 software package [3] for electronic energy predictions. Extraction of these energies combined with reaction kinetic tools such as potential energy surface development and transition state theory (TST) led to the development of rate expressions. To ensure mastery of the software, an in-class computer-based exam was given seven weeks into the course, i.e., three weeks after the software was introduced.
During the last four weeks of the course, students were asked to choose a topic for a final project. It was required that the final project relate to a student’s research project, i.e., within their senior thesis, M.S. thesis, or Ph.D. dissertation. The goal of this final project was to apply the computational and kinetic tools learned throughout the course to an aspect within their chemical engineering research. This final exercise served as a method for evaluating students’ understanding of the material, with a measure of the course success dependent upon whether a student was able to effectively apply the knowledge gained from the course in a novel way to their research. Some examples of this application include:

- Electrochemical water-gas shift reactions on platinum and ruthenium catalysts - Application: fuel cell chemistry
- Adsorption mechanisms of MTBE, Chloroform, and 1,4-dioxane with cations - Application: separation of contaminants from groundwater using zeolites
- Mechanism development of sulfur’s role in poisoning palladium - Application: hydrogen separation using Palladium membranes

If one wished to integrate molecular modeling and computational chemistry techniques into a graduate curriculum to supplement the chemical engineering background traditionally acquired, carrying out this reaction assignment would ensure student mastery of the computational tools necessary for gaining a molecular perspective into their graduate research. Therefore, it is this aspect of the course that will be described in detail within this article.

In the “Learning through a Reaction Example” assignment, elementary gas phase reactions were considered for a complete thermodynamic and kinetic analysis. The goal was to produce a high-level potential energy surface based upon ab initio energetics, and to derive accurate rate expressions for the reaction using transition state theory. Computational-based ab initio techniques were employed to solve approximations to the Schrödinger wave equation (SWE), which describe the location and energetics associated with the electrons in a given system. The “level of theory” chosen to investigate the species within a given reaction requires two components, i.e., a mathematical method to solve the approximation to the SWE and a wave function (spatial description of the electrons in space).

**DESCRIPTION OF REACTION ASSIGNMENT**

One of the following elementary gas phase reactions was assigned to each pair of students in the class.

1. \( \text{H}_2 + \text{Cl} \rightarrow \text{HCl} + \text{H} \)
2. \( \text{D}_2 + \text{Cl} \rightarrow \text{DCl} + \text{D} \)
3. \( \text{H}_2 + \text{F} \rightarrow \text{HF} + \text{H} \)
4. \( \text{D}_2 + \text{F} \rightarrow \text{DF} + \text{D} \)

5. \( \text{F}_2 + \text{H} \rightarrow \text{HF} + \text{F} \)

Two students investigating the same reaction were doing so for validation of the molecular results generated with each investigation being performed at a unique level of theory, i.e., method and basis set combination.

**Step One:** Students were asked to retrieve experimentally-based chemical properties of the species within their assigned reaction in addition to experimental thermochemical and kinetic data for the total reaction. The chemical properties included equilibrium bond distances, vibrational frequencies, dipole moments, and rotational constants.

**Step Two:** Within this step of the assignment students performed geometry optimization and spectroscopic calculations on their assigned reaction species. They were required to perform the calculations at varying levels of theory, including the density functional method, i.e., Becke 3 parameter Yee Lang and Parr (B3LYP), as well as Hartree-Fock, and the second order perturbation method, Moller-Plesset (MP2). Additionally, higher electron-correlated methods such as quadratic configuration interaction (QCI) and coupled cluster (CC) techniques were also explored. Both Pople and Dunning basis sets were considered with each of these calculational methods. The complexity of the basis sets assigned ranged from minimal such as the double zeta Pople basis set, 6-31G, to more extensive including both diffuse and polarization functions, such as the triple zeta Pople basis set, 6-311++G**. Students were assigned nine levels of theory for the energetic and spectroscopic predictions, and asked to consider three additional others.

**Step Three:** Within this step students compare their theoretical predictions to the experimental data that was compiled in step one of the assignment. It is this aspect of the assignment, which allows the students to control their learning; they are able to see how well a chosen level of theory agrees to experiment. There is flexibility as well since the students are asked to choose three levels of theory to consider in addition to those assigned.

**Step Four:** This step involves the development of a high-level potential energy surface (PES). In order for a student to proceed with this step, two criteria must be met, i.e., students must first choose a level of theory that accurately predicts the heat of reaction and equilibrium constant. Once a student obtains a level of theory which predicts a heat of reaction to within 2 kcal/mol to experiment and an equilibrium constant to within an order of magnitude of experiment, they can proceed to develop a PES at this chosen level of theory.

**Step Five:** The last step of the assignment involved the calculation of rate expression parameters, i.e., the rate constant, using the hard sphere collision model (HSCM) for an upper bound and transition state theory (TST) for a more accurate rate prediction.
CONCLUSIONS

A graduate-level course in molecular modeling was developed which served to provide chemical engineering students with an introduction to a molecular approach in understanding chemical reactivity. Often there exists a disconnect between the topics in an applied engineering discipline and the fundamental chemical and physical principles on which applications are based. This course served as a means to provide students with additional tools to supplement their graduate research projects. This connection was established through the development of a reaction assignment which led students through a series of steps ranging from an introduction to quantum mechanics to the development of a potential energy surface, from which activation energies were extracted for rate expression calculations. These series of steps ensured students’ comprehension of the concepts covered, which was evident based upon final projects that required the students to implement these tools of computational chemistry into their individual research projects.

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REFERENCES

