

Incorporating **COMPUTATIONAL CHEMISTRY** *into the ChE Curriculum*

JENNIFER WILCOX

Worcester Polytechnic Institute • Worcester, MA 01609

In many engineering curricula it is difficult to cover the fundamental concepts that are required to provide all students with an optimum base for the solution development of new problems and applications. Although this task is daunting, replacing the learning and understanding of fundamental concepts with starting parameters and a list of equations to use as tools is not a solution. Such an approach subsequently limits the capabilities and potential accomplishments of the students.

This trap is easy to fall into, however, since it is nearly impossible to cover all of the fundamentals in addition to the applications. Yet a failure to emphasize these basics could mean putting chemical engineers at a disadvantage against chemists or physicists, who may be able to develop new ideas more readily because their training through education has taught them to derive the equations they are using. Engineers are typically admired for their ingenuity and creativity, but with a curriculum that does not obligate them to derive and to consistently ask “why” and “from where,” engineers will soon lose the merits of which they are so well known.

Within a graduate-level chemical engineering course, fundamental chemical principles combined with computational chemistry software were used as a tool to bridge the gap that often exists between chemistry and 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 computational chemistry course. The theoretical 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] The current methodology, however, is different from its typical inclusion within a chemistry course since it has been incorporated into a chemical engineering curriculum, where it serves to couple fundamental chemical principles to applications in chemical engineering through a combination of ab initio theory and reaction kinetics. During the fall 2005 semester this course

Jennifer Wilcox is an assistant professor in the Chemical Engineering Department at Worcester Polytechnic Institute. She received her B.S. degree from Wellesley College in mathematics and her M.A. and Ph.D. from the University of Arizona in chemical engineering.



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was offered for the first time in the Chemical Engineering Department at Worcester Polytechnic Institute. A six-week assignment termed, "Learning through a Reaction Example," served as the main driving force throughout the course and was reflected both in lecture material and 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.

COURSE OVERVIEW

The course spanned more than 14 weeks and was held for 1.5 hours twice a week; homework was assigned on a weekly basis. The course was divided into the following sections with less than half taking place outside the computer lab:

- ▶ **Principles by which ab initio-based methods and basis sets are comprised.** Background of key features and concepts of quantum mechanics (QM) were taught. Homework assignments included the following: 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. Homework assignments throughout this aspect of the course required a background in calculus and differential equations. A brief review of complex numbers and differential-equation solution types was given. These topics comprised four weeks of the course, culminating with a closed-book in-class exam.
- ▶ **"Learning through a Reaction Example."** This assignment included five weekly projects and a take-home exam that required students to compile the individual components into the form of scientific papers (so that students could gain familiarity with writing in a scientific manner). An additional manuscript is being submitted for publication which describes further details and results of this assignment, purely through the students' perspective.^[3] In addition, students reflect on each of these four sections of the course in detail, determining which exercises were more beneficial than others and why. Throughout the "Learning Through a Reactions Example," topic, a combination of lecture and interactive learning through computational in-class lab exercises was used, *i.e.*, using the Gaussian98 software package 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.

- ▶ **Final project.** 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. In some cases, the research area of focus required an advanced background in molecular modeling that the course was not able to provide in just 14 weeks, and in these cases the students gained mastery of the literature available on the computational chemical aspect of their research. Additionally, the students used what was learned from the course to provide insight into the chemical mechanisms that may play a role in the explanation of experimentally observed phenomena. The goal of this final exercise was to provide a way to evaluate 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 to their research in a novel way. 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

With regard to several of the student projects—such as the one involving the application of ab initio theory for modeling complicated catalytic processes such as those involved in fuel cell research—the student completed the final project with an

understanding of the computational literature in this field and a visual interpretation of the mechanisms involved within the complexities of the process, which will likely benefit him by providing focused direction when deciding which experiments to carry out in the lab. This theoretical understanding became the goal of this student's project since heterogeneous modeling was outside the scope of the course. With respect to the second project listed above, the student used *ab initio* energetic predictions along with electrostatic potential and molecular orbital maps to understand the reactivity between groundwater contaminants and zeolite exchange ions. This student has since had a paper accepted and will be presenting her research at the International Conference in Engineering Education in Puerto Rico in July 2006.^[4] Therefore the measure of success spans a wide range, whether it is based on the direct inclusion of *ab initio*-based calculations in a student's work or based on an appreciation and understanding of the *ab initio* language to a level that allows for material retention from a peer-reviewed article within the student's specific research area.

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 incorporating a molecular perspective into their graduate research. Therefore, it is this aspect of the course that will be described in detail within this article.

COURSE SPECIFICS

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 describes 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).

This computational chemistry course was highly technologically based with approximately two-thirds of the classes involving active learning through the use of computers. Students used the software package Gaussian98^[5] to calculate the electronic energies from approximations to the SWE. To visualize vibrational frequencies, chemical bonding, electron density maps, and molecular orbital maps, gOpenMol soft-

ware was employed. In a traditional course in introductory chemistry these topics are covered in detail, but oftentimes teaching students about them is difficult due to the underlying abstract quantum chemistry involved. Using the visualization software, the students were responsible for developing electron density and molecular orbital maps to gain understanding into the chemical reactivity of various species. Straightforward molecules such as water and methane were introduced, and in additional assignments students explored molecules of increasing interatomic bonding complexity such as cyclohexane and 1,4-dioxane. For the development of the quantum mechanical-based potential energy surfaces, MATLAB software was used. A Sun Microsystems Sun Fire V20z server with a dual AMD Opteron™ 64 bit processor and 4 gigabytes of memory with a 73 Gigabyte hard disk was devoted specifically for the course. The software program WebMO 4.1 was used as an interface to submit jobs to Gaussian98 through the Sun server. Students were able to submit their calculations to the server such that the local desktop computers could remain active throughout each class period; this also provided students with the flexibility to work on homework assignments and submit jobs from any computer with Internet capabilities.

DESCRIPTION OF REACTION ASSIGNMENT

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



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. Seeking these experimental data required students to gain familiarity with standard references such as JANAF^[6] tables, the *Handbook of Chemistry and Physics*,^[7] and Herzberg spectroscopy texts.^[8] The experimental thermochemical data included reaction enthalpies, entropies, Gibbs free energies, and equilibrium

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constants using the *NIST Chemistry WebBook*.^[9] To locate experimental kinetic data for the reaction, students were encouraged to perform literature searches in addition to accessing the data available in the NIST kinetic database.^[9]

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-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 compared their theoretical predictions to the experimental data that was compiled in step one of the assignment. It is this aspect of the assignment that allows the students to be in control of 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. An example of equilibrium geometry and spectroscopic predictions for Reaction (2) is shown in **Table 1**. Thermochemical predictions, including reaction enthalpies, entropies, and Gibbs free energies, at varying levels of theory, are presented for Reaction (5) in **Table 2**. In most cases, the students would choose more than three additional levels of theory for investigation in an effort to obtain a theoretical prediction with minimal deviation from experiment. Within this step of the assignment students learned how the addition of polarization and diffuse functions to a basis set can influence the theoretical predictions. Of course, lecture material

TABLE 1
Comparison of Chemical Properties of Species from $D_2 + Cl \rightarrow DCl + D$

Theory	Bond Length (Å)		Vibrational Frequency (cm ⁻¹)		Dipole Moment (Debye)	Rotational Constant (cm ⁻¹)	
	DCI	D ₂	DCI	D ₂	DCI	DCI	D ₂
B3LYP/LANL2DZ	1.3149	0.7435	1943	3153	1.80	5.11	30.28
HF/6-31G	1.2953	0.7297	2097	3289	1.87	5.27	31.44
HF/STO-6G	1.3112	0.7105	2097	3886	1.77	5.14	33.16
MP2/6-31G	1.3174	0.7376	1970	3206	1.88	5.10	30.77
MP2/6-311+G	1.3269	0.7376	1943	3149	1.89	5.02	30.77
MP2/6-311+G(d,p)	1.2731	0.7383	2214	3206	1.44	5.46	30.71
MP2/6-31+G*	1.2810	0.7375	2177	3206	1.53	5.39	30.77
MP2/6-311(3df,3pd)	1.272	0.7367	2190	3195	1.17	5.47	30.84
QCISD/6-31G	1.3262	0.7462	1901	3089	1.88	5.03	30.06
QCISD/6-311+G	1.3262	0.7465	1875	3018	1.71	5.03	30.04
QCISD/6-311+G**	1.2758	0.7435	2183	3126	1.33	5.43	30.28
QCISD/6-311++G**	1.2762	0.7435	2181	3126	1.32	5.43	30.29
CCSD/6-31G	1.3261	0.7462	1901	3089	1.88	5.03	30.06
CCSD/6-311+G	1.3365	0.7465	1876	3018	1.89	4.95	30.04
CCSD/cc-pVDZ	1.2905	0.7609	2144	3100	1.16	5.31	28.91
CCSD(T)/6-311G**	1.2772	0.7435	2174	3127	1.46	5.42	30.28
CCD/aug-cc-pVDZ	1.2897	0.7610	2151	3084	1.16	5.32	28.90
CCD/cc-pVTZ	1.2748	0.7421	2172	3127	1.18	5.44	30.39
Experimental[†]	1.2746	0.7420	2145	311	-	5.44	30.44

[†] Ref^[7,8,14]

included a discussion of the details of methods and basis sets; however, the interactive experience of testing, checking, and comparing to experiment was far more valuable, allowing these concepts to sink in to a deeper level of understanding from the student perspective. Class at this time included discussions concerning the difference in accuracy of the various levels of theory and the reasons associated with why some levels work better than others. Additionally, discussions also included why at times some levels of theory work, but not

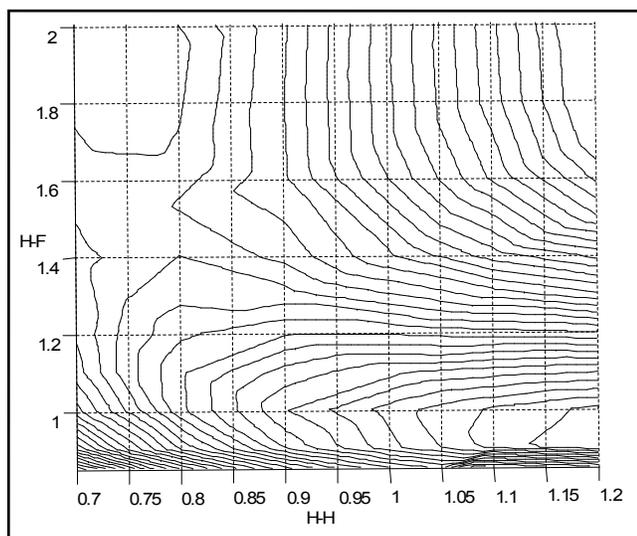


Figure 1. PES for the reaction $H_2 + F \rightarrow HF + H$ generated at the QCISD/6-311G(3df,3pd) level of theory.

necessarily for the right reasons, *i.e.*, cancellations in error could provide a reasonable heat of reaction prediction in one case, but may deviate from experiment in terms of the predicted equilibrium geometry. The goal of matching the experimental data provided a motivation for the students to push forward through obstacles that are typical of a traditional lecture-formatted curriculum. For example, traditional teaching methods such as Microsoft Office PowerPoint presentations or conventional rote lectures tend to neglect participation of the students, consequently allowing their minds to wander, losing the ability to grasp the material at hand. Providing a motivated student with an objective and the responsibility for her own learning through a series of interactive exercises ensures active participation, which undoubtedly enhances the likelihood of material retention.

Step Four: This step involves the development of a high-level potential energy surface (PES). 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. A PES generated from the class for Reaction (3) at the QCISD/6-311G(3df,3pd) level of theory is presented in Figure 1. The software program MATLAB was employed for the PES plots. Most of the surfaces generated in the class consisted of approximately 200 single-point energies. Since the reactions assigned were

all elementary gas-phase reactions involving, at most, three atoms, the largest transition structures were three-atom complexes. It was assumed that each activated complex was linear so that two degrees of freedom could be considered along two dimensions of the three-dimensional PES plot, with the third dimension serving as the potential energy. From the PES plots students extracted the relative geometry of the reaction's activated complex. As a further check that this activated complex corresponded to a true transition structure, a frequency calculation was performed to ensure the existence of one negative frequency along the reaction coordinate. Oftentimes this additional calculation would provide more accurate

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TABLE 2
Thermochemistry Comparison for $F_2 + H \rightarrow HF + F$

Theory	ΔH_{rxn} (kcal/mol)	ΔS_{rxn} (cal/mol*K)	ΔG_{rxn} (kcal/mol)	K_{eq}^\dagger
B3LYP/LANL2DZ	-91.61	1.841	-92.16	3.87(+67)
HF/6-31G	-121.20	1.904	-121.7	2.01(+89)
MP2/6-31G	-82.76	1.677	-83.26	1.16(+61)
MP2/6-311+G	-91.99	1.586	-92.46	6.48(+67)
MP2/6-311+G(d,p)	-103.8	1.787	-104.3	3.44(+76)
QCISD/6-31G	-84.52	1.578	-84.99	2.14(+62)
QCISD/6-311+G	-94.24	1.510	-94.69	2.82(+69)
CCSD/6-31G	-84.65	1.577	-85.12	2.68(+62)
CCSD/6-311+G	-94.44	1.513	-94.89	3.91(+69)
CCSD/aug-cc-pVDZ	-104.4	1.798	-104.9	9.08(+76)
CCSD(T)/6-311G**	-98.96	1.607	-99.44	8.56(+72)
QCISD(T)/6-311G**	-98.92	1.612	-99.40	7.92(+72)
Experimental [‡]	-98.27	3.596	-99.34	7.20(+72)

[†]Numbers in parenthesis denote powers of 10.

[‡] Ref [6, 9, 15]

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coordinates of the transition structure, ensuring accuracy in the barrier-height calculation.

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. In determining the rate constant for each reaction, the value predicted by transition state theory,^[10] Eq. (6), was modified with the tunneling correction of Wigner^[11] given by Eq. (7) (where ν represents the single imaginary frequency value of the transition structure), so that the final rate constant value was given by Eq. (8),

$$k^{\text{TST}} = \frac{k_b T}{h} \frac{Q_{\text{TS}}}{Q_1 Q_2} e^{\left(\frac{-E_a}{RT}\right)} \quad (6)$$

$$k_T = 1 + \frac{1}{24} \left[\frac{h\nu}{k_b T} \right]^2 \quad (7)$$

$$k = k^{\text{TST}} \cdot k_T \frac{\text{cm}^3}{\text{mol} \cdot \text{s}} \quad (8)$$

where ν represents the single negative frequency value of the transition structure and the partition function, $Q_{\text{Total}} = Q_{\text{trans}} Q_{\text{rot}} Q_{\text{vib}} Q_{\text{elec}}$. Two lectures and one homework assignment were dedicated to providing the students with an introductory background in statistical mechanics so that they could understand the assumptions that are made in Gaussian to obtain the partition function data. Three to four lectures were dedicated to reaction kinetics in which the HSCM and TST were taught. Students were required to work through two TST problems in a homework assignment before applying the knowledge to their reaction example. Further details of TST can be found in standard kinetic texts, which served as references for the course.^[12,13] In addition, the barrier heights required for Eq. (6) were extracted from the previously developed high-level PES.

The barrier height was calculated by taking the energy difference between the thermal-corrected (including zero-point energies) transition structure and the sum of the thermal-corrected reactant species.

The calculation of the rate constant based upon the hard-sphere collision model was performed using Eq. (9).

$$k^{\text{Coll}} = \pi \sigma_{12}^2 N_A \sqrt{\frac{8k_b T}{\pi \mu_{12}}} e^{\left(\frac{-E_a}{RT}\right)} \frac{\text{cm}^3}{\text{mol} \cdot \text{s}} \quad (9)$$

where the barrier height, E_a is the same as for k_{TST} , μ_{12} is the reduced mass, and σ_{12} is the collision diameter. Since E_a is already known, and μ_{12} can be determined with a simple calculation, the only difficulty was in determining the collision diameter. Here, the lack of experimental data required the use of estimation techniques to find an approximate value of σ . The primary technique utilized was a traditional approach based on the critical properties of the species in the reaction as shown in Eq. (10), in which V_c and Z_c are the critical volume and critical compressibility parameters, respectively.

$$\sigma = 0.1866 V_c^{\frac{1}{3}} Z_c^{\frac{6}{5}} \text{ \AA} \quad (10)$$

An example of the predicted reverse rate expressions for Reaction (1) calculated at the CCSD/6-311G(3df,3pd) level of theory compared to literature predictions and experiment is presented in Table 3. Figure 2 is a graphical representation of the rate prediction for the forward direction of Reaction (1), showing that this high level of theory with a modest kinetic tool such as TST provided a fairly accurate kinetic prediction.

CONCLUSIONS

A graduate-level chemical engineering course in computational chemistry was developed that served to provide chemical engineering students with an introduction to a

Temp Range (K)	A^\ddagger (cm ³ /mol*sec)	E_a (kcal/mol)	Reference
291–1192	2.999(13)	5.10	Adusei and Fontijn ^[16]
1000–1500	3.114(13)	4.84	Allison, <i>et al.</i> ^[17]
600–1000	2.318(13)	4.25	Allison, <i>et al.</i> ^[17]
200–1000	7.94(12)	4.39	Lendvay, <i>et al.</i> ^[18]
298.15–2500	5.015(13)	4.39	Present work (TST) CCSD/6-311G(3df, 3pd)
298.15–2500	6.134(14)	4.67	Present work (HSCM)

[†]Numbers in parenthesis denote powers of 10.

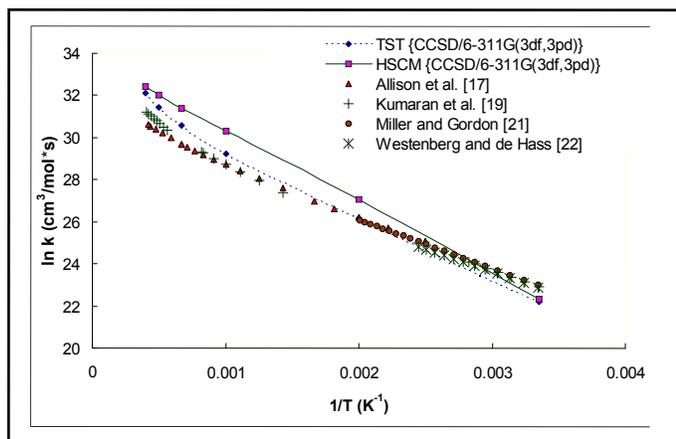


Figure 2. Rate Constant Comparison for the Reaction, $\text{Cl} + \text{H}_2 \rightarrow \text{HCl} + \text{H}$.

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 barrier heights were extracted for predicted rate expression calculations. This 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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