Chapter #1

Theory, Computation, and Modeling of Experimental Observables

Theory

A theory is a rule ("law"), or a group of rules, that describe physical systems.

Theories are tested by experimentation.

Theories are valid within an "applicable range".

Theories should be "complete".

Einstein, mass-energy equivalence: $E = mc^2$

Coulomb, electrostatic interaction: $E = q_1 q_2 / r_{12}$

Model

A model is a rule, or a group of rules, that describe physical systems approximately.

Semi-quantitative or merely qualitative.

Not necessarily reflective of true physical nature. Empirical rather than causal.

Validity depends very much on similarity.

Arrhenius Equation: $k = A \exp(-E_A/RT)$

Computation

The use of digital technology to solve the mathematical equations that define a particular theory or model.

Computational Chemists May Be…

Concerned mainly with chemistry.

Concerned mostly with algorithms.

Concerned mostly with programming.

Types of Theories

In ab initio theory, observables are computed based on more or less rigorous evaluation of the rigorous quantum-mechanical equations.

In empirical theory, observables are computed based on an intuitively adopted or adapted equation. The equation may or may not be justified by *a posteriori* derivation from QM.

Observables

[1] Structure

[2] Energy

[3] Properties

Spectroscopy: MW, IR, UV/Vis, NMR, ESR,…

Thermochemistry and Kinetics

Potential Energy Surface, PES

$$\text{Energy} = E(x_1, y_1, z_1, x_2, y_2, z_2, \ldots x_M, y_M, z_M)$$

Nonlinear: $M = 3N - 6$

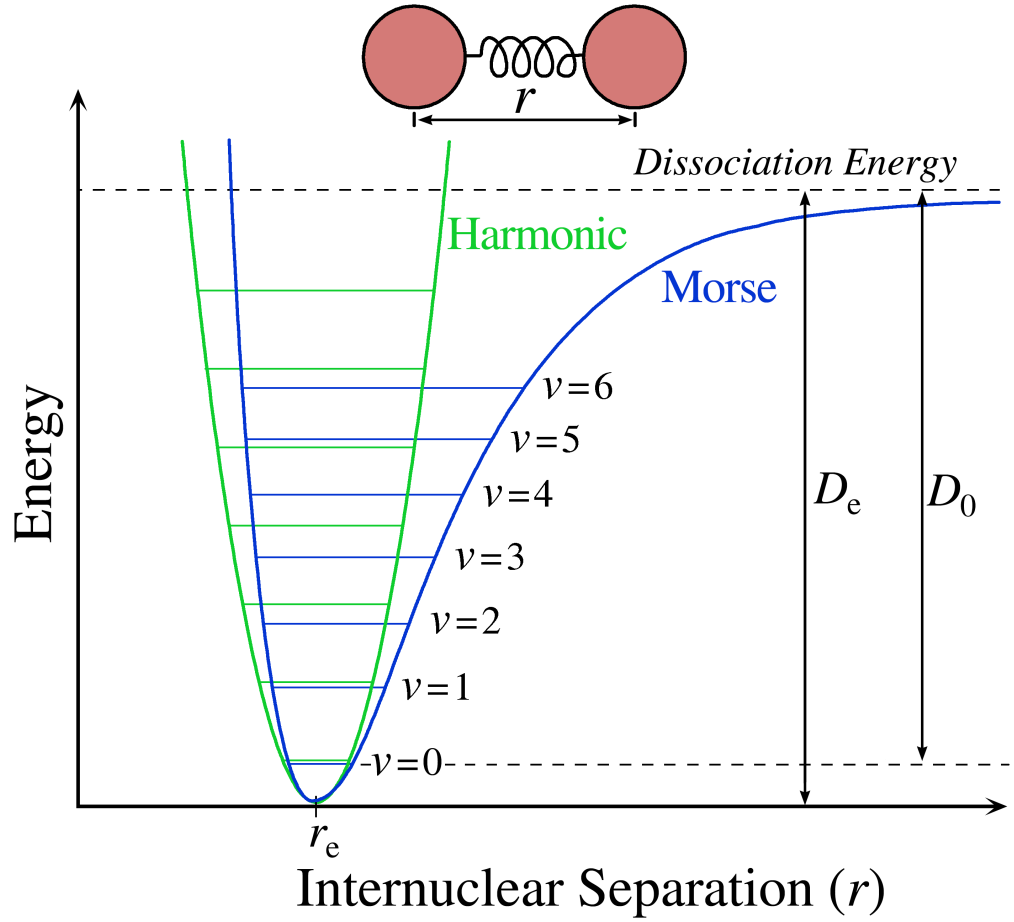
Linear: $M = 3N - 5$

N is the number of atoms. M is the number of internal coordinates.

The remaining coordinates describe the motion of the molecule as a whole.

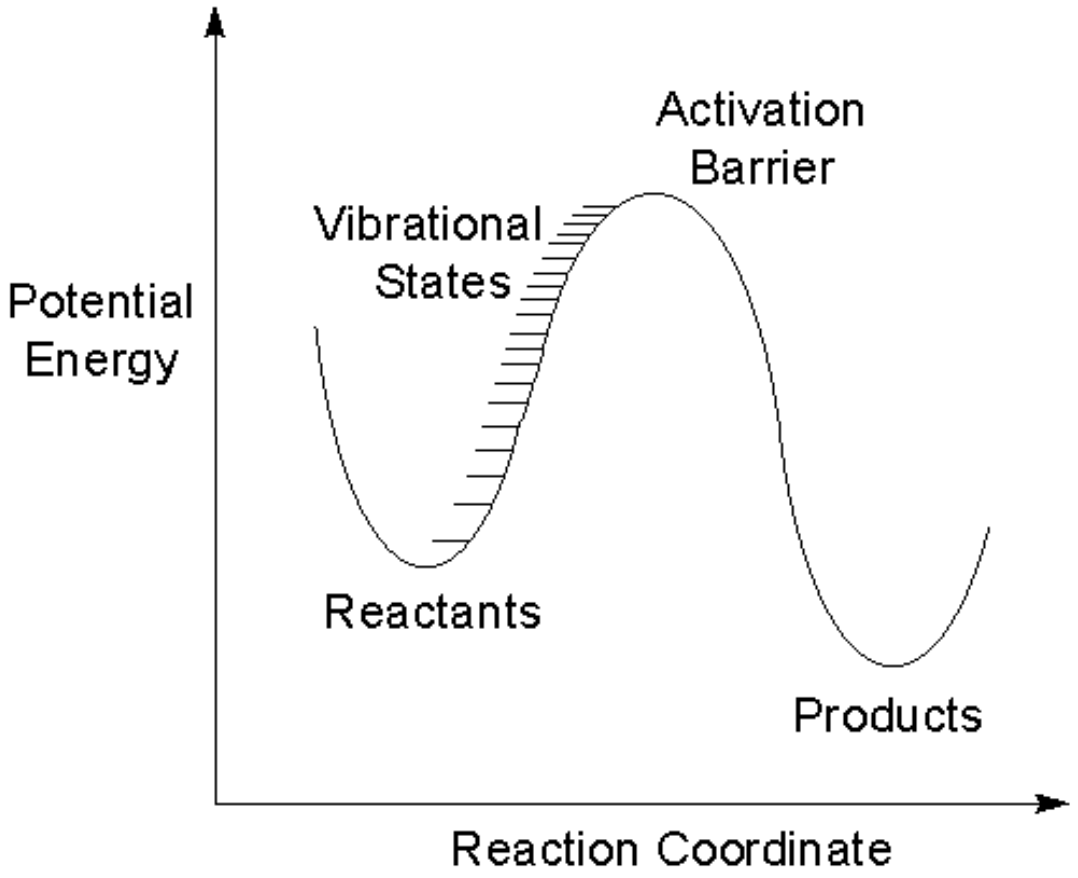
HARD TO VISUALIZE. MORE ON THIS SOON.

Potential Energy Surface, PES



https://upload.wikimedia.org/wikipedia/commons/7/7a/Morse-potential.png

Reaction Diagram: PES(Rxn. Coord.)



www.chem.hope.edu/~polik/poster/polyad96.htm

Approaches to the Combination of Theory and Experiment

[1] *Post facto* application. Theory clarifies the interpretation of experimental data.

- mechanisms, kinetics,…

[2] *A priori* application. Theory is applied to generate best expectations about experimental measurements.

- spectra, solubility properties,…

[3] *Ante facto* application. Theory is applied to explore chemistry not yet amenable to measurement.

- properties of toxins, explosives,…
- chemistry in exotic places, exotic conditions,…

Hardware

[1] Nodes (Board) and Cores (CPU).

- The more the better.
- Typical HPC: 24 – 28 cores per node (PC: 2-4)

[2] Memory. Memory on chip. Lost on power-off.

- The more the better. The faster the better.
- Typical HPC: 128 - 256 GB per node (PC: 2-8 GB)

[3] Storage. Memory on disk. Stays on power-off.

- The more the better.
- Typical HPC: TB range (terabyte, 10^{12})

https://doit.missouri.edu/services/research/high-performance-computing/

Scaling

If your problem doubles in size (n), the computations required

- might double (linear scaling, n^1, scaling factor 1).
- grow 4-fold (n^2)
- or worse (n^m).

Linear scaling is desirable, but hard to realize. Size still creates hard limits for computational chemists.

There are many Measures of "Size." The important ones include:

- Number of atoms.
- Number of basis functions.
- Number of degrees of freedom.

Atomic Units

Energy (Hartree)	E_h
Length (Bohr)	a_0, Bohr radius for H.
Charge (electron)	e
Mass	m_e
Angular Momentum	$\hbar$
Vacuum Permittivity	$4\pi\varepsilon_0$

Unit Conversion

Length: 1 a_0 = 0.529 Å = 52.9 pm

Electron Charge: $1.60217662 \times 10^{-19}$ Coulombs

Electron Rest Mass: $9.10938356 \times 10^{-31}$ kg

Energy per system: 1 E_h = $4.360 \bullet 10^{-18}$ J

Avogadro Number: N_A = $6.0221415 \bullet 10^{23}$ mol^{-1}

Energy per mole:

1 E_h = 2626 kJ/mol = 627.51 kcal/mol