INCORPORATING MOLECULAR MODELING INTO THE CHE CURRICULUM

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Computers have long been used in the teaching of chemical engineering in order to facilitate complex calculations required for the design and analysis of chemical process equipment (plug-flow reactors, multistage distillation columns, etc). The use of computer-based process simulation using commercial software (Aspen Plus, ProVision, Hysim, etc.) is commonplace in most modern chemical engineering curricula. Today, the availability of powerful molecular modeling software is adding an entirely new vehicle for predicting the behavior of systems and processes based on molecular-scale properties. While the principles are not new, only recently has the computational hardware and software become available that can bring these tools (Gaussian, Spartan, Cerius^2, etc) into the chemical engineering classroom. The capability of combining computation with visualization presents chemical engineering educators with important new opportunities for enhanced teaching and learning.

PARADIGMS IN CHE EDUCATION

Wei[1] commented on the two paradigms that shaped chemical engineering education during the 20th century. The first of these was based on classification of processes and systems as the familiar unit-operations lexicon; this approach dominated the early stages of chemical engineering teaching. The publication of *Transport Phenomena*[2] marked the beginning of the second paradigm, that of the fundamental analytical approach based on rigorous mathematical models of physical systems. Recently, a third paradigm for chemical engineering was proposed by Landau,[3] that of a closer relationship with practice and industry.

It is our opinion, however, that the third paradigm could and should be cast in the context of better integration of the fundamental molecular processes of chemical physics into chemical engineering. Other educators have discussed the importance of the microscopic viewpoint in our teaching and research[4,5] but in today's chemical engineering curriculum the basic atomistic concepts learned in organic and physical chemistry are too often left to languish as soon as the specific courses dealing with these subject areas have been completed. This is caused in large part by a lack of continuity between subject matter and by poor integration in terms of teaching of the two disciplines. Important concepts in organic synthesis and molecular structure are rapidly forgotten by third- and fourth-year chemical engineering students, just at the time that these concepts should be applied (for example, in the process design and/or reaction engineering courses).

At the Colorado School of Mines (CSM), we have recently completed a top-to-bottom school-wide redesign of our undergraduate curriculum. As part of this exercise, the undergraduate chemical engineering curriculum was significantly updated and revised. A key philosophical component in this revision process was our desire to incorporate molecular modeling and simulation into the chemistry and chemical engineering course sequence in order to foster a better ap-

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preciation of the relationship between microscopic and macroscopic phenomena and a better understanding of the importance of chemical physics in determining how molecules interact and react:

$$\text{molecular properties} \xleftrightarrow[\text{modeling}]{\text{molecular}} \text{macroscopic processes}$$

As described above, we believe that computer-aided molecular modeling can serve as the catalyst that allows students to make and understand these connections.

MOLECULAR MODELING AND SIMULATION

The two main components of our microscopic approach to understanding macroscopic processes are molecular modeling and molecular simulation. The distinction between these two is somewhat arbitrary, but in our case we define molecular modeling to be the investigation of isolated molecular assemblies (*e.g.,* single molecules, dimers, etc.) and molecular simulation to be the investigation of collections of interacting molecules. The primary tools used to perform molecular modeling are *ab initio* and semi-empirical quantum mechanics and molecular mechanics,[7] while molecular simulation incorporates the use of molecular dynamics and, for example, Monte Carlo methods.[8]

The primary use of molecular mechanics is to make empirical estimations of equilibrium molecular geometry (*e.g.,* the most energetically favorable structure) and energy by using parameterized force fields. For homogeneous systems, molecular mechanics describes the total energy of a molecule as the sum of a distortion energy from an "ideal" geometry of connected atoms (E_1)

$$E_1 = \sum_{\text{bonds}} E^{\text{stretching}} + \sum_{\substack{\text{bond}\\\text{angles}}} E^{\text{bending}} + \sum_{\substack{\text{dihedral}\\\text{angles}}} E^{\text{torsion}} \tag{1}$$

and the contribution due to non-bonded interactions (E_2) that arise from van der Waals and electrostatic interactions

$$E_2 = \sum_i \sum_j E_{ij}^{\text{VDW}} + \sum_i \sum_j E_{ij}^{\text{electrostatic}} \tag{2}$$

The total energy is just $E_1 + E_2$. Examples of molecular mechanics force fields are SYBYL[9] and MMFF.[10] Depending on the nature and applicability of the force field being used to carry out the calculation, this procedure may work well or can give rise to structures, geometries, and hence equilibrium energies that are significantly in error. In so-called computational chemistry programs, force field calculations are often employed to give a refined structure as a starting point for the *ab initio* quantum mechanics calculations.

Today, the availability of powerful molecular modeling software is adding an entirely new vehicle for predicting the behavior of systems and processes based on molecular-scale properties.

The second type of computation that is often used for molecular modeling directly involves quantum mechanics, with the general mathematical relationship given by the Schrödinger equation

$$\left(-\frac{h^2}{8\pi^2}\sum_N \frac{1}{m_N}\nabla_N^2 - \frac{h^2}{8\pi^2 m_e}\sum_i \nabla_i^2 - \sum_N\sum_i \frac{Z_N e^2}{r_{iN}} + \sum_N\sum_M \frac{Z_N Z_M e^2}{R_{NM}} + \sum_i\sum_j \frac{e^2}{r_{ij}}\right)\Psi(\{R\},\{r\}) = E\Psi(\{R\},\{r\}) \tag{3}$$

In this equation, ∇ is the momentum operator, m refers to a mass, Z is a charge, e is the unit measure of charge, R denotes nuclear positions, and r denotes electronic positions. Ψ is the quantum mechanical wave function for the molecule, and E is the energy of the molecule. According to quantum mechanics, solution for the wave function enables one to calculate the energy and other structural properties of a molecule.

Although this equation may be written down rather simply, it cannot be solved exactly except for the hydrogen atom (one electron, one proton). While exact solution of this equation for polyatomic molecules is still not feasible, application of a series of approximations (in particular, the Hartree-Fock approximation) and the advent of powerful desktop computers using high-speed microprocessors has made numerical solutions possible.[6]

A high degree of computational efficiency can be obtained by using *semi-empirical* quantum mechanical methods that consider only the valence electrons in a molecule and reduce the number of electron-electron interactions by neglecting "overlaps" between atomic orbitals. In addition, these models introduce parameters that have been optimized with experimental data.

In contrast to molecular mechanics and *ab initio* quantum mechanics, molecular simulation techniques examine the behavior of systems composed of a small collection (typically 100 to 10,000) of interacting molecules. The methods used include molecular dynamics (in which the time evolution of the molecular system is simulated and monitored) and Monte Carlo simulation (in which statistical methods are used to sample states of the system according to some pre-defined probability distribution).

The basic method used in molecular dynamics is to solve numerically the classical equations of motion of the molecules (structured mass points) and calculate time averages of quantities such as the configurational energy, pressure, self-diffusion coefficients, local structure, etc. Typically, the molecular system is simulated for picosecond time intervals, which may involve solving the coupled differential equations of motion for several hundred thousand time-steps.

The accuracy of these simulations is governed by the numerical techniques used and the accuracy of the interaction potential(s) that govern the motion and time evolution of the molecules in the system. For structured (polyatomic) molecules, these potentials might include intra-molecular vibration, rotation, and non-bonded interaction potentials as well as non-bonded intermolecular potentials. The non-bonded potentials are typically parameterized intermolecular potential functions such as the Lennard-Jones or Exponential-6 models. An advantage of molecular dynamics is that non-equilibrium properties may be calculated with relative ease.

In Monte Carlo simulations, the energy of the molecular system is minimized by randomly moving molecules according to some desired probability distribution. Again, the user must specify the potential functions, and equilibrium properties can be calculated by statistical (rather than time) averages. A great advantage of this method is the relative ease with which it can be used to calculate phase equilibria.[11]

Molecular modeling and simulation is finding widespread applicability and increased acceptance in chemical engineering practice. Estimation of thermophysical properties has become routine.[12]

Simulation of rheological properties of complex fluids has been demonstrated by Cummings and co-workers[13,14] and molecular simulation of water has been shown to give structural information that is more reliable than even the most precise measurements can yield.[15]

In addition, use of molecular mechanics and quantum chemistry calculations to determine orbital occupancy has been shown to be important in understanding and design of new materials such as catalysts,[16] sorbents,[17] and reactive polymer membranes.[18]

MOLECULAR SIMULATION IN THE UNDERGRADUATE CHEMISTRY CURRICULUM

At CSM, students first encounter applications of molecular modeling in their sophomore-level organic chemistry course sequence. Calculations are facilitated using Spartan, which is a user-friendly computational quantum chemistry software package.

Computational quantum chemistry problems are assigned essentially as self-paced "discovery" exercises in Organic I and II. Students first use Spartan to carry out quantum calculations in order to investigate structure/stability relationships for typical hydrocarbons, functional groups, and reactive intermediates (radicals, carbocations, carbenes, etc.). Most calculations are carried out using geometry optimization at the semi-empirical AM1* level: some calculations require *ab initio* methods with higher levels of theory (3-21G)**. In either case, the computations can be rapidly completed using either Spartan's PC-based software or the Unix workstation version; a total of approximately sixty licensed copies of Spartan are available to chemical engineering students in open computer labs on both platforms.

Spartan's ability to calculate and display electron density and molecular orbital surfaces is exploited in the organic course sequence where the focus is on understanding the mechanisms of chemical reactions.

The relationships between electronic structure, molecular orbital density, and chemical reactivity are also developed using the visualization capabilities of the software. For example, when studying nucleophilic substitution reactions, the students use Spartan to compute HOMO (highest occupied molecular orbital) and LUMO (lowest unoccupied molecular orbital) surfaces for the reactants, and then relate the electron transfer taking place in the frontier orbitals to the observed regiochemistry and selectivity of the reaction.

For both the organic and physical chemistry sequences, Spartan's capabilities of calculating and graphically rendering electron density molecular orbital surfaces greatly facilitates the student's understanding of the relationship between molecular properties and such important concepts

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* *Austin Method 1: a semi-empirical molecular orbital method.*

** *A basis set in which each inner-shell atomic orbital is written in terms of three Gaussian functions and each valence-shell atomic orbital is split into two parts, written in terms of two and one Gaussians, respectively.*

as stability and reactivity.

These concepts are further elaborated during the third-year physical chemistry sequence. Here, the students are exposed in class to the theory and some of the mathematical details associated with setting up and arriving at approximate solutions to the Schrödinger equation. As an example, the Morse potential energy diagram for a diatomic molecule is first calculated using measured spectroscopic (IR) data from the lab, and then simulated using Spartan.

MOLECULAR MODELING IN THE CHE CURRICULUM AT CSM

Incorporation of molecular modeling in the chemical engineering curriculum was first accomplished two years ago in our senior-level reaction engineering course. As an example of the approach being used, an outline for one of the computational chemistry homework problems assigned in this class is shown in Table 1.

The problem deals with synthesis of chemical-grade ethanol via a S_N2 nucleophilic substitution reaction in aqueous solution. The objective of the problem is to illustrate use of quantum mechanics and computational chemistry in order to generate the thermochemical information required to carry out an analysis of a simple industrial reaction. Two possible reactions are proposed, differing only in choice of substrate:

$$C_2H_5Cl + OH^- \leftrightarrow C_2H_5OH + Cl^-$$

$$C_2H_5Br + OH^- \leftrightarrow C_2H_5OH + Br^-$$

As a first step, students are asked to investigate the thermodynamics of the reactions. For this part of the problem, heats of formation of all products and reactants (including solvation energy effects) are estimated by semi-empirical quantum chemistry methods, and the heat of reaction computed in the normal fashion:

$$\Delta H_R = \sum_j^{\text{products}} \nu_j \Delta H_{F,j} - \sum_i^{\text{reactants}} \nu_i \Delta H_{F,i} \qquad (4)$$

Calculation of the equilibrium constant requires the free energy change for the reaction

$$K = \exp\left(-\Delta G_R^0 / RT\right) \qquad (5)$$

but if entropic effects are not important (a reasonable assumption in this case)

$$\Delta G_R^0 = \Delta H_R^0 - T\Delta S^0$$
$$\Delta G_R^0 \approx \Delta H_R^0 \qquad (6)$$

and the standard free energy change and hence the equilibrium constant for each reaction can be readily estimated

TABLE 1
Example Problem in Reaction Kinetics

Synthesis of chemical-grade ethanol can be achieved by a nucleophilic substitution reaction using hydroxide ion as the nucleophile and a haloethane as the substrate. For this problem, we will investigate the rates of two synthesis reactions, differing only in the nature of the halogen atom (bromine vs. chlorine):

$$C_2H_5Cl + OH^- \leftrightarrow C_2H_5OH + Cl^-$$

$$C_2H_5Br + OH^- \leftrightarrow C_2H_5OH + Br^-$$

The reaction takes place under aqueous conditions. Both reactions can be assumed to follow a S_N2 (substitution/nucleophilic/bimolecular) mechanism. Hence the geometry and configuration of the transition state can be assumed to be the same for both reactions. We wish to estimate the ratio of the rates of these two reactions.

1. Estimate the activation energies for both the forward and reverse reactions using Spartan. This will require several assumptions regarding the exact geometry of the transition state, namely
    - Assume that the nucleophile (the attacking group) and leaving group are both attached to the same carbon atom and are in axial positions (*e.g.*, 180° apart)
    - For S_N2 reactions, trigonal bi-pyramidal geometry at the carbon atom where the nucleophile is attacking gives a reasonable approximation to the transition state.

   To obtain the energy of the transition state, have Spartan carry out a Semi-Empirical Transition Structure calculation using AM1 as the model and water (Water C-T) as the solvent. Remember to set up the correct charge and multiplicity for your assumed transition state. Obtain heats of formation from Spartan for the ionic species (Semi-Empirical, Single Point Energy, AM1, Water C-T). Obtain heats of formation for the other reactants and products using Semi-Empirical Geometry Optimization as the task, AM1 as the model, and Water C-T as the solvent.

2. Using data on heats of formation of the reactants and the products from Spartan, calculate the heat of reaction for both nucleophilic substitution reactions. Which reaction is favored if the reactions are under thermodynamic control? Calculate the ratio of the equilibrium constants for these two reactions at 25°C.

3. Calculate the ratio of the rate of the substitution reaction for bromoethane as the substrate to the substitution reaction when chloroethane is the substrate in the temperature range from 25°C to 100°C. What assumptions are necessary to carry out this calculation? Are these assumptions reasonable? Does the ratio change with temperature? Why?

4. a) If you were going to engineer a reactor for manufacture of chemical-grade ethanol using one of these two reactions, which haloethane would you recommend be used and why? Are there any important factors that you are not considering in your choice for a substrate?*
   b) Would you suggest the process be carried out at low temperature or high temperature, and why?

* *You may want to consult the Chemical Marketing Reporter (reference room, CSM library) for data that will help answer this question. Up-to-date information on some chemicals can also be found at <www.chemexpo.com> and <www.chemweek.com>.*

based on the heat of reaction. Using ratios for the two equilibrium constants in evaluating the thermodynamic feasibility makes this assumption much less restrictive.

This analysis shows that both reactions are favorable thermodynamically, with a preference to chloroethane as the substrate (larger equilibrium constant). The reactions are also shown to be under kinetic control, hence the next step is to see what differences may exist in the activation energies for the two reactions.

This is accomplished by constructing a hypothetical transition state for the nucleophilic substitution reaction for both reactions, and by using Spartan to estimate the energy of these species. This part of the solution process draws heavily on the student's background in organic chemistry theory where substitution reactions are concerned.

Once the transition states for both reactions have been constructed, values for the heats of formation of the reactive intermediates are determined using the Transition Structure Optimization routine (searching for a saddle point on the reaction potential energy surface) in Spartan.

Students can include a calculation of the vibrational spectrum at this point in order to verify that a reasonable approximation for the transition state species has been found by this procedure (at least one imaginary frequency that corresponds to the reaction coordinate of interest). Animation of the largest imaginary frequency in the calculated table of normal mode frequencies provides convincing evidence that the reaction coordinate of interest corresponds well to the transition state structure. Finally, the activation energies for both reactions can be readily estimated from the semi-empirical heats of formation as

$$E_A = \Delta H_{f,TS} - \sum^{\text{reactants}} \Delta H_f \tag{7}$$

Comparison of the relative rates at any temperature, T, then follows directly from

$$\frac{r_{Cl}}{r_{Br}} = \exp\left[\left(E_{A,Br} - E_{A,Cl}\right)/RT\right] \tag{8}$$

From this process, the students find that the activation

TABLE 2
Course Outline and Instructional Modules
Molecular Perspectives in Chemical Engineering

Learning Objectives

The class introduces students to the use of molecular-scale techniques for the prediction of physical properties, transport properties, and reaction energetics.

Content Summary

This class introduces modern methodologies for the estimation of physical, transport, and reaction properties and parameters needed in the design of chemical processes. In addition, it serves to enhance students' molecular-scale intuition through the use of group contribution methods, molecular simulations, quantum mechanical calculations, and molecular visualization. The class begins with a review of the microscopic world of atoms and molecules; fundamental length, time, and energy scales are discussed. Molecular-scale forces and their representative potentials are presented. Case studies are pursued involving topics such as the estimation of diffusion coefficients, viscosity, and phase equilibria, as well as transition-state theory for the estimation of rate constants in chemical reactions. Relevant experimental techniques that can serve to verify the molecular-scale calculations are covered. Significant hands-on experience in a computer laboratory and case-study projects is emphasized.

Topics Covered

1. Computers and computer simulation in chemical engineering
2. Properties of fluids and solids; molecular structure prediction methods
3. Computational quantum chemistry, intramolecular properties
4. Intermolecular properties and forces
5. Intermolecular forces and configurational properties
6. Equilibrium molecular dynamics
7. Monte Carlo techniques
8. Nonequilibrium molecular dynamics

Module	***Description***
Ideal Gas Properties	Simulation and text to illustrate how molecular motions give rise to ideal gas properties.
Vapor-Liquid Equilibria	Simulation to illustrate how inter-molecular interactions affect the dynamics and VLE of mixtures.
Group Contributions	Quantum mechanical calculation of Benson groups.
Diffusion in Polymers	Molecular dynamics simulation and visualization of nitrogen diffusion in polysiloxane.
Thermochemical Properties	Use of computational chemistry to estimate thermochemical properties.
Structure-Property Relationships	Free radical polymerization of vinyl chloride to form PVC.
Activation Energies	Use of quantum mechanics to investigate thermal cracking of ethane.
Intramolecular Quantum Behavior	Quantum mechanics of molecules: potentials, vibrations, IR spectra, and equilibrium geometries.
Intermolecular Forces	Estimation of intermolecular force using quantum chemistry.
Thermodynamics of Rare Gas Mixtures	Application of molecular dynamics simulations to the estimation of mixture properties.

energy for the synthesis using bromoethane as the substrate is significantly lower, thus suggesting that the reaction will be much faster if this compound is used as the reactant. Finally, costs of the two reactants are compared using data from the commodities literature.

The approach to solving this problem relies exclusively on the use of molecular modeling to obtain information that is not readily available from any of the standard data sources—hence the use of quantum chemistry to estimate parameters that are of considerable practical utility for both reactor and process-design purposes is well illustrated.

We have recently added a new senior-level course to our curriculum, "Molecular Perspectives in Chemical Engineering." This course presents students with a comprehensive overview of the use of molecular modeling and simulation techniques in several different applications, including estimation of thermophysical and reaction rate data, sorption equilibria and diffusion rates, phase equilibrium simulation, and prediction of transport properties.

An outline for this course, including descriptions of the computational exercises that are currently in use, is given in Table 2. Examples of molecular modeling exercises used in the capstone chemical engineering molecular simulation course can also be found by accessing the CSM website at <http://www.mines.edu/Academic/chemeng>.

CONCLUSIONS

Molecular-scale modeling has reached a level of sophistication and accuracy that makes it an essential and highly useful tool for chemical engineers, yet the methods, capabilities, and limitations of this tool are not yet well known across the chemical engineering profession. The use of molecular-scale modeling is becoming increasingly important in industry as researchers and product developers look for ways to cut the costs and time associated with development of new products.

At CSM, we have addressed this problem by incorporating atomistic modeling methods throughout our curriculum at the undergraduate level in both the chemistry and chemical engineering course sequences. We believe that this approach represents a new educational paradigm in chemical engineering, and we are committed to integration of these concepts across the curriculum.

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ChE letter to the editor

Dear Sir:

The article by Rugarcia, et al., titled "The Future of Chemical Engineering Education" [*CEE,* **34**, 16, (2000)] is interesting and thought provoking. However, it begins with a caricature of a poor lecture and returns to the theme of the inferiority of the lecture format later in the paper with the assertion that "the superiority of alternative methods. . .has been demonstrated in thousands of empirical research studies." This view has become widely accepted among the proponents of "new" teaching methods. At the risk of being branded as a Luddite (probably true), I am compelled to offer a modest and purely anecdotal defense of the lecture format.

Looking back on my own experience as an undergraduate, the classes that I most enjoyed were all formal lectures in physics, chemistry, and even geology. These lectures were given to large classes (sometimes several hundred students) and I am sure that the lecturers would have been horrified at the thought of following a course textbook or of presenting worked examples during a lecture. What was presented was an in-depth review stressing the fundamental principles and the logic and coherence of our understanding of the subject. It is perhaps ironic that the notes from several of these courses were later published as successful textbooks! Well-thought-out and well-rehearsed demonstration experiments, performed by a teaching assistant, were sometimes included. Questions, assignments, and practice examples were handled in parallel tutorial sessions, given by either a faculty member or a PhD student, each with no more than

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