

# A Course to Tie Chemical and Molecular Principles into Chemical Engineering

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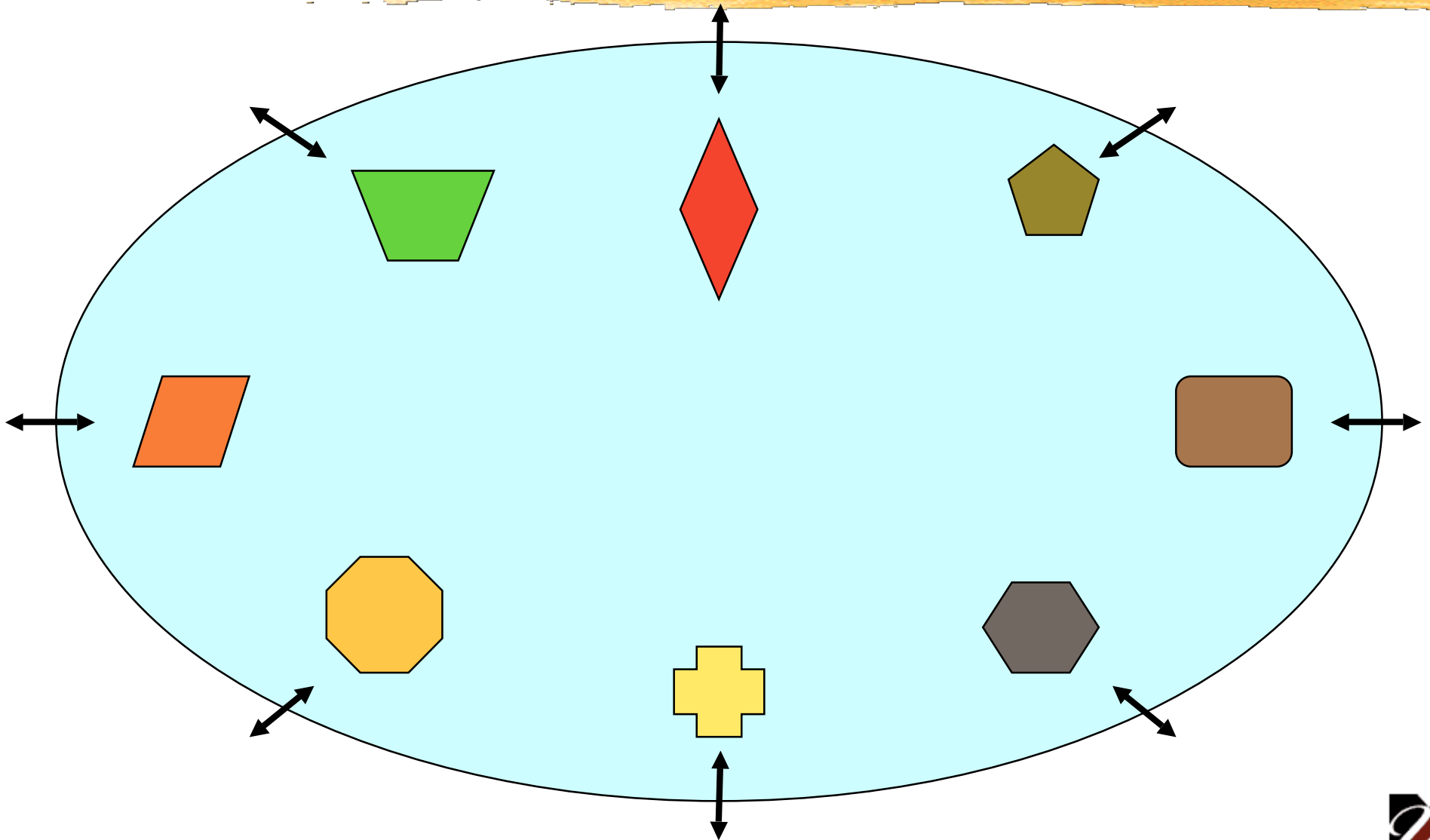
See also:

- <http://www.ecs.umass.edu/che/che697> [username & password che697]
- CoMSEF Web site, <http://www.comsef.aiche.org/>
- CACHE's Molecular Modeling Task Force (Web modules and text), <http://zeolites.cqe.nwu.edu/Cache/>
- "Chemistry and life sciences in a new vision of chemical engineering," *Chemical Engineering Education*, **35**(4), 248-255 (2001).

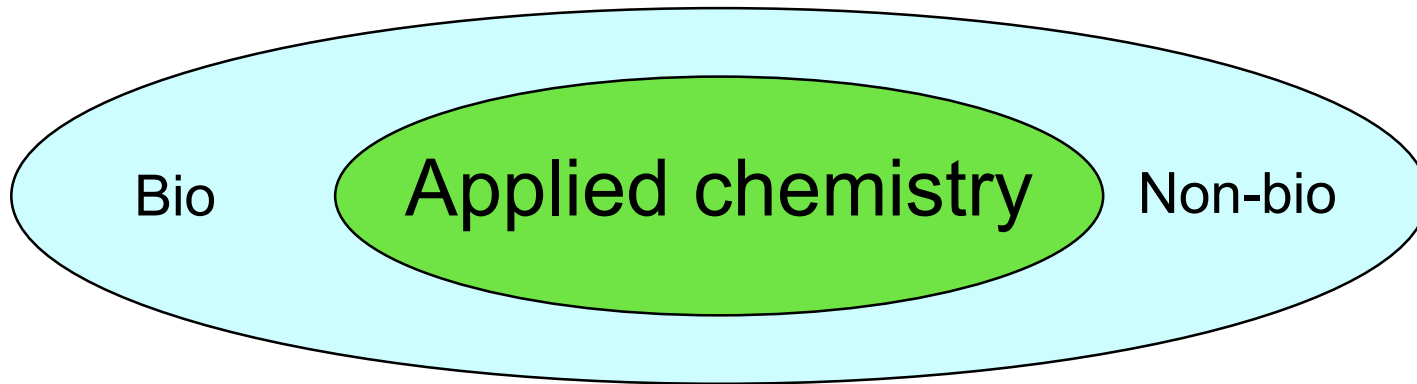
The subject is “Chemical Principles of Engineering,” not molecular modeling.

- Fits in the historic tradition of Industrial Chemistry courses.
  - They disappeared when they turned into flowsheet courses.
  - However, their purpose was to connect chemistry to application.
- It is unrealistic to expect Chemistry Departments to teach chemistry in the way that ChE’s need it.
  - They still teach that reaction rate =  $-dc/dt$  !
  - But after all, we don’t expect Physics to teach Transport, either.
- Our students need biochemical principles as well.
  - A key message of the past fifteen years has been that molecular chemistry is the underpinning of life sciences.
- Molecular modeling is already a powerful aid for teaching and for engineering use.

Another way to look at it:  
What are Chemical Engineering's core ideas?



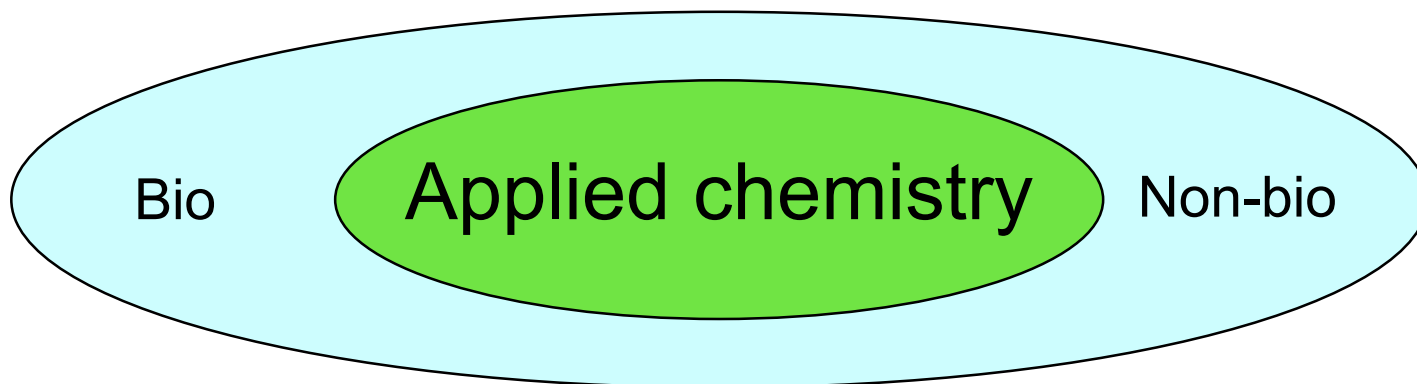
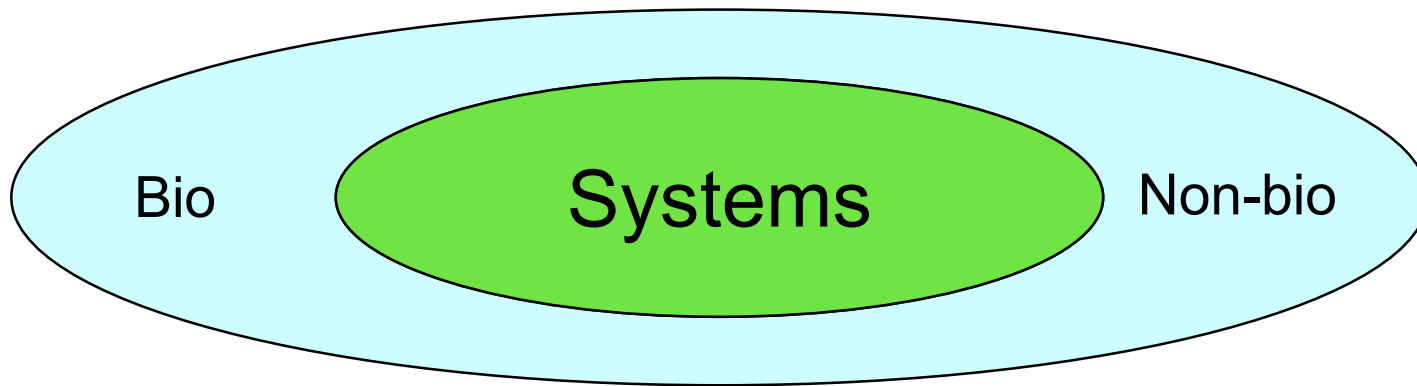
# What are Chemical Engineering's core ideas?



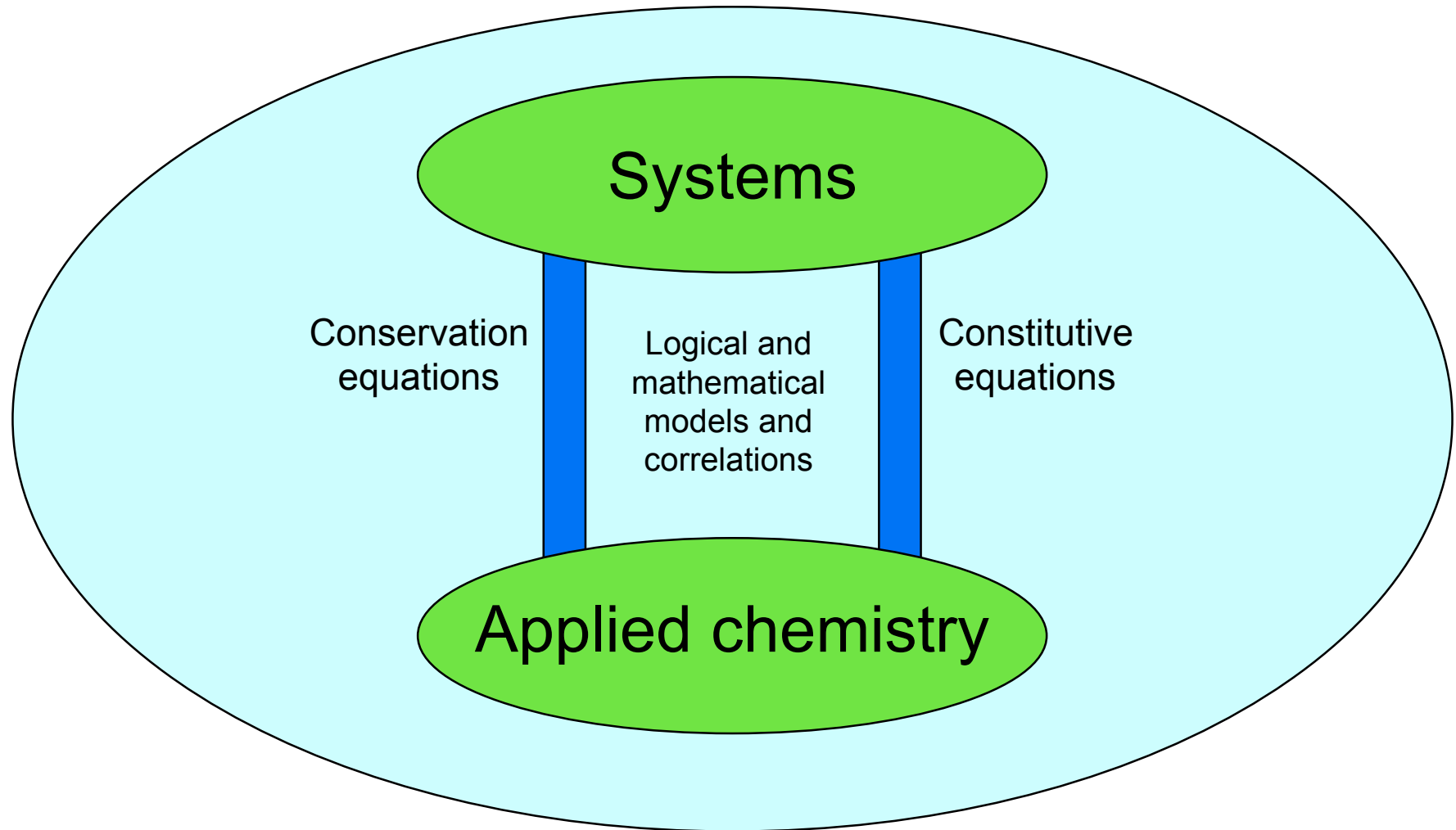
Not just reaction chemistry, but also properties and behaviors of materials that depend on chemical structure



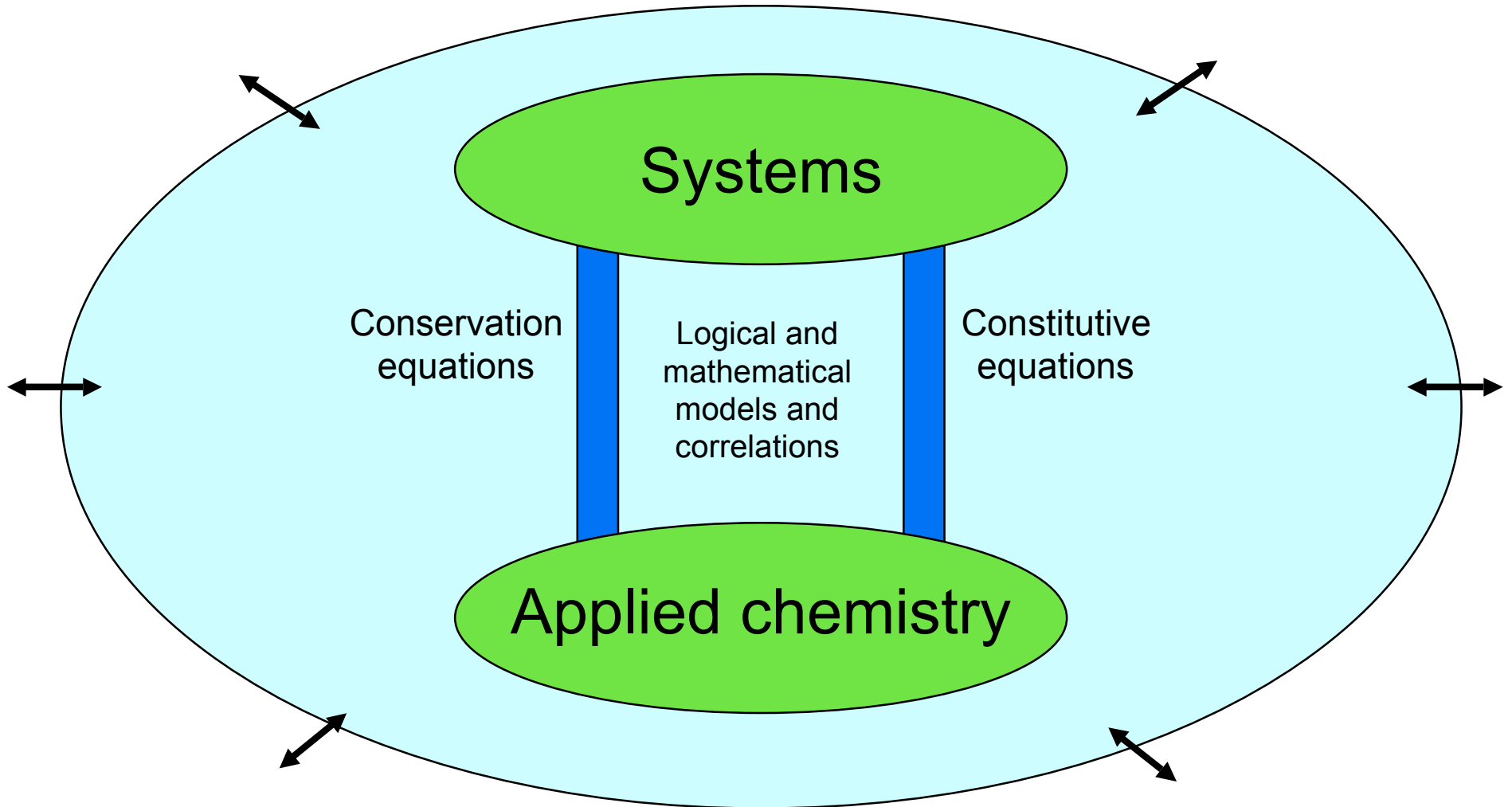
# What are Chemical Engineering's core ideas?



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# What are Chemical Engineering's core ideas?



Thus, the aim of the course is to teach applicable chemical principles and how to use them.

- To model and design processes and products,
- We need properties of substances
- To solve balances,
- We need properties of substances ...
- and properties have their origins in electronic and molecular structures,
- which are the bases for correlation and prediction.


# Properties are often the critical information needed for process and product design.

- Maybe require accurate, precisely known numbers
  - Necessary for accurate design, costing, safety analysis
  - Cost and time for calculation may be secondary
- Often, accurate trends and estimates are at least as valuable
  - Can be correlated with data to get high-accuracy predictions
  - Can identify relationships between structure and properties
  - A quick, sufficiently accurate number or trend may be of enormous value in early stages of product and process development, for for operations, or for troubleshooting
- Great data are best; but also theory-based predictions

The course is carried out with parallel lines of instruction.

- Review nomenclature, structures, and stoichiometry.
- Construct molecular models by type and molecular mechanics.
- Teach about “correlation,” in this case including fundamental theory.
- Calculate molecular structures and frequencies with computational quantum chemistry.
- Teach theory behind predictive techniques.
- Predict thermochemistry, kinetics, transport properties, binding / docking.
- Study applications.

Consider “correlation” component;  
Begin with attempts to build naïve correlations.



## ChE 697, Chemical Principles of Engineering - Problem Set 2

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 <sub>4</sub>	-17.9	44.5	8.5	0.0	3.758	148.6
Ethene, C <sub>2</sub> H <sub>4</sub>	12.5	52.4	10.3	0.0	4.163	224.7
Ethane, C <sub>2</sub> H <sub>6</sub>	-20.2	54.9	12.7	0.0	4.443	215.7
Propene, C <sub>3</sub> H <sub>6</sub>	4.9	63.8	15.3	0.4	4.678	298.9
Propane, C <sub>3</sub> H <sub>8</sub>	-24.8	64.5	17.6	0.0	5.118	237.1
n-Butane, C <sub>4</sub> H <sub>10</sub>	-30.2	74.1	23.4	0.0	4.687	531.4
2-Methylpropane (isobutane), C <sub>4</sub> H <sub>10</sub>	-32.2	70.4	23.3	0.1	5.278	330.1
Methanol, CH <sub>3</sub> OH	-48.0	57.3	10.5	1.7	3.626	481.8
Ethanol, C <sub>2</sub> H <sub>5</sub> OH	-56.2	67.5	15.7	1.7	4.530	362.6

This information may also be downloaded as [an Excel spreadsheet](#).

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Last update: September 11, 2001.

Contact [westm@ecs.umass.edu](mailto:westm@ecs.umass.edu) for corrections or inquiries.

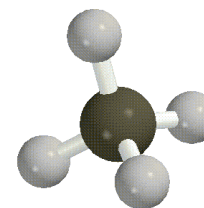
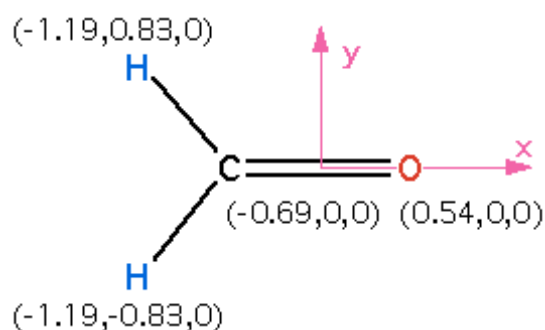
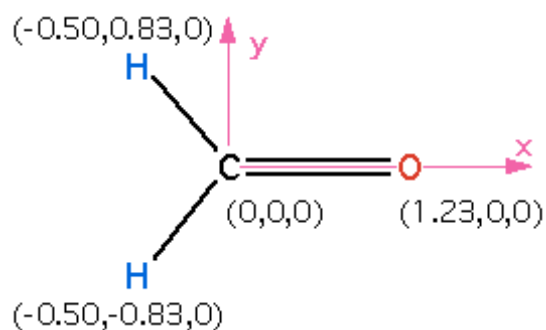


# Students try trends within functional groups and (maybe) linear regressions on stoichiometry or MW.

- Atom additivity (correlation based on simple stoichiometry) is not particularly useful
- However, group additivity is a widely used, valuable correlation / estimation technique for many molecularly based properties:
  - Propane ( $\text{CH}_3\text{-CH}_2\text{-CH}_3$ ) becomes  $\text{C-(C)}_2(\text{H})_2 + 2 \text{ C-(C)}(\text{H})_3$
- When based on quantitative molecular structures or properties like bond lengths or dipole moments, these are “Quantitative Structure-Property Relationships.”
  - QSPR and QSAR (activity relationships) have become widely used in pharmaceutical and industrial chemistry.

# Our recognition of molecular structures is more sophisticated correlation.

- From the outset, students calculate structures of some molecules by computational quantum chemistry:
  - Initially sketch and optimize with Gaussview (or Spartan, Hyperchem or Accelrys) molecular mechanics software
  - Review classes and nomenclature using these sketches and the fragments provided for molecular drawing
  - Promptly begin ab initio calculations (we use Gaussian for Windows)
  - Bond lengths, angles, dihedrals for  $\text{CH}_2\text{O}$ , isooctane, fructose
  - Emphasize 3-D structural nature with molecule viewers



# Naturally develop patterns and utility.

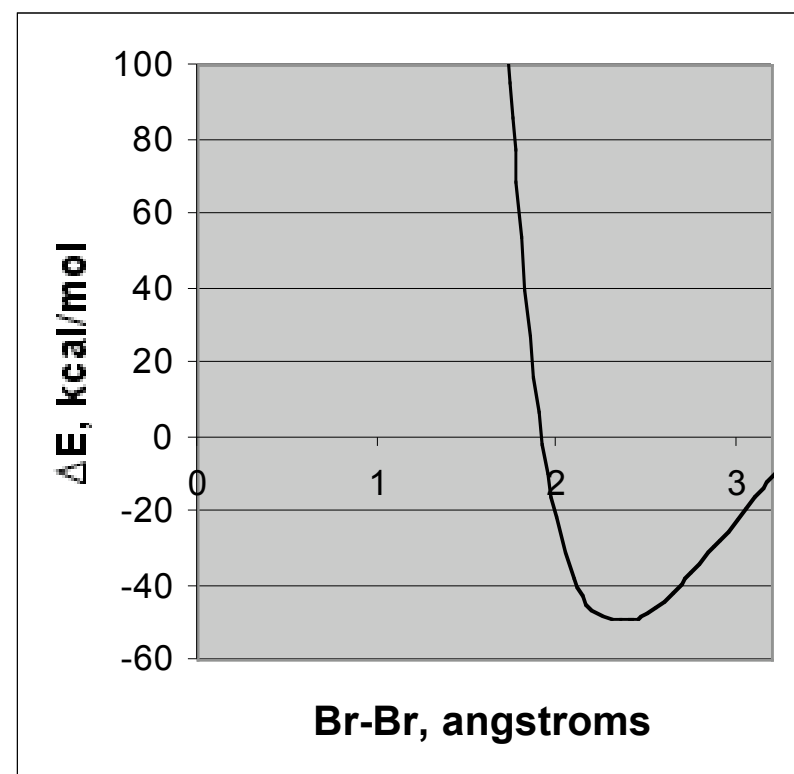
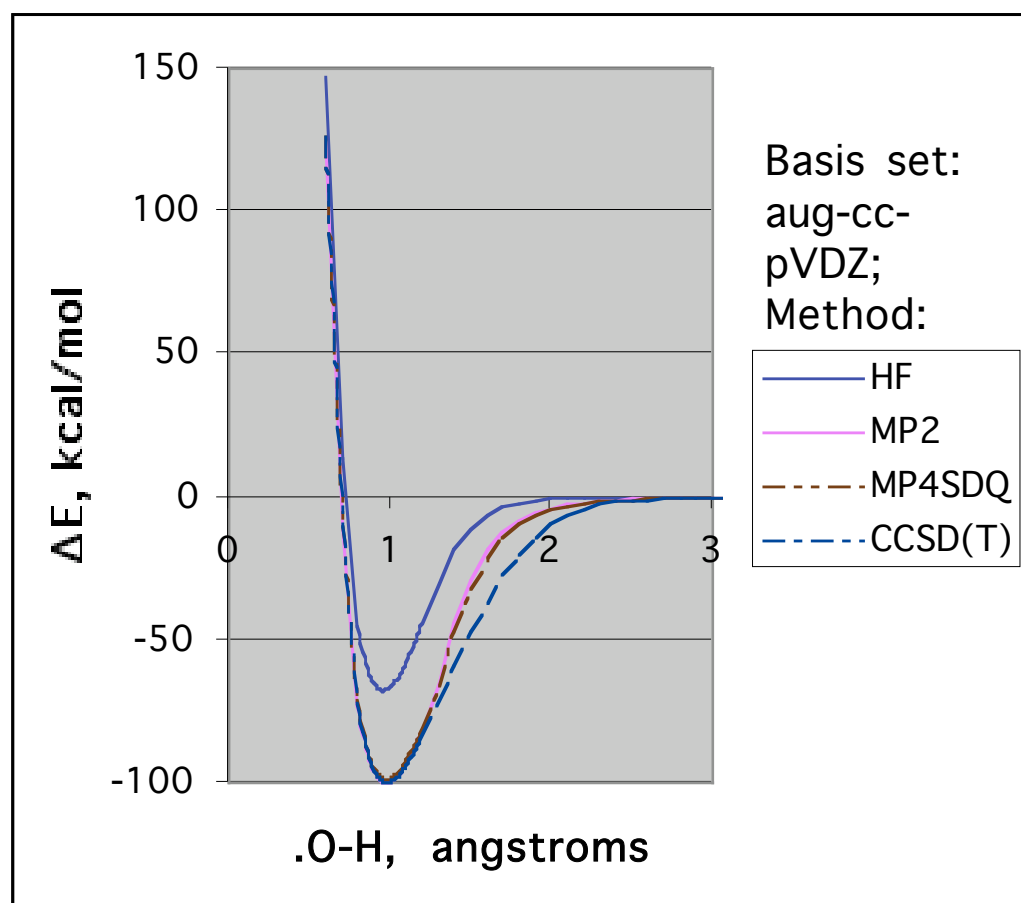
## ■ Generalizations arise.

- Bond lengths (C-H 1.08 Å, C-C 1.54 Å, C=C 1.35 Å, CC at 1.20 Å)
- Bond angles (Tetrahedral  $\sim 109.7^\circ$ ,  $sp^2 \sim 120^\circ$ ) and dihedrals

## ■ Frequencies of internal vibrations are easily computed and some generalizations are apparent.

- e.g., C-H stretches are all about  $3100\text{ cm}^{-1}$ , even though real motions are more complex than simple two-atom motions
- Different motions may be triggered by absorbing energy from photons of the right energy ( $E=h\nu$ ) although with differing effectiveness
- When IR spectrum is shown, students quickly grasp that these molecular properties can be used for identification and even quantitation.

Bond energies and interaction energies are likewise found from data or computation.



UB3LYP/6-311++G(3df,3dp) with  
basis-set superposition error correction

Developing statistical mechanics for ideal-gas thermochemistry is then readily accepted.

- The partition function  $q(V, T) = \sum \exp(-\epsilon_i / kT)$  arises naturally in the development of Maxwell-Boltzmann and Bose-Einstein statistics
- Quantum mechanics gives the quantized values of energy and thus the partition functions for:
  - Translational degrees of freedom
  - External rotational degrees of freedom (linear or nonlinear rotors)
  - Rovibrational degrees of freedom (stretches, bends, other harmonic oscillators, and internal rotors)
- Electronic d.f. require only  $\Omega_{\text{electronic}}$  and degeneracy.

Entropy, energy, and heat capacity can be expressed in terms of the partition function(s).

$$S = Nk_B \left[ \ln \frac{q(V, T)}{N} + T \frac{\partial \ln q(V, T)}{\partial T} \right]_{V}$$

$$\begin{aligned} S(\text{molar}) &= R \cdot \ln(q_{trans} q_{rot} q_{vibr} q_{elec} e) + T \frac{\partial \ln q_{trans} q_{rot} q_{vibr} q_{elec}}{\partial T} \\ &= S_{trans} + S_{rot} + S_{vibr} + S_{elec} \end{aligned}$$

$$H = E + PV = E + (RT)_{ideal\ gas}$$

$$E = RT^2 \left[ \frac{\partial \ln q(V, T)}{\partial T} \right]_{V}$$

$$(C_p)_{ideal\ gas} = \left[ \frac{\partial E}{\partial T} \right]_{N, V} + R = C_{v,trans} + C_{v,rot} + C_{v,vibr} + C_{v,elec} + R$$

Simplest treatment is of ideal gas, beginning with the translation degrees of freedom and then so on.

- Quantum mechanics for pure translation in 3-D gives:

$$\epsilon_{\text{translation}} = \frac{h^2 n^2}{8ml^2} \quad \text{where } n = 1, 2, \dots \text{ [particle in a box]}$$

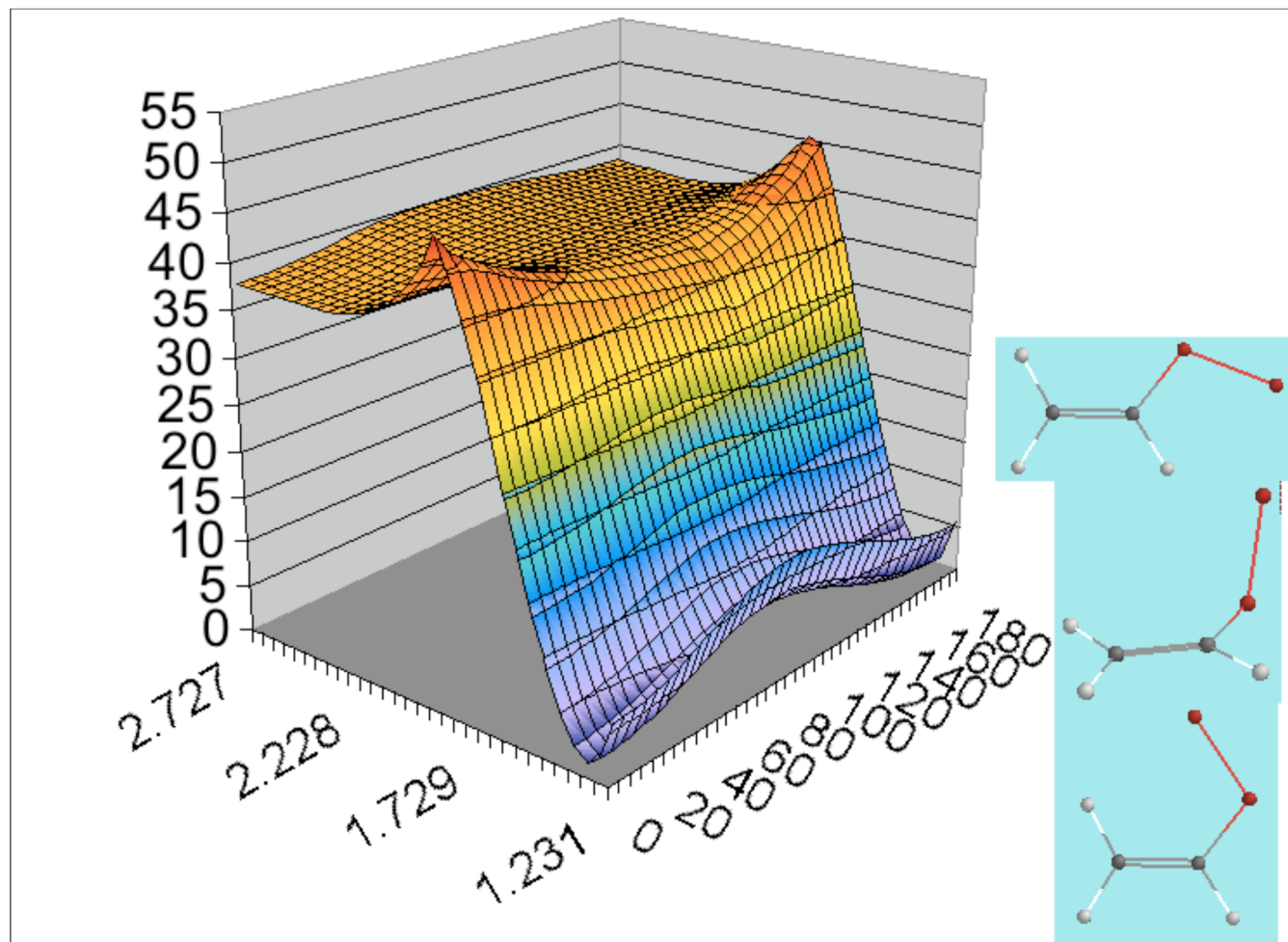
$$q_{\text{trans}(3D)} = \left( \frac{2\pi m T}{h^2} \right)^{3/2} \cdot V$$

$$C_{v,\text{trans}(3D)}^o = 3 \frac{R}{2}$$

$$S_{\text{trans}(3D)}^o = R \ln \left( \frac{2\pi m T}{h^2} \right)^{3/2} \cdot \frac{RT}{P} + \frac{5}{2} R$$

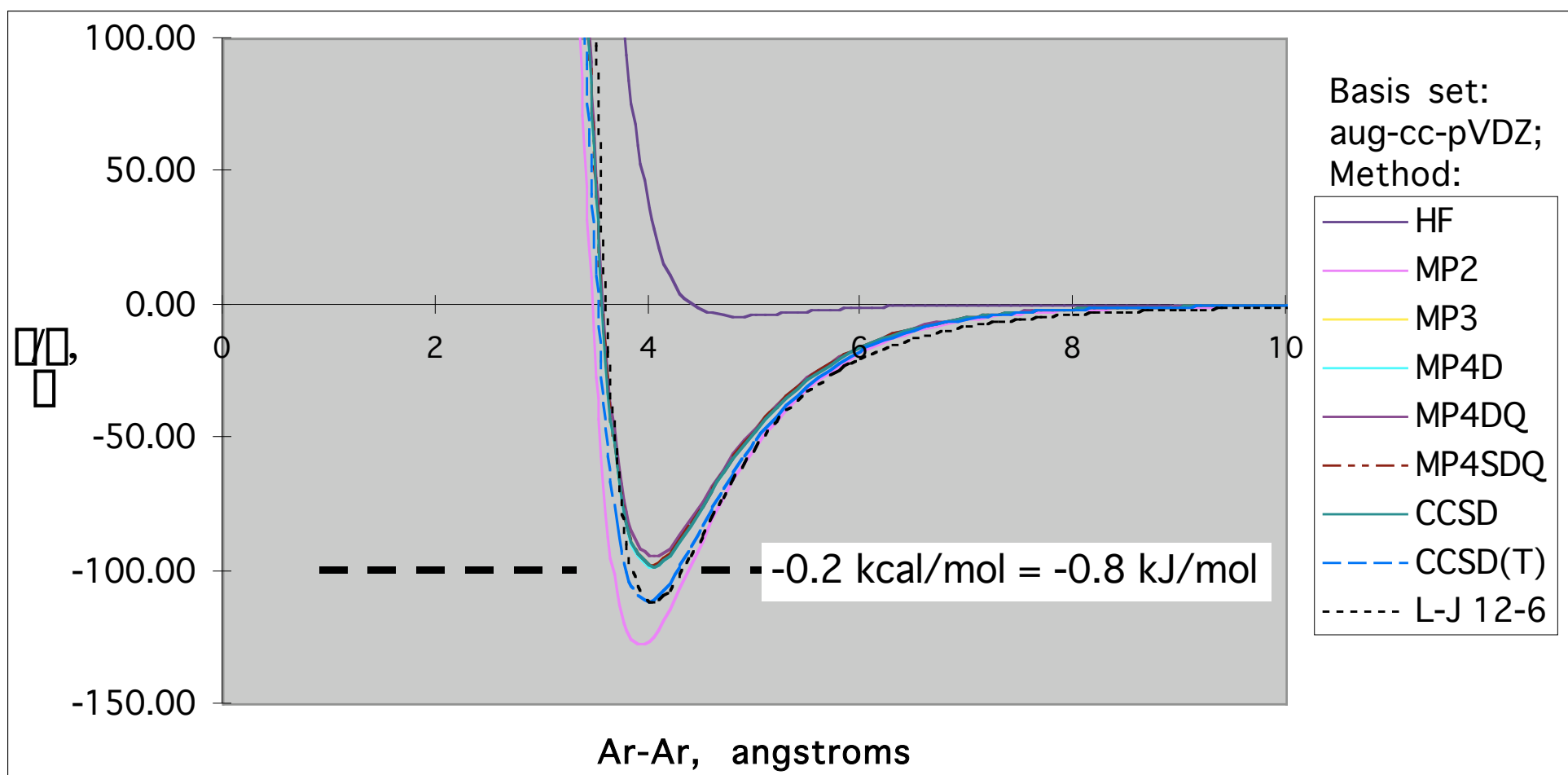
Transition-state theory is developed easily once we have this statistical mechanics background.

Potential energy surface for O-O bond fission in  $\text{CH}_2\text{CHOO}\cdot$   
B3LYP/6-31G(d);  
*Kinetics analysis based on O-O reaction-coordinate-driving calculation at B3LYP/6-311+G(d,p)*



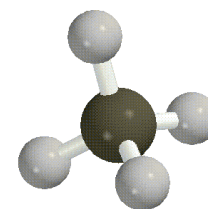


Likewise, gas kinetic theory provides a theoretical structure for correlating simple transport properties.

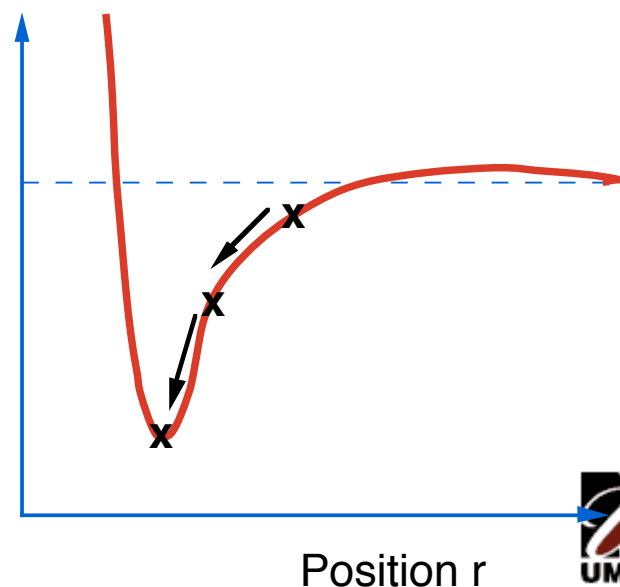


Obtain molecular properties from quantum chemistry;  
Initially restrict discussion to an isolated molecule.

- Equivalent to an ideal gas, but may be a cluster of atoms, strongly bonded or weakly interacting.
- Easiest to think of a small, covalently bonded molecule like  $H_2$  or  $CH_4$  *in vacuo*.
- Most simply, the goal of electronic structure calculations is energy.
- However, usually we want energy of an optimized structure and the energy's variation with structure.



Energy  $E$   
[from  
 $E_0 = \mathcal{H}[\psi]$ ]



From classical Hamiltonian ( $E=T+V$ ), develop Hamiltonian operator for quantum mechanics.

- Obtain a Hamiltonian function for a wave using the Hamiltonian operator:

$$\mathcal{H} = -\frac{\hbar^2}{2m} \nabla^2 + U(x, y, z)$$

to obtain:

$$E\psi = \mathcal{H} \{ \psi(\vec{q}, t) \} = \frac{i\hbar}{2m} \frac{\partial \psi(\vec{q}, t)}{\partial t}$$

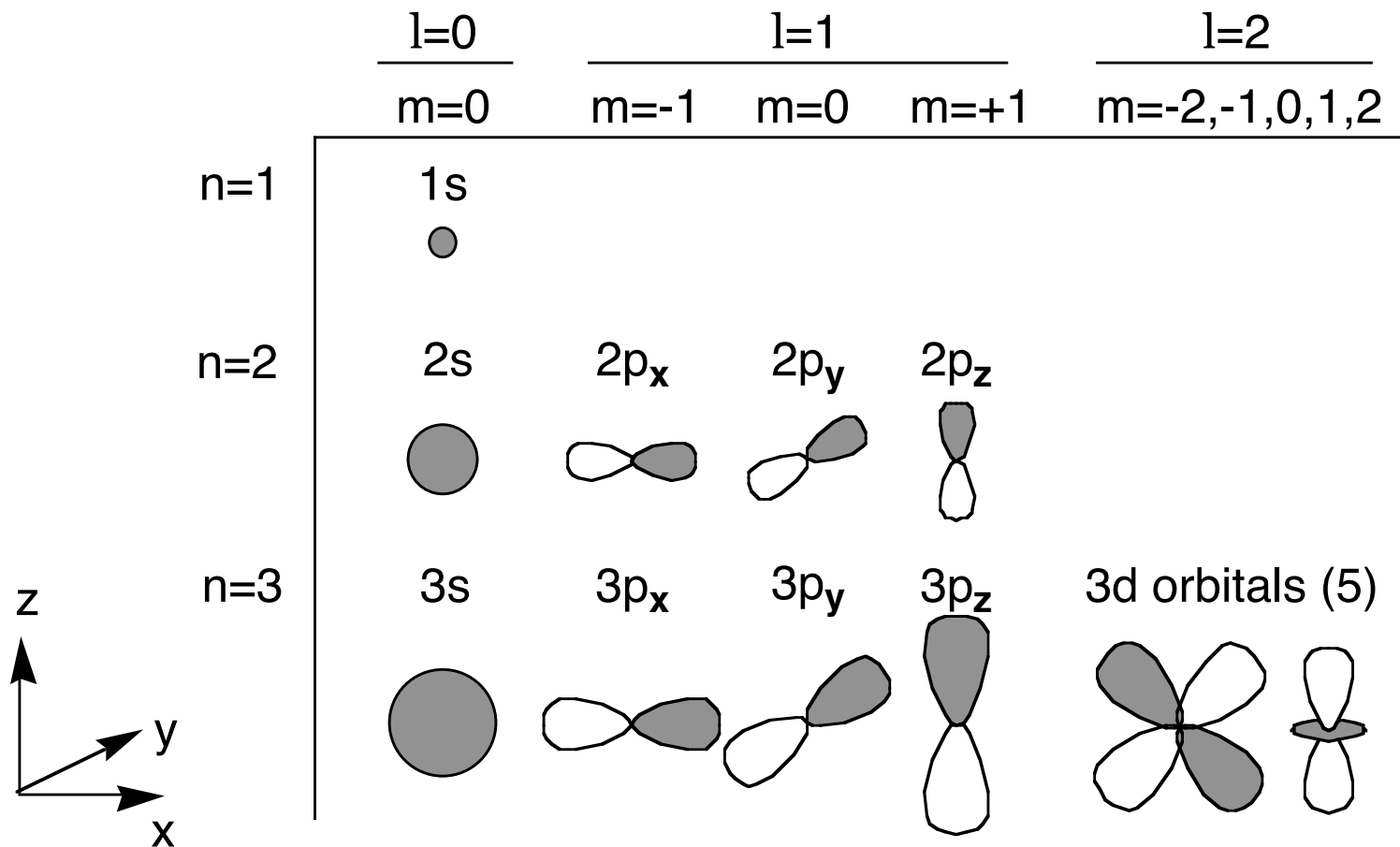
where  $\psi$  is the “wavefunction,” an eigenfunction of the equation

- Born recognized that  $|\psi|^2$  is the probability density function

Three key features of theory are required for *ab initio* calculations.

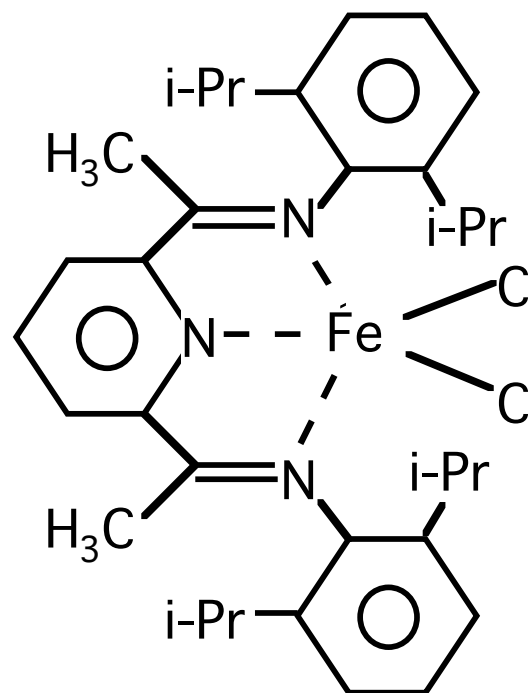
- Understand how initial specification of nuclear positions is used to calculate energy
  - Solving the Schrödinger equation
- Understand “basis sets” and how to choose them
  - Functions that represent the atomic orbitals
  - e.g., 3-21G, 6-311++G(3df,2pd), cc-pVTZ
- Understand levels of theory and how to choose them
  - Wavefunction methods: Hartree-Fock, MP4, CI, CAS
  - Density functional methods: LYP, B3LYP, etc.
  - Compound methods: CBS, G3
  - Semiempirical methods: AM1, PM3

H-atom eigenfunctions  $\psi$  correspond to hydrogenic atomic orbitals.

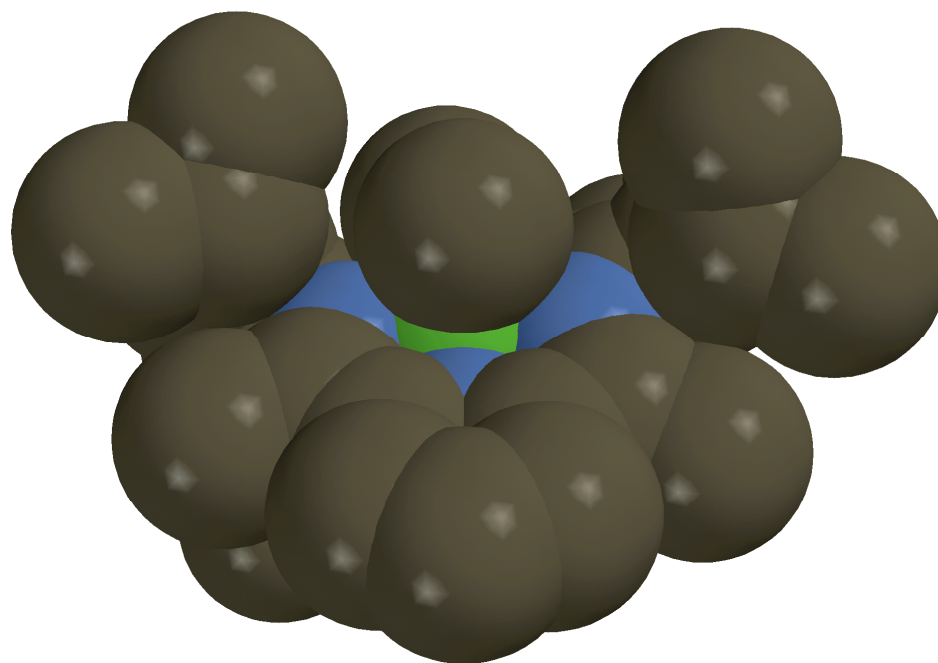
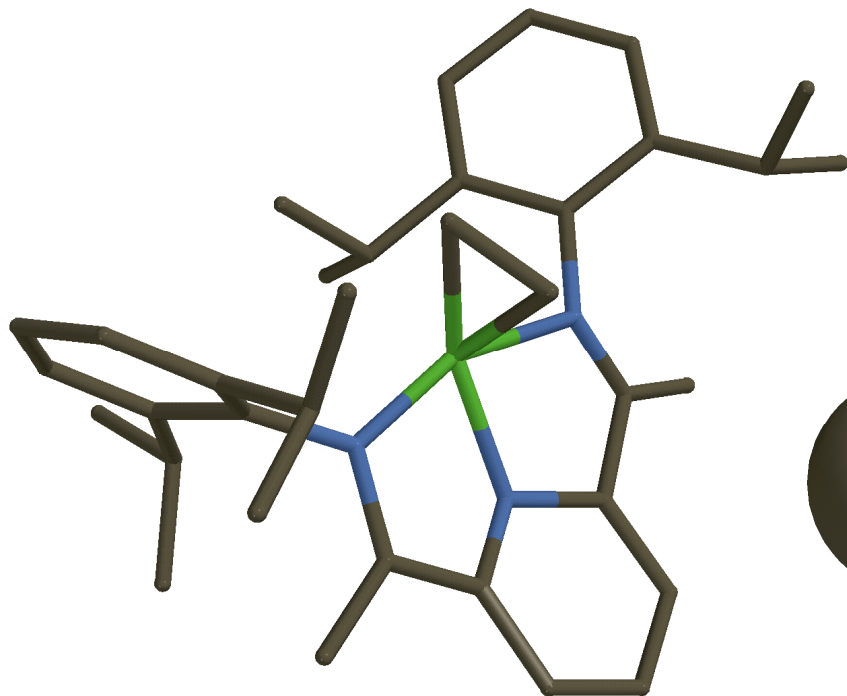


With these theoretical tools, we can move from  
overall formulas... to sketches...

$(C_{33}N_3H_{43})FeCl_2$ ,  
a liganded  
di(methyl imide  
xylenyl) aniline ...

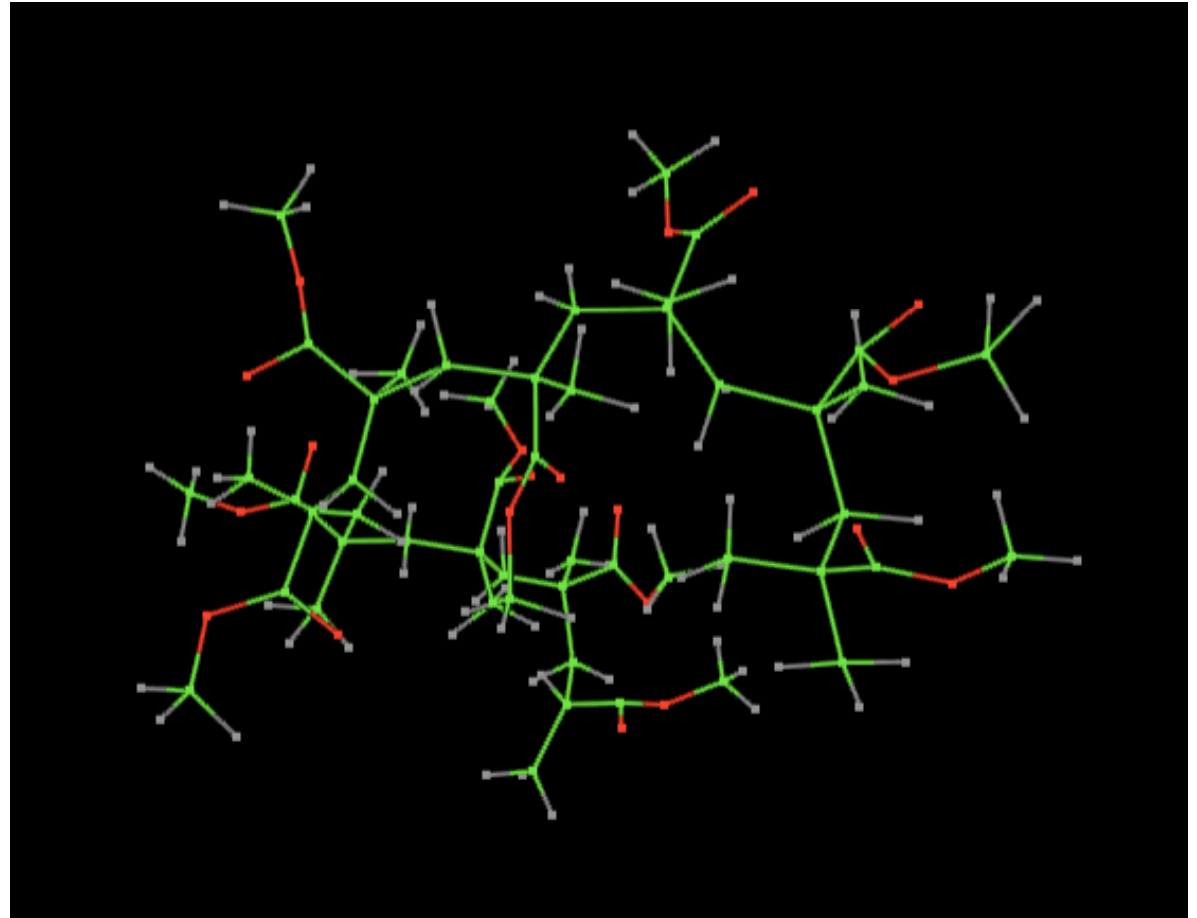


To quantitative 3-D functionality and properties.



# “Molecular simulations” handle larger scales.

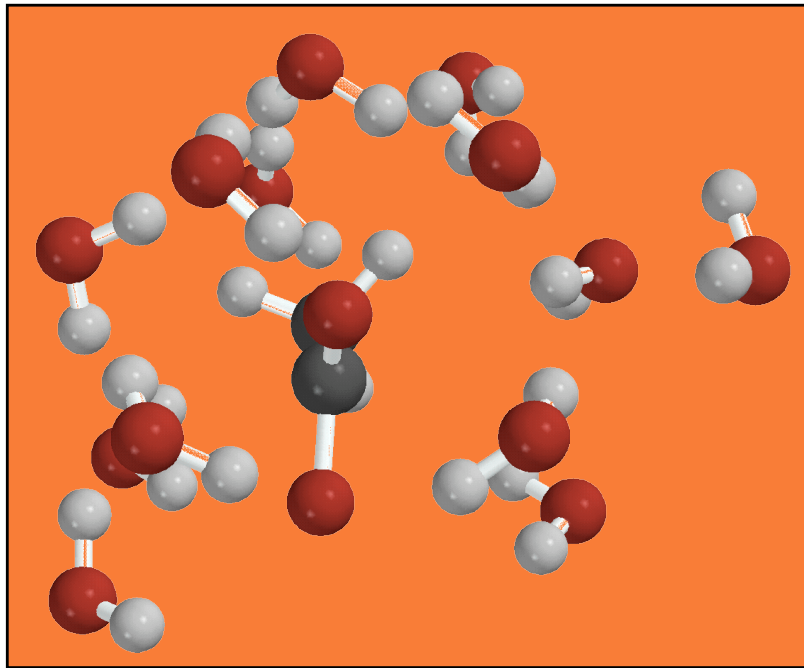
- System behaviors, based on forces between bodies.
- Accurate force-field functions are crucial.
- Statistical mechanics gives properties from system averages at constant NVT or NPT.
- Solvation is handled by molecular interactions.



Stoliarov, Westmoreland, Nyden, and Forney, “A reactive Molecular dynamics model of thermal decomposition in polymers: I. Poly(methyl methacrylate),” *Polymer* 44, 883-894 (2003).



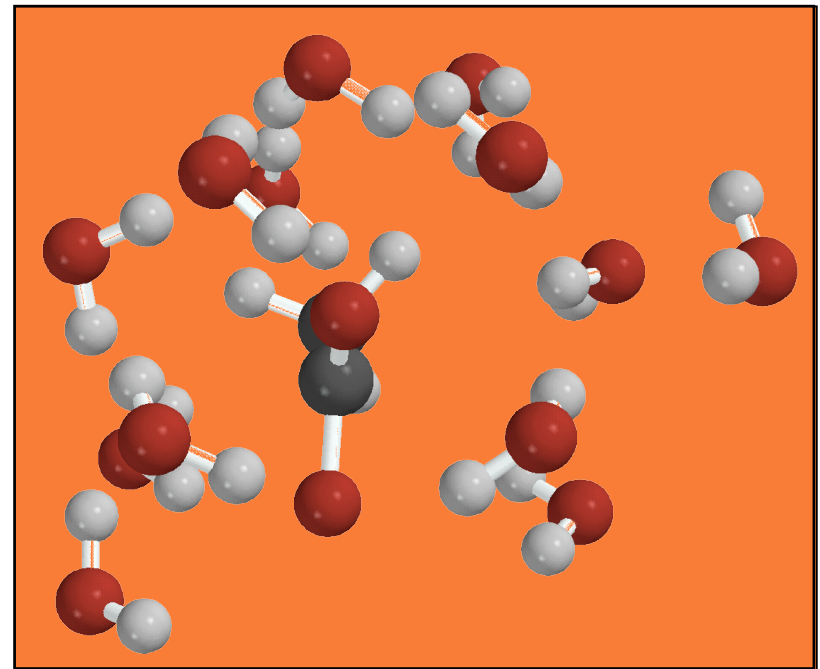
**Molecular dynamics** applies motions from Newtonian physics.



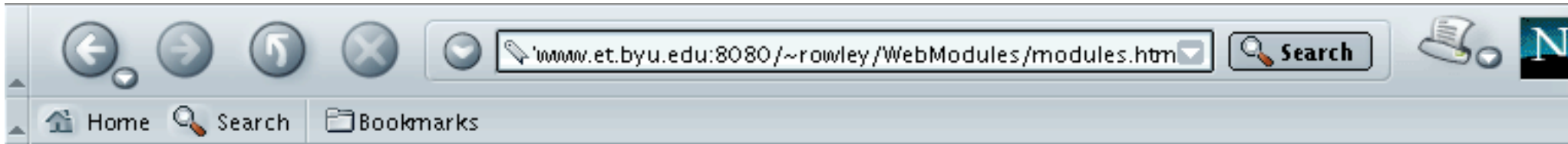
- $F = ma$  is used to compute positions and velocities over time
- Especially suited to evolving configurations:
  - Protein folding
  - Substrate docking (non-covalent)
  - Transport phenomena
  - Material morphology changes

“**Monte Carlo**” simulation samples phase space with random numbers.

- Select a probability-weighted move using a random number
- Effective for phase equilibrium, like VLE by **Gibbs-Ensemble Monte Carlo**
- Effective for processes with known step-wise parameters, like adsorption / surface diffusion with **Kinetic Monte Carlo**



# CACHE and NSF have sponsored development of simulation-based Web modules.



## WWW- Based Modules for Introduction of Molecular Simulation into the Chemical Engineering Curriculum

Modules accessible from this page are freely distributed. Their purpose is to introduce molecular simulation into the standard chemical engineering curriculum with the intent of addressing two issues:

- Fostering molecular understanding of phenomena and processes commonly taught in standard chemical engineering courses
- Improving abilities of chemical engineering students and faculty members to use and interpret molecular simulations

Both objectives are designed to help prepare students to meet the demands of emerging technologies that are dependent upon molecular processes without introducing new courses into an already full curriculum.

This project has been a multi-institutional endeavor by Chemical Engineering faculty at various universities. The modules are can be used by faculty members in standard chemical engineering courses. Provided with each module are:

- Background materials on the concepts taught by the module
- A molecular simulation that permits the user to explore the concepts taught
- Tutorial material that illustrates the use of the simulation applet
- Additional problems for use as homework problems
- Instructor materials
- Assessment form



Funded by the [National Science Foundation](#) under grant DUE-9752243



Sponsored by [CACHE](#) of AIChE



Developed by the [MMTF \(Molecular Modeling Task Force\)](#) of [CACHE](#)

### [Etomica: General Simulation Design Tool](#)

Purpose:	Visual environment for quickly designing and constructing simulation applets by dragging and dropping simulation components including the type of: simulation cell, molecules, interactions, numerical integrator, boundary conditions, display monitors, etc.
Applicable Classes:	unlimited
Author:	David Kofke
Affiliation:	State University of New York at Buffalo
Date Posted:	July 2, 2001

### [Multicomponent Phase Equilibrium](#)

Purpose:	Molecular simulations are used to elucidate the concept of chemical potential in multicomponent systems, and how the chemical potential relates to multicomponent phase equilibrium.
Applicable Classes:	Thermodynamics
Author:	Daniel Lacks
Affiliation:	Tulane University
Date Posted:	July 2, 2001

### [Vapor Liquid Equilibrium](#)

Purpose:	Provide a molecular visualization of the equilibrium vapor and liquid phases corresponding to real binary mixtures. Students at any level in their curriculum can get a better feel for the relationship between the interactions between molecules and the resultant extent of the phases (mass balances) and the equilibrium compositions (equality of component chemical potentials).
Applicable Classes:	Separations, Material and Energy Balances, Thermodynamics
Author:	Richard Rowley
Affiliation:	Brigham Young University
Date Posted:	July 2, 2001

### [Molecular Aspects of Thermal Conductivity](#)

Purpose:	Using an interactive simulation applet, the module attempts to strengthen the link between traditional macroscopic engineering approaches to heat transfer and the concepts from kinetic theory that students learn in physical chemistry courses. Students will learn what properties influence the ability of different materials to conduct energy, as well as how the transport coefficients can be calculated from knowledge of the molecular-level structure and energetics of the material.
Applicable Classes:	Heat Transfer, Fundamentals of Transport Phenomena, Molecular Modeling
Author:	Randall Snurr
Affiliation:	Northwestern University
Date Posted:	July 2, 2001

### [Joule-Thomson Effect](#)

Purpose:	In this module, you will investigate the Joule-Thomson effect, using classical thermodynamics along with molecular simulation. You will explore how the relationship between temperature, pressure and intermolecular forces leads to a given temperature change upon expansion. At the completion of the module, you should be able to answer Joule and Thomson's question!
Applicable Classes:	Thermodynamics
Author:	Edward Maginn

Other properties are predicted or correlated if we have information from data or computation.

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- Good semi-empirical and *ab initio* calculations for excited states give pigment and dye behaviors
- Solvation models by Tomasi and others make liquid-phase behaviors more calculable
- Hybrid QM / Mol Sim'n methods have proven powerful
  - QM/MM for biomolecule structure and *ab-initio* molecular dynamics for ordered condensed phases; calculate interactions as dynamics calculations proceed
  - Spatial extrapolation such as embedded-atom models of catalysts and Morokuma's ONIOM method; connect or extrapolate domains of different-level calculations

# Leads smoothly to features of molecular biology.



- Build on earlier review of biochemical nomenclature, calculation of structures, and homogeneous catalysis
- Examine four behaviors with related properties and calculations:
  - DNA and genomic structure
  - Protein structure and folding
  - Small-molecule docking into receptors
  - Ion-channel transport

# Throughout, include examples ranging from Dow and classical ChE applications...

- Dow case study: Six months to identify and produce high-T organic solid with low dielectric constant (SiLK)
  - Also, homogeneous and heterogeneous results and patents
  - Computational thermochemistry is routine
    - | Dave Frurip (part of the JANAF team) described calculation of  $\Delta H_{\text{reaction}}$  for safety analysis as having reached “maintenance mode”
    - | For the same accuracy, measurement of  $\Delta H_{\text{reaction}}$  was estimated to cost \$125,000 vs. \$2,000 for a G3 calculation
    - | Includes calculations to generate new additivity groups
- Molecular modeling beginning to deliver physical properties to design accuracy: densities, viscosities, critical points
  - | e.g., 2002 AIChE CoMSEF “First Industrial Fluid Properties Simulation Challenge”, <http://www.cstl.nist.gov/FluidSimulationChallenge/>)

# To Vertex Pharmaceutical's anti-HIV drug.

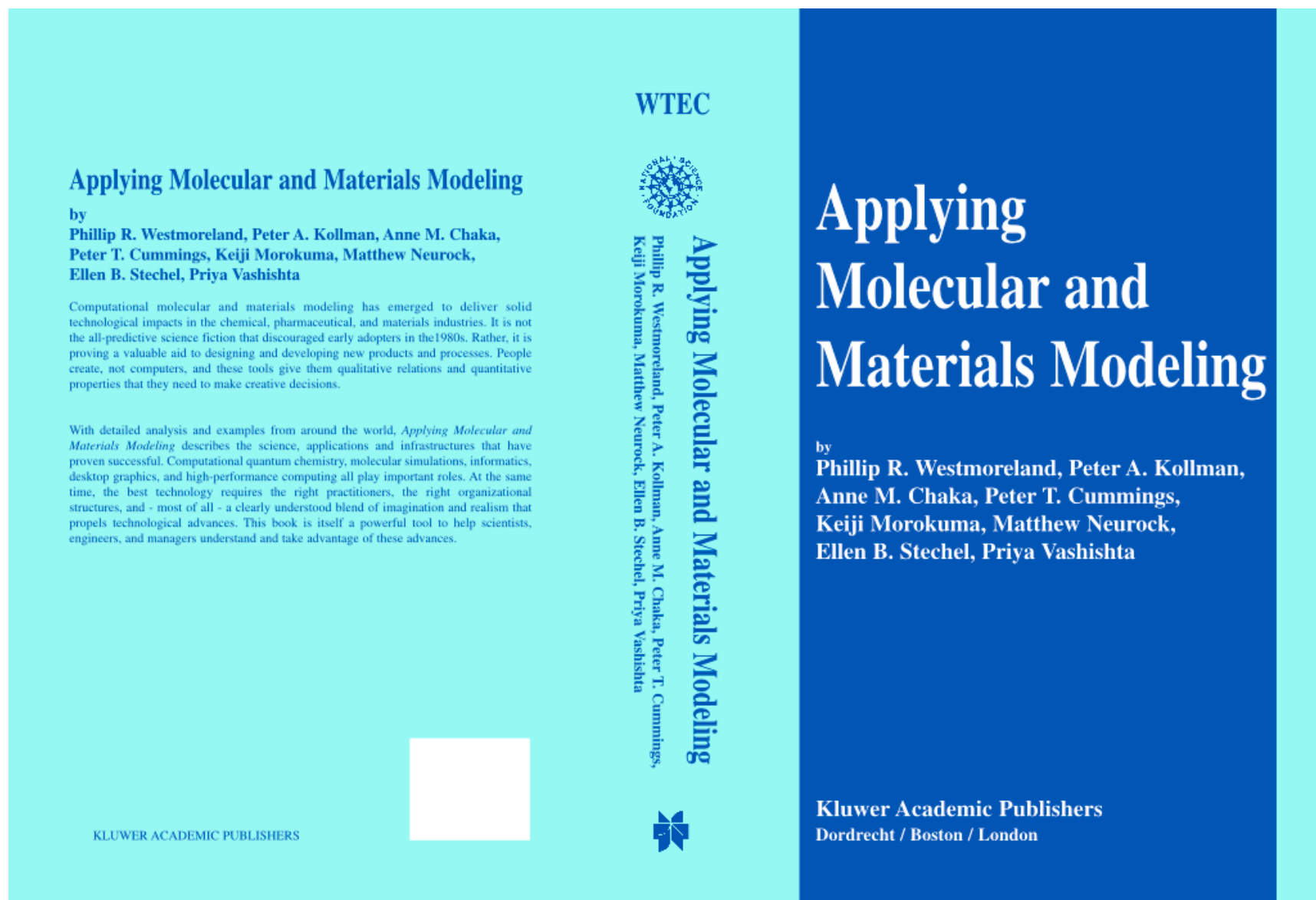
- Agenerase is on the market, developed using computational chemistry as a central tool



HIV protease inhibitor Agenerase®  
(Vertex Pharmaceuticals, 1999)



Our recent book describes activities at 600+ sites.  
(Online version is at <http://www.wtec.org/loyola/molmodel/>)



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