

Putting Chemistry in ChE Classes
2017 Chemical Engineering Summer School
Wednesday, August 2, 2017, North Carolina State University in Raleigh

Goals:

In a condensed form, provide insights and teaching material about understanding and predicting properties for use across the curriculum, especially in thermodynamics, kinetics, transport, separations, and biotechnology. Content will be provided that can be used in core ChE courses, as well as reporting on a full-semester course that the presenter has given.

Scope and Content:

- I. **Introduction: Molecule-based properties** define the usefulness of products and the ability to use design/analysis equations. We need property relations based on composition, recognizing that composition and other factors may determine structure and function. Contrast conservation equations and constitutive relations. Introduce molecule-viewing software (GaussView) to show molecule structures and how to assemble them computationally.
 - a. Provide examples of properties and property trends, showing that they depend on molecular structure and interactions.
 - b. Introduce molecule-viewing software (GaussView) to show molecule structures and how to assemble them computationally. Also helps refresh memories of chemical nomenclature from alkanes to polymers to biomolecules.
- II. **Empirical correlations** may be linear – or not.
 - a. Use Excel to devise empirical correlations of selected pure-compound properties: Gas-phase heats of formation and entropies at 298 K, dipole moments, viscosity.
 - b. Provide examples of correlations, pointing toward the causes of their forms: Ideal gas law / compressibility, ideal solution / activity coefficients, pressure-dependent rate constants, gas & liquid mass diffusivities, Flory-Huggins polymer solution theory, Kovats relations for chromatography.
 - c. Introduce group additivity for thermochemistry and VLE relations.
 - d. Provide tables and descriptions of estimating molecular geometries and vibrational frequencies.
- III. **Statistical mechanics** are practically useful for understanding and predicting properties, often using **molecular simulations** for VLE, soft matter, and biological environments.
 - a. Outline (and give references and teaching material) for fundamentals of pure-species ideal-gas statistical mechanics.
 - b. Provide and discuss simple tables for pure-species ideal-gas thermochemistry and their basis (UG level with references for Grad level), introducing moments of inertia, types of molecular vibrations, and electronic states.
 - c. Show how molecular simulations -- molecular dynamics and Monte Carlo methods -- use mechanical physics and force fields to capture molecule interactions for mixture properties. Cite David Kofke's Etomica <etomica.org> and the Molecular Simulation workshop here.
- IV. **Computational quantum chemistry** can be understood using molecular structure-property interactions.
 - a. Outline (and give references and teaching material) for fundamentals of electronic structure theory and solution methods.
 - b. Have students use Gaussian to predict rotational moments, dipole moments, and vibrational spectra. Generate pure-species thermochemistry.
- V. **Correlating and predicting kinetics** applies statistical mechanics (transition-state theory) to a modest number of classes of reactions.
 - a. Categorize reactions as radical vs. ionic vs. pericyclic vs. *d*-orbital-based; and as abstraction vs. association/dissociation. Attendees will correlate rate coefficients within reaction classes.
 - b. Introduce impact of gas-phase density (Master Equation), supercritical behavior, solvent shells, and catalytic surface chemistry.
- VI. **Transport properties** are correlated by Lennard-Jones relations that rely on spherically symmetrical molecules but extend to capture real-substance behaviors.
 - a. Class-active comparison of mass-diffusivity correlations from simple gases and transport in pores to biomolecule transport through membranes; contrast with correlations of mass-transfer coefficients, which depend on both diffusivities and fluid mechanics.
- VII. **Biological functions** can be understood using molecular structure-property interactions.

- a. Illustrate with protein structure, lipid bilayer structure, ion-channel transport, molecule-enzyme docking, and G-protein-coupled receptors.

VIII. **Summary** will point to uses of the material in various courses and to sources of software and content.

Method of Delivery:

Use a mix: (1) Introductory materials to organize attendees' prior and new experiences with organic and physical chemistry, (2) references for in-depth background, (3) small-group in-class examples, and (4) hands-on data use and computation.

Participants will engage in active learning by tackling some property-correlation exercises, drawing molecules with GaussView molecular-viewing software, and calculating some simple structures, energies, thermo, and transition states with Gaussian and related tools. For calculations, we will use some web-based software on attendee laptops and additionally will set up a class-group access to the NC State henry2 supercomputer.

Take Home Materials:

Physical handouts and supplements, all provided electronically through the Summer School USB drive and a Google Drive folder <<https://drive.google.com/drive/folders/0B4vpFSLMDvShc0gtblgtY3hXTXM?usp=sharing>>. The handouts will include background resources, homework examples with answer discussions, and references to software sources.

Presenter:

Professor Phil Westmoreland (biosketch attached) will present the module. He has developed a class and class materials for the topic; taught short courses on computational quantum chemistry for Gaussian Inc., PPEPPD, and AIChE; and presented earlier versions of this material at the 1999 and 2006 ASEE Summer Schools.

Biosketch:

Phil Westmoreland is a Professor of Chemical and Biomolecular Engineering at North Carolina State University. He is also Director of the Southeast Regional Center for a new DOE Smart Manufacturing Institute. He worked previously at Oak Ridge National Laboratory (1974-79), UMass Amherst (1986-2009), and NSF (2006-09). His degrees are in chemical engineering from N.C. State (BS '73), LSU (MS '74), and MIT (PhD '86).

His group uses flame and pyrolysis experiments, molecular-beam mass spectrometry, computational quantum chemistry, data science, and reactive-flow modeling for research on clean energy from fossil and biofuels, chemical looping, and the international data cyberinfrastructure PRiME. He is author or co-author of 113 peer-reviewed publications and five books.

He was 2013 President of AIChE and is a trustee of the educational nonprofit CACHE Corporation, serving as its president in 2004-06. He is a past board member of the Combustion Institute (2002-14), Council for Chemical Research (2005-07), and AIChE (2009-11) and is the winner of the 2017 Institute Award for Excellence in Industrial Gases Technology.



Putting Chemistry in ChE Classes

Part I: Strategies (Part II: Resources)

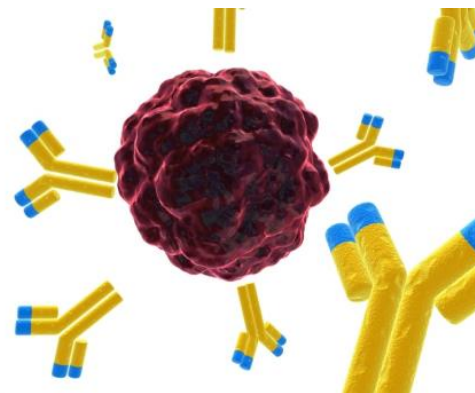
Phil Westmoreland, NC State University (prwestmo@ncsu.edu)

2017 ASEE Summer School for Chemical Engineers
North Carolina State University, Raleigh NC
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Preview the workshop:

- I. Strategies: By chemistry, ChEs mean **molecularly based properties**.
 - Examine properties and molecular structures *[demo]*.
 - Where in the ChE curriculum? Or throughout?
 - How is it being done?
- II. Teaching resources:
 - Products; Structure-based property relations by **correlation** *[demo]*.
 - Properties from **statistical mechanics** *[demo?]*.
 - Properties from computational **quantum chemistry** *[demo]*, including **thermochemistry and kinetics**.
 - Examples: Transport, solid-state chemistry, and cellular biology.

Part 1. Frame the questions about chemistry and ChE.



<http://www.bbe.caltech.edu/content/monoclonal-antibody-facility>

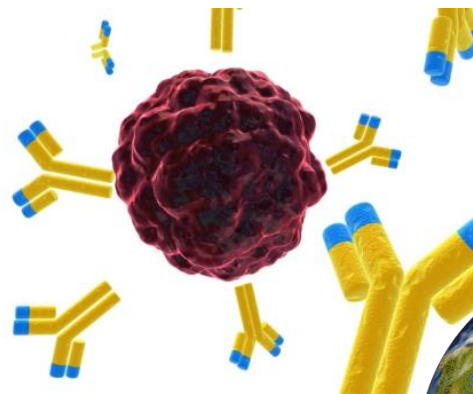
Many students choose ChE because they like chemistry.

- What does that mean?



Many students choose ChE because they like chemistry.

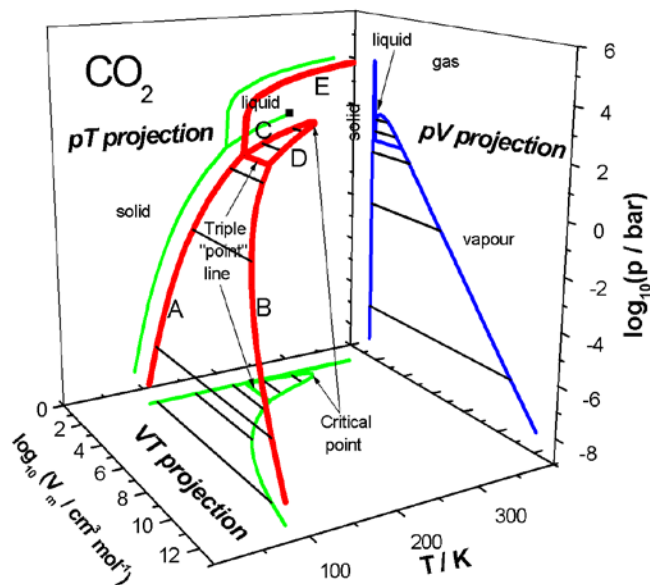
- They usually mean **chemicals** and what the chemicals can do (learned in a class they liked)...
- ...which often means **reactions**.



- And often they want the chance to **use chemistry meaningfully.**



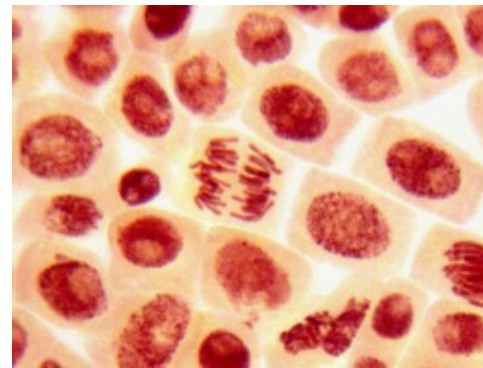
Reactions are important, but ChE chemistry is more.



PVT behavior and
phase equilibria

PVT: Glasser, *J. Chem. Educ.* **79** (2002) 874-876.
<<http://biomodel.uah.es/Jmol/plots/phase-diagrams/inicio.htm>>

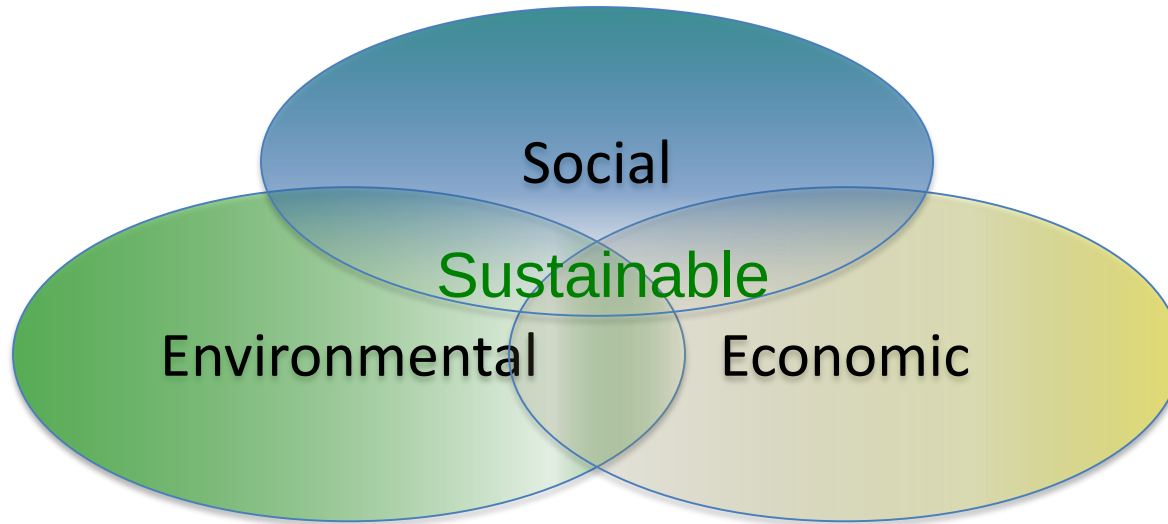
Transport and other physical
properties of chemical origin,
like miscibility, color and
specific heat



Biochemistry and
biological functions

Let's back up: Consider what engineering is.

- Production of practical devices, structures, materials, and processes by applying mathematics and science.
- Framed within the “triple bottom line” of cost/benefit.



Core engineering disciplines are all the same:



Systems



Tools of analysis



Foundational science

What is the scientific basis for ChE / ChBE?
Express it as the “**molecular sciences**.”

- Chemistry – physics – biology.
- Physical chemistry – Chemical physics – Biochemistry;
- Physical organic chemistry – Biophysical chemistry;
- Quantum mechanics – Statistical mechanics;
- Semiconductor physics – Organic semiconductors.
- These are all rooted in the “molecular sciences.”
- That’s a useful description! [Even recognizing that ionic solids aren’t molecular, nor are monatomic noble gases.]

Applied molecular sciences are ChE's foundation.



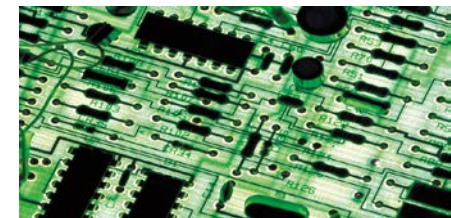
System: Oil refinery with supply chain and environmental/safety



Tools: Unit operations, control, transport phenomena, analytics, reaction engineering



Molecular sciences: Chemistry, biology, materials



A practical view is Chemistry = Properties.

- A bottom line is that we all need properties, and a lot of them are molecular in origin.
- Molecule-based properties define the usefulness of products and the ability to use design/analysis equations.
- We need property relations based on composition, recognizing that composition and other factors may determine structure and function.
- Contrast conservation equations and constitutive relations.

Exercise 1: What properties of substances do we need as engineers?

Some suggestions:

- Phase and reaction equilibria
 - Bond and interaction energies
 - Ideal-gas thermochemistry
 - Thermochemistry and equations of state for real gases, liquids, solids, mixtures
 - Adsorption and solvation
- Reaction kinetics
 - Rate constants, products
 - Metabolic pathways
- Transport properties
 - Interaction energies, dipole
 - μ , $k_{thermal}$, D_{AB}
- Analytical information
 - Spectroscopy: Frequencies, UV / Vis / IR absorptivity
 - GC elution times, NMR shifts
 - Mass spectrometric ionization potentials and cross-sections, fragmentation patterns
- Protein folding and misfolding, docking, ADMET, drug discovery
- Mechanical properties of hard and soft condensed matter
- Electronic & optical properties

ChE/CBE isn't the only engineering profession that applies molecular sciences.

- Obviously, Materials Science and Engineering.
- More subtly, mechanical engineers use many properties that are molecular in origin.
 - Thermochemistry: $\Delta_f H^\circ$, C_p° , S° ; P - V - T relations; Strength of materials.
- So do civil and environmental engineers:
 - Chemical and biological treatment; Air, water, soil properties.
 - Effects of environment on materials.
- Likewise, electrical and computer engineers:
 - Semiconductor band gap (system HOMO-LUMO difference).
 - Chip-manufacturing kinetics.

Again, we all need properties.

- Sometimes accurate, precisely known numbers.
 - Necessary for accurate design, costing, safety analysis.
 - Cost and time for calculation may be secondary.
- Sometimes “merely” accurate trends and estimates.
 - Often more valuable.
 - Correlate with data to get high-accuracy predictions.
 - Use to identify relationships between structure and properties.
 - Valuable for product and process development, operations, and troubleshooting.
- Great data are best (with uncertainty characterization!).
 - Especially good: NIST Webbook (<http://webbook.nist.gov>).
- We must understand enough molecular structure and theory to **correlate and predict unmeasured properties**.

How can we best put chemistry into ChE classes?

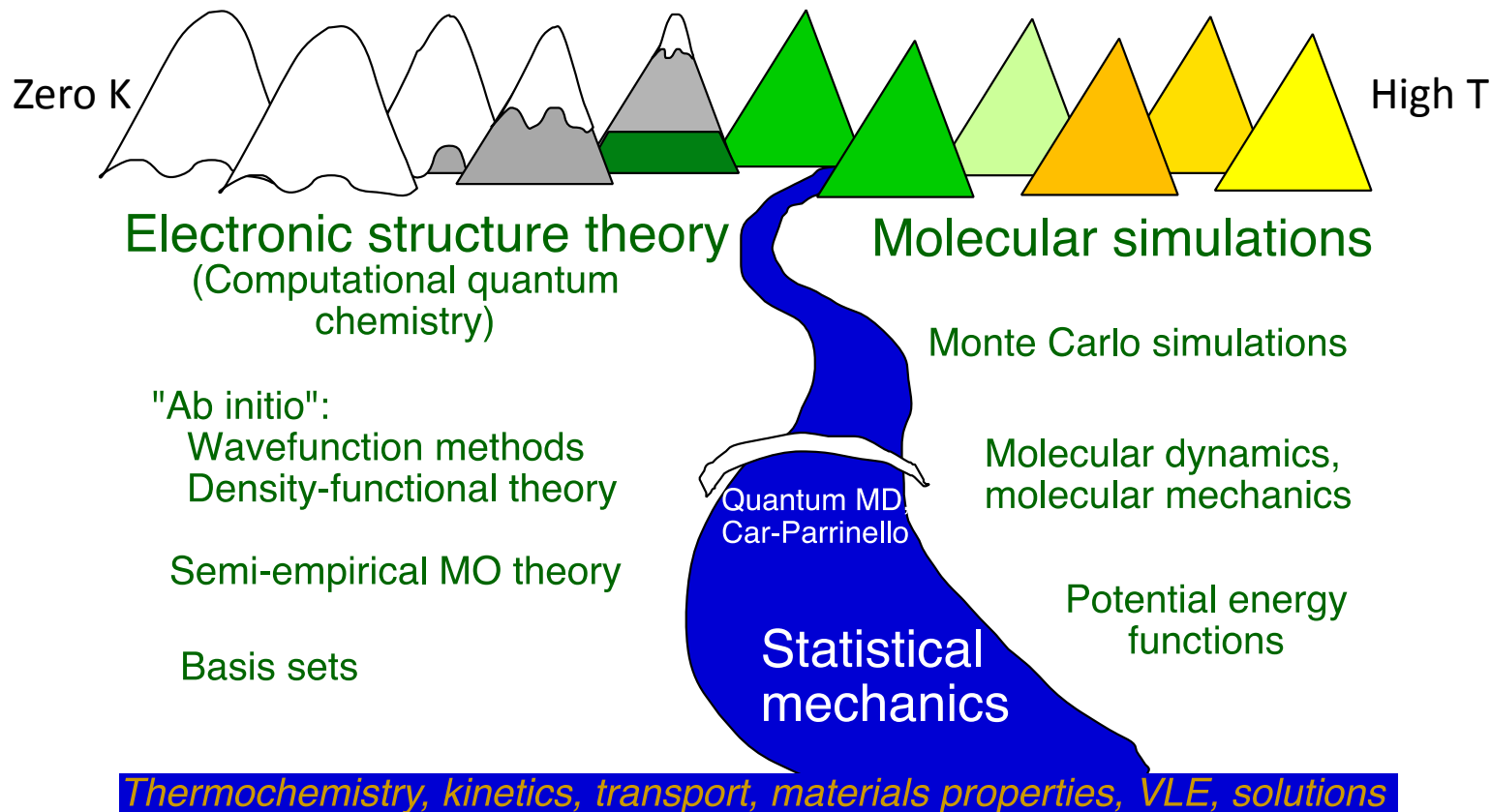
By incorporated and/or focused material.

- **Incorporated material:** Weave into courses.
 - Find ways to incorporate chemically specific information.
 - Introduce theory or skills to find course-dependent needed properties.
- **Focused material:** Special-topics course.
 - Provide specific course or a course segment on how to understand or obtain properties.

Let's focus on how to insert molecular sciences.

- Applications first and throughout, but ...
- Use real molecules; real reactions and other properties.
- Molecular-scale viewing.
- Correlations – which must have some fundamental basis to work well, including identity and form of the independent and dependent variables.
- Molecular modeling & simulation: An aid to understanding and a tool.
 - “Molecular modeling” = Computational quantum chemistry, molecular mechanics.
 - “Molecular simulation” = Molecular dynamics, molecular mechanics; maybe Monte Carlo.
 - Statistical mechanics link most physicochemical properties to molecular properties.
 - Reaction theories, solid-state physics/chemistry, biochemistry.
- Applications especially in thermo, kinetics, transport, materials, bio.

Molecular and material structure



Two ways are focused or incorporated material.

- Focused material: Special-topics course.
 - A specific course or a course segment on how to obtain properties.
- Incorporated material: Weave into courses.
 - Find ways to incorporate chemically specific information.
 - Introduce theory or skills to find course-dependent needed properties.

In core UG classes: Material and energy balances

- Use real chemical species.
 - Useful aid: ChemSpider data at <http://www.chemspider.com>
- Use real reactions (maybe lumped reactions, but describe pieces).
- Call out the ties to basic freshman chemistry and organic chemistry.

In core UG classes: Thermodynamics

- P-V-T behavior and the molecular reasons the ideal-gas law is powerful – and limited.
- Kofke's <http://www.etomica.org> modules: Easy, useful aids.
- Ideal-gas thermochemistry for C_p° and S° (rooted in practical statistical mechanics).
- VLE phase equilibria, critical points, and non-ideal behaviors – and their molecular origins.

In core UG classes: Transport

- Concentration-gradient effects in Fick's Law (go where the going is good; etomica.org's Lennard-Jones Molecular Dynamics module); origin of thermal diffusion.
- Temperature-gradient effects in Fick's Law (spreading of rovibrational energy); phonon transport in solids.
- Prediction and correlation of viscosity and thermal and mass diffusivity from gas kinetics theory.

In core UG classes: Kinetics

- Ties between thermodynamics and kinetics, especially microscopic reversibility.
- Molecular origins of rate laws (etomica.org's Reaction Equilibrium module) and rate coefficients (Transition-state theory and “thermochemical kinetics”).
- Physico-chemical origin of pressure fall-off (Lindemann-Hinshelwood, RRK, Quantum-RRK, RRKM, Master Equation, RRKM)
- Classes of reactions.
 - Linear Free-Energy Relations
 - NIST Chemical Kinetics Database, <http://kinetics.nist.gov/kinetics>

Elective course on *Chemical Principles of Engineering*

- **Introduction: Molecule-based properties.** Contrast conservation equations and constitutive relations. Introduce molecule-viewing software ([GaussView](#)) to show molecule structures and how to assemble them computationally.
- **Empirical correlations** and the need for them to rest on real bases for forms, like ideal linear mixing.
- **Basics of statistical mechanics** and **molecular simulations.**
- **Basics of quantum mechanics and computational chemistry** (aided by black-box [Gaussian](#) or [Spartan](#), escalating to show how the principles are used).

Chemical Principles of Engineering (part 2)

- **Correlating and predicting kinetics**, categorizing reactions as s,p-orbital-based radical or ionic or pericyclic vs. *d*-orbital-based; and as abstraction vs. association/dissociation.
 - Examine both derivations of TST; application across reaction classes; fall-off and inverse fall-off.
 - Reaction-mechanism-generator methods (use Green/West's Reaction Mechanism Generator code rmg.mit.edu).
 - Impact of gas-phase density (Master Equation), supercritical behavior, solvent shells.
 - Kinetic Monte Carlo; Reactive Molecular Dynamics.

Chemical Principles of Engineering (part 3)

- **Transport properties**, correlated by Lennard-Jones relations (spherically symmetrical molecules) that extend to capture real-substance behaviors.
- **Molecular catalysis and adsorption**: Enzyme kinetics and sites, surface and solid-state chemistry.
- **Biochemistry and function**, emphasizing protein structure, lipid bilayer structure, ion-channel transport, molecule-enzyme docking, and G-protein-coupled receptors.

Other approaches: First, Tom Manz of NMSU.

CHME 491: Special Topics: Calculation of Material and Molecular Properties

Fall 2014 (elective course)

14 students (graduate and undergraduate)

Class held in computer lab so students can work problems during class

Main software tools used: **Gaussian 09** (quantum mechanics of molecules) and **Chargemol** (for atomic population analysis to find net atomic charges, atomic spin moments, bond orders, etc.)

Required textbook: James Foresman and Aeleen Frisch, Exploring Chemistry with Electronic Structure Methods, Second Edition, Gaussian INC, ISBN 978-0-9636769-3-1. (Note: Now there is a third edition of the book out.)

Catalog description:

CH E 491. Special Topics: Calculation of Material and Molecular Properties 3 cr.

The aim is to describe and apply techniques for computing common properties of materials and molecules: optimized geometries, transition states, vibrational spectra, energies (electronic, internal energy, enthalpy, and Gibbs free energy), heat capacities, net atomic charges, atomic spin moments, and effective bond orders. These techniques allow one to estimate the thermodynamic properties of a chemical, as well as to compute the mechanisms and energy barriers for chemical reactions and catalytic processes, and to quantify the electronic, magnetic, and chemical ordering in materials. The theory behind these techniques will be described and students will perform hands-on computer exercises using common computational chemistry programs. Prereq: CHEM 116, MATH192G, and (PHYS 214 or PHYS 216G)

Grading:

Attendance 5%; Reading and review of journal articles and book chapters 15 %; Computer projects 20%; Quizzes 15%; Oral presentation 10 %; Mid-term exam 15%; Final exam 20%

Other approaches: Erik Santiso of NCSU.

ChE 596-025: Introduction to Molecular Simulation

1. *Introduction.* Current challenges; different methods.
2. *Basic computing and scripting.*
3. *Brief review of probability, Quantum Mechanics and Statistical Mechanics.*
4. *Ab Initio methods.* Overview of quantum chemical methods. Self-consistent field theory. Variational and perturbation methods. Density Functional Theory.
5. *Classical potentials and force fields.* Simple fluids: continuous and discontinuous potentials. Complex molecules and force fields. Multibody effects. Electrostatics. Polarization. Reactive force fields. Bulk systems and periodic boundary conditions.
6. *Optimization and molecular mechanics.* Gradient methods. Quasi-Newton methods. Finding transition states and transition paths.
7. *Molecular dynamics.* Integration of classical equations of motion. Calculating properties. Sampling and stability. Improving performance. Thermostats and barostats. Constraints and restraints. Ab Initio molecular dynamics.
8. *Stochastic dynamics.* Brownian motion. The Langevin equation. The Fokker-Planck equation. The fluctuation-dissipation theorem. Dissipative particle dynamics.
9. *Monte Carlo simulation.* Markov processes. Detailed balance. Monte Carlo moves for different ensembles. MC versus MD. Monte Carlo simulation of complex molecules.
10. *Calculating interfacial properties.* Anisotropic systems. Pressure tensor and surface tension. The test-area method.
11. *Calculating transport properties.* Green-Kubo equations. Nonequilibrium molecular dynamics.
12. *Free energy calculations.* Widom particle insertion. Biased sampling. Metadynamics. Histogram methods. Perturbation methods.
13. *Coarse-graining.* Coarse-grained force field fitting. Iterative Boltzmann inversion. Force matching. Relative entropy minimization. Top-down coarse graining.
14. *Rare events.* Bennett-Chandler method. Transition path sampling. The string method. Milestoning. Calculating reaction rates.
15. *Chemoinformatics and the Materials Genome.* Introduction to machine learning. Regression and classification. Neural networks. Support vector machines. Data mining. Metaheuristics.

Or both: David Hibbits



UF
UNIVERSITY of
FLORIDA

Using Computational Chemistry to Improve Understanding of Chemical Reactions, Kinetics, and Catalysis.

David Hibbits
Chemical Engineering
University of Florida

ASEE

Courses

Molecular Understanding of Catalysis

- Elective graduate course (~15 students).
- Semester-long research project on a topic of their choice:
 - Critique published literature.
 - Perform DFT calculations using CCI and VASP.
 - Discuss their results in a written report.
 - Present their projects to the class.
- Two students continued to use DFT after course ended.

Chemical Engineering Kinetics

- Required graduate course (~70 students).
- Lecture topics assisted by CCI:
 - Chemical bonding potentials
 - Molecular vibrations
 - Potential energy surfaces
 - Transition state theory and kinetic isotope effects
 - Adsorption/desorption on uniform/nonuniform surfaces
 - Surface reaction kinetics

Chemical Kinetics and Reactor Design

- Required undergraduate course (~130 students).
- Lecture topics assisted by CCI:
 - Quasi-equilibrated and rate-determining steps
 - Potential energy surfaces

High School Chemistry Classes

- Beginning Summer '18 (pending CAREER proposal)
- 3-week on-campus collaboration with 2 high school teachers
 - Develop interactive educational and outreach CCI modules
 - Potential topics:
 - Chemical Bonding (educational)
 - Greenhouse Gases (educational)
 - Zeolites and Fuels (outreach)
 - Lesson plans will be implemented (tablets and classroom monitoring technology will be provided by university)
 - Disseminated at in-service workshops
 - Year 3: switch to on-campus dissemination
 - Tracking and surveys will assess and improve program.

Computational Catalysis Interface (CCI)

View 3D periodic structures of catalytic reactions alongside reaction coordinate diagrams showing potential energies.

View particle charges on atoms and how electrons move during reaction.

Submit supercomputer calculations directly from website.

No Programming Required

User-Friendly Startup

Efficient Multi-step Calculations

Easy Submit to Various Supercomputers

Command Line Interface

DFT, QM, KMC

Web Interface

Interact Lesson

Movies and Voiceover

Build and Manipulate Molecules and Catalysts

Enhance Learning Showcase ST

Two ways are focused or incorporated material.

- Focused material: Special-topics course.
 - A specific course or a course segment on how to obtain properties.
- Incorporated material: Weave into courses.
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Putting Chemistry in ChE Classes

Part II: Teaching Resources

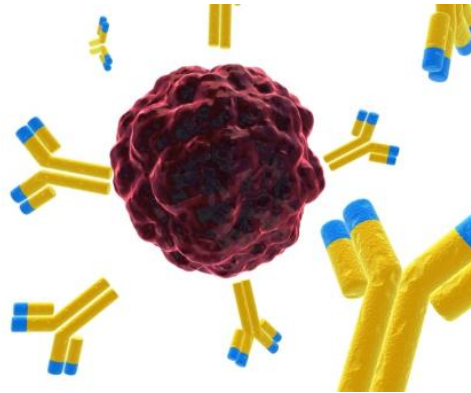
Phil Westmoreland, NC State University

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Many valuable aids are on the web.

- <http://cache.org/teaching-resources-center/molecular-modeling>
- International Comparative Study on Applying Molecular and Materials Modeling (2002) with many examples of industrial applications: <http://www.wtec.org/loyola/molmodel/>
- *Chem & Eng News* “What’s That Stuff?”:
<http://pubs.acs.org/cen/whatstuff/>
- Search [Patrick Di Justo Wired “What’s Inside?”](#)

Part 2. Describe molecules and other chemicals.

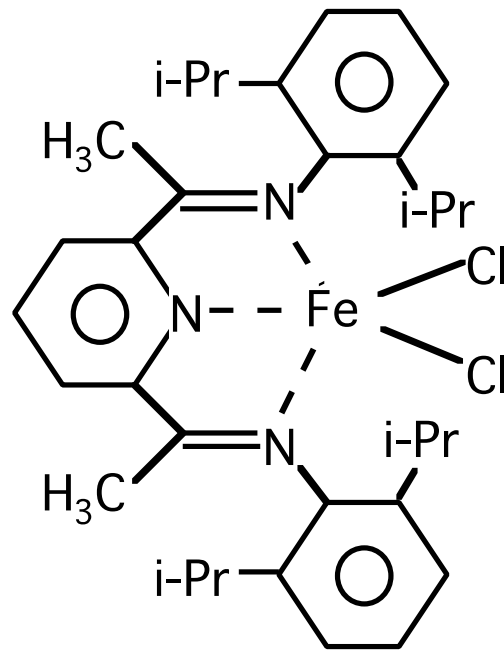


Drawing software has aided visualization.

- Chemspider (<http://www.chemspider.com>) is a database rather than a drawing program, but it provides 2D and 3D images as well as various properties and useful links.
- ChemDraw Professional can be downloaded free if you are at a participating institution.
 - <http://www.cambridgesoft.com/sitesubscription/academic/>
- ACD/Chemsketch can be loaded free – period.
 - <http://www.acdlabs.com/resources/freeware/chemsketch/>
- GaussView from Gaussian Inc is widely available and also serves as a generator of input for Gaussian quantum-chemistry calculations.

It provides transformative visualization.

- Consider the homogeneous catalyst $(C_{33}N_3H_{43})FeCl_2$.
 - What does that suggest to you about its catalytic function?
- Consider it as a liganded di(methyl imide xylenyl) aniline.
 - What does that suggest to you about its catalytic function?
- Consider a 2-D sketch:
 - What does that suggest to you about its catalytic function?

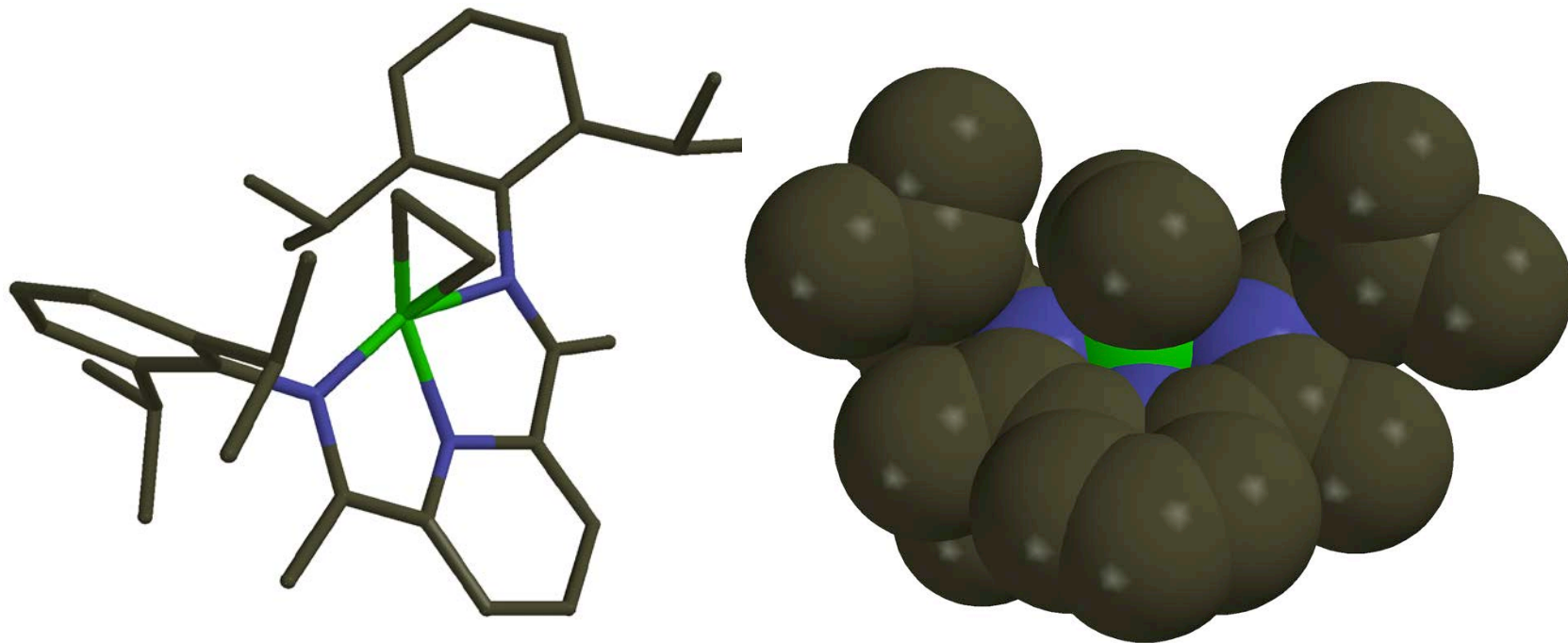


Let's draw it with Gaussview.

- Atom by atom, plus some ready-made groups.
- Construct with x-y-z coordinates? Uh, no.
 - Start from one atom and build up. Specify “Z-Matrix”:
 - Atom1 [implicit 0 0 0]
 - Atom2 1 A2A1 [bond length, attached to #1]
 - Atom3 1 A3A1 2 A3A2A1 [bond angle]
 - Atom4 1 A4A1 2 A4A2A1 3 A4A2 [dihedral]...
- Different bond types – what lengths and angles are used?
- Ethylenes (ethenes) are liganded to the iron.
- Draw it, and clean it up.

It provides transformative visualization.

- Examine two other 3-D views; the “paddles” steer polymer tactoid:



Measure the bond lengths, angles, dihedrals.

- You'll see that the initial estimates are based on mean bond lengths like C-C single bond = 1.54 Å, C=C double bond = 1.355 Å.
- Likewise for bond angles of 109.47° or 120° or 180°.
- Dihedral angles are usually 60° or 180°.
- When cleaned up by molecular mechanics ("sweeping broom" icon) or when optimized at a higher level, they will be slightly different.
- Likewise, calculated frequencies will be somewhat different.
- For a comprehensive comparison, see NIST's Computational Chemistry Comparison and Benchmark DataBase Release 18 (October 2016) Standard Reference Database 101 <<http://cccbdb.nist.gov>>.

Second: Property correlations require underlying principles.

Develop correlations for the following species' properties. I suggest using Excel or some such spreadsheet program with regression and solver methods. **I expect at least one correlation, good or bad, for each property.** If there is not a clean correlation, describe the trends you observe.

Note: Your cover memo and comments should be in word-processed form.

Ideal gases at standard state of 1 atm and 298.15 K

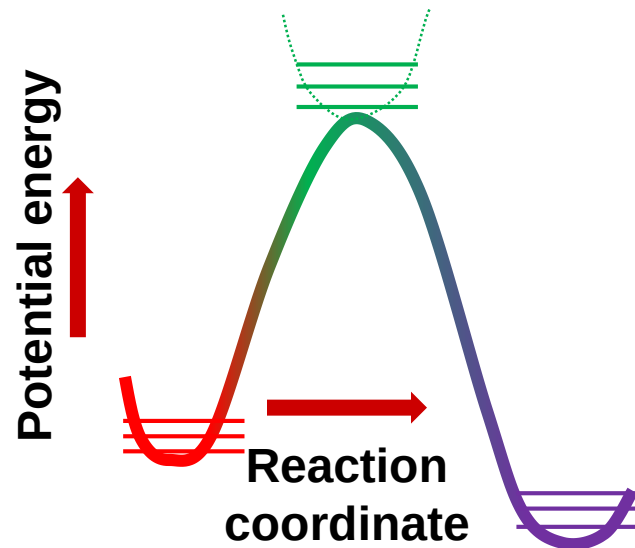
Species	Heat of formation, kcal/mol	Standard entropy, cal / mol K	Specific heat, cal / mol K	Dipole moment, debye	Lennard-Jones sigma, angstroms	Lennard-Jones epsilon/kappa, K
Methane, CH ₄	-17.9	44.5	8.5	0.0	3.758	148.6
Ethene, C ₂ H ₄	12.5	52.4	10.3	0.0	4.163	224.7
Ethane, C ₂ H ₆	-20.2	54.9	12.7	0.0	4.443	215.7
Propene, C ₃ H ₆	4.9	63.8	15.3	0.4	4.678	298.9
Propane, C ₃ H ₈	-24.8	64.5	17.6	0.0	5.118	237.1
n-Butane, C ₄ H ₁₀	-30.2	74.1	23.4	0.0	4.687	531.4
2-Methylpropane (isobutane), C ₄ H ₁₀	-32.2	70.4	23.3	0.1	5.278	330.1
Methanol, CH ₃ OH	-48.0	57.3	10.5	1.7	3.626	481.8
Ethanol, C ₂ H ₅ OH	-56.2	67.5	15.7	1.7	4.530	362.6

Third: Use of computational quantum chemistry

- We'll use Gaussian (note my disclaimers and COI), who are providing the software used in this workshop.
- Molecular structures.
- Transition states.
- Must use stat-mech software and reaction-theory software to get most properties.

Search for transition states (QC) and compute thermo and k s with stat mech.

- Confirm reactants and products by Internal Reaction Coordinate calculations.
- Correct for hindered rotors.
- Compute rate constants $k(T)$ directly or with CHEMRATE, then fitted to Arrhenius expressions.



Let's do some simple ones.

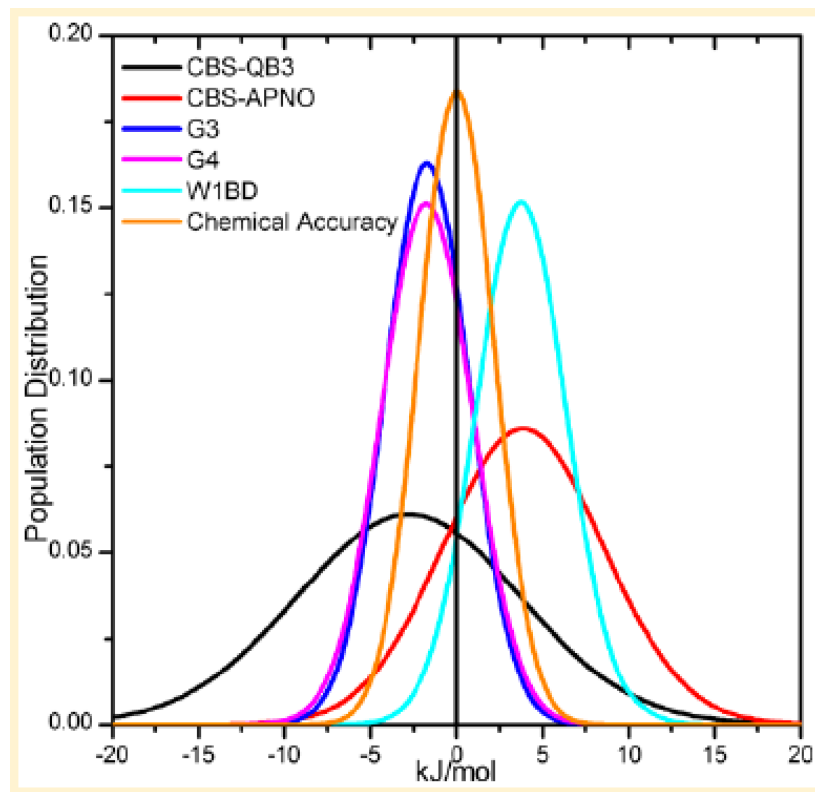
- $\text{CH}_4 + \text{H} = \text{CH}_3 + \text{H}_2$
- $\text{C}_2\text{H}_4 + \text{H} = \text{C}_2\text{H}_5$
- $\text{C}_2\text{H}_4 + 1,3\text{-C}_4\text{H}_6 = \text{Cyclohexene}$
- ...

Let's use a slide set from the supporting material.

- ChemicalPrinciples_Session14_15.ppt

As a note on accuracy of compound methods:

John M. Simmie, Kieran P. Somers, "Benchmarking Compound Methods (CBS-QB3, CBS-APNO, G3, G4, W1BD) against the Active Thermochemical Tables: A Litmus Test for Cost-Effective Molecular Formation Enthalpies" *J. Phys. Chem. A* 2015, 119, 7235–7246; DOI: 10.1021/jp511403a



Finally, let's review some molecular biochemistry.

- ChemicalPrinciples_Session22_23.pptx

In summary:

- Be clear on your goals.
 - Do you want to teach the science and understanding of the methods and/or their underlying theory?
 - Do you want to teach about specific chemical principles?
 - Do you want to predict properties or teach about pertinent chemistry?
- Your goals should dictate what you do.
- Meanwhile, use the CACHE Teaching Resources and engage in its Molecular Modeling Task Force and in AIChE programming.
- Thanks!!!