

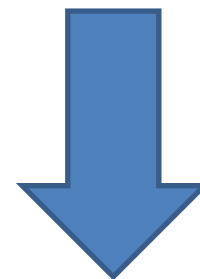
Materials design and selection for circular economy

Mod. 2 Design and selection of functional molecules and materials
for sustainable synthesis and circularity

Laura Orian
DiSC UNIPD Via Marzolo 1 35131 Padova (IT)
laura.orian@unipd.it



Molecular modeling and chicken cooking...



CONSIDERATIONS	CHICKEN	MOLECULES
STARTING SHAPE: What does the thing look like?	What is the shape of the chicken? Legs, breast, wing, strips?	What is the geometry of the molecule? Atoms, bonds, angles and lengths?
FINAL PRODUCT: What do I want at the end?	How do I want the chicken cooked? Fried, baked, BBQ, stir-fry, etc.	What properties do I want to know? Energy, vibrations, thermodynamics, transition state
AVAILABLE TOOLS: What tools do I have to work with?	What cooking devices? Microwave, stove, oven, grill, open fire?	What computational software do I have? Gaussian, GAMESS, MOPAC, Tinker
INSTRUCTIONS: What method(s) do I have or know?	Which recipe(s) do I know or have?	Which methods do I know or have? Ab initio, semi-empirical, MM, DFT, etc.
RESOURCES: What resources do I have at my disposal?	What ingredients do I have? Sauces, spices, etc.	What type of basis sets do I know and have? Minimal, split-valence, polarized, diffuse, etc.

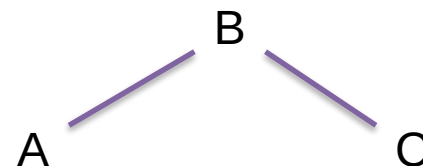
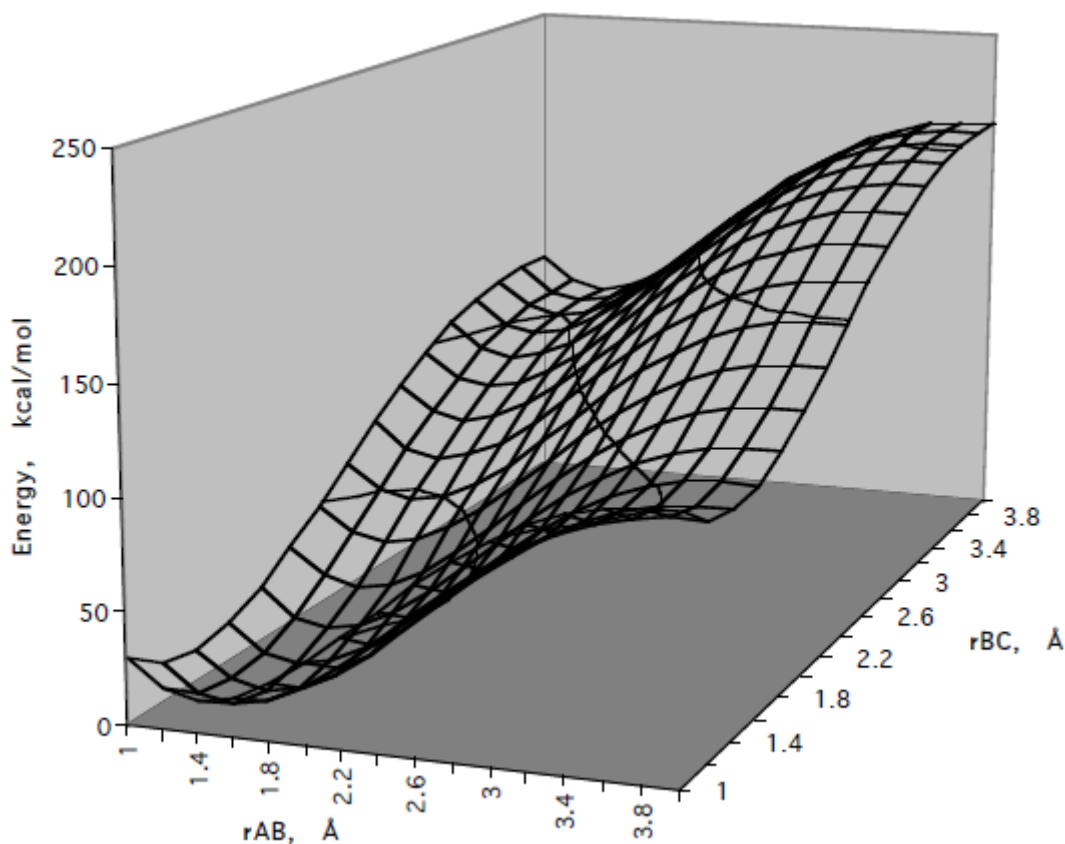
The potential energy surface (PES)

- Unique energy associated to each structure (geometry)
- Smooth energy landscape: chemistry $\rightarrow$ topology

Dimensionality of the PES

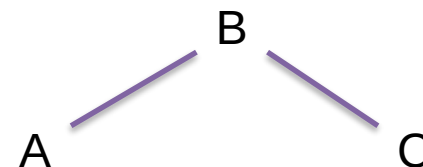
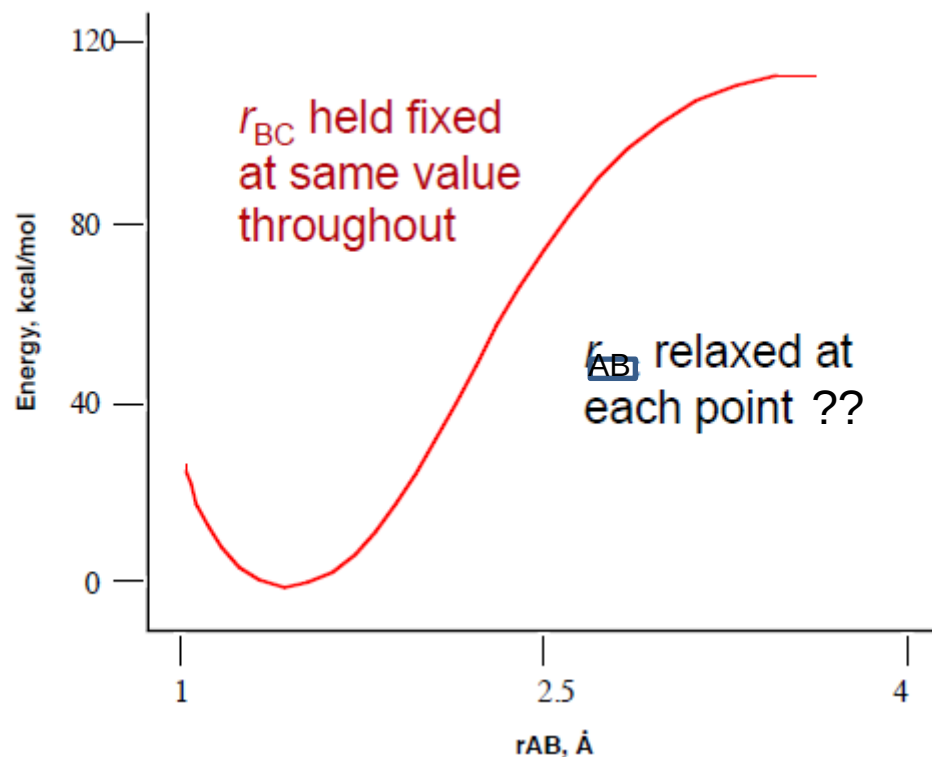
- To define an atom's location in 3-dimensional space in principle one needs 3 coordinates (e.g., x , y , and z in some laboratory reference frame)
- The PES should not depend on the *absolute* location of the atoms, but only on their location *relative to one another* (i.e., the **molecular geometry**)
- A typical PES has the same dimensionality as the number of *geometric degrees of freedom* of the (not everywhere linear) molecule ($3N-6$, where N = number of atoms and $N > 2$)

Usually *slices* of the PES are considered:



2D slice of a
molecule with 3 degrees
of freedom;

It is the bond
angle that is being held
fixed that defines the
slice.

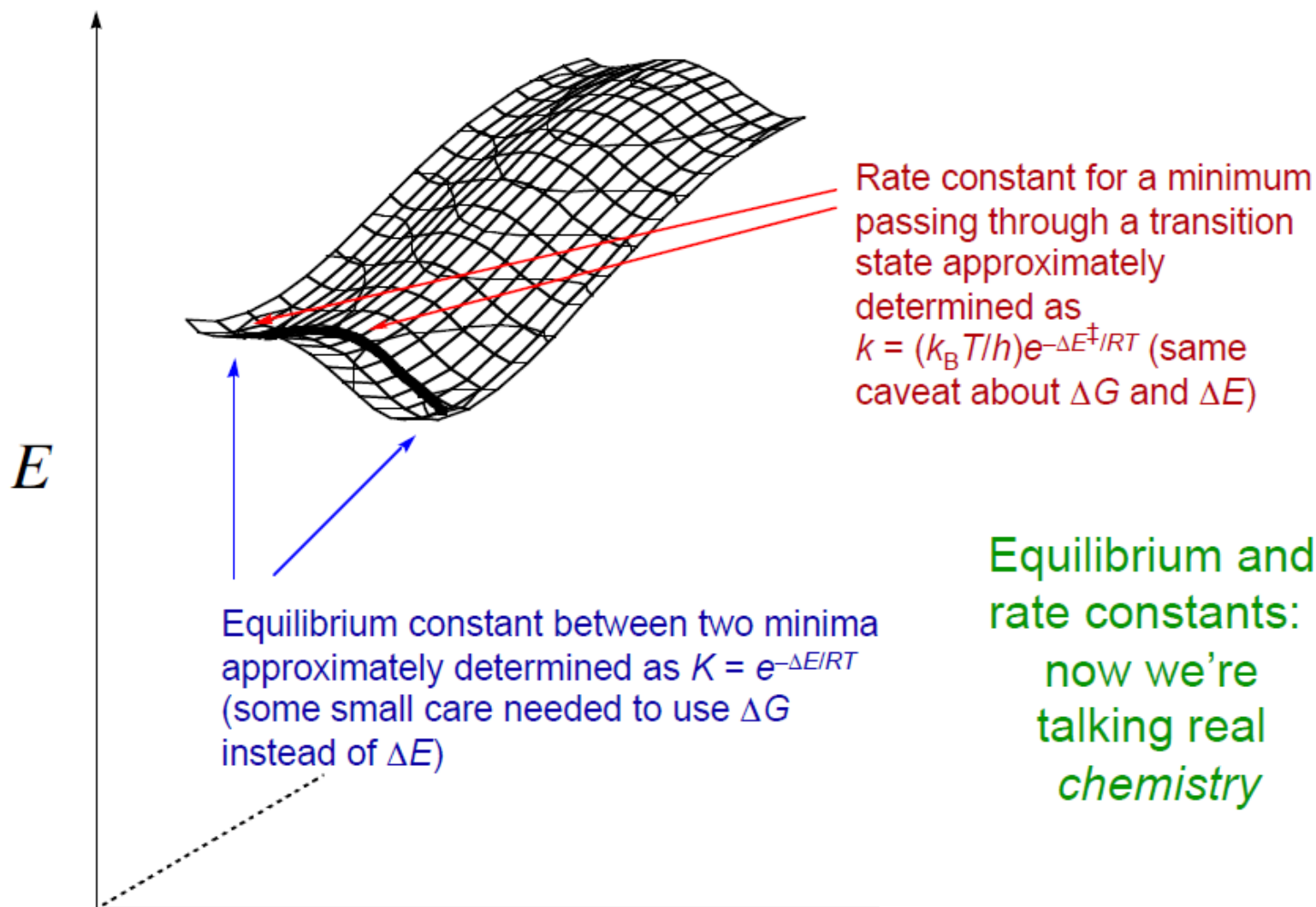


This is a slice of the surface from the last slide now not only holding the ABC angle to some fixed value, but also controlling r_{BC}

A *true* reaction coordinate implies that all other degrees of freedom are *relaxed*, not held fixed

The PES:

- Depends in a fundamental way on the *Born-Oppenheimer* approximation
- Inherently a classical construct with respect to the nuclei (but quantum in the electronics)
- Corresponds to a single molecule; thinking about a *collection* of molecules requires us to bring in thermodynamics
- Does not show *kinetic* energy! So, everyone's favorite picture of a dynamic molecule being a ball rolling on the surface is misleading if you think of the energy decreasing as you go downhill. *Total* energy (PE + KE) is conserved at a constant value.
- At $T = 0$ K (no KE), the rules of our universe say that our molecule will want to be at the lowest possible potential energy, i.e., at a *minimum* on the PES. It surely would be nice to have ways of finding the locations of minima efficiently...
- Between any two minima (valley bottoms) the lowest energy path will pass through a maximum at a saddle point. In chemistry, we call that saddle point a transition-state structure. They'd be nice to find too...

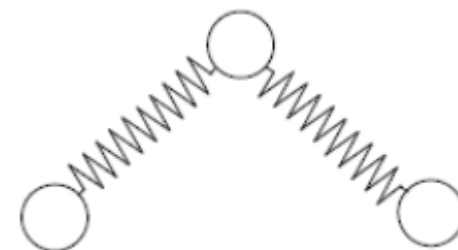


It's clear the PES is useful, so how can I construct it for an arbitrary system (defined simply by the molecular formula)?

- It seems that for equilibrium and rate constants, I don't actually need to know the whole surface, only the energies of critical points (minima and saddle points)—is there a way to find these without mapping out the entire surface in detail?
- If I *don't* do the whole surface, can I be sure that I know about the locations of *all* the critical points and how they relate to one another?

How do we calculate the energy?

- **Quantum mechanics**
 - Electrons are the smallest particle represented.
 - Solves the Schrödinger equation.
- **Molecular mechanics**
 - Atoms are the smallest particles.
 - Atoms are represented by balls.
 - Bonds are represented by strings.
 - “balls and springs” model



Force fields

Equations and parameters that relate the
chemical structure and conformation to energy.

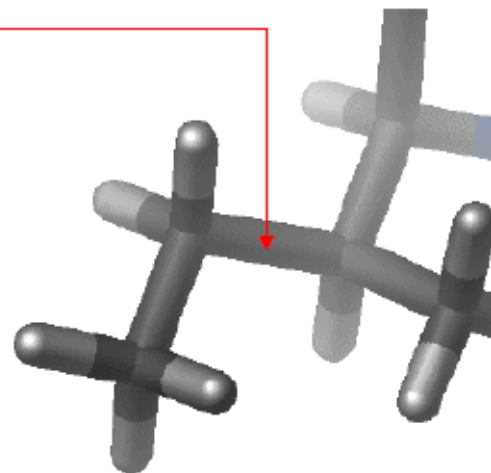
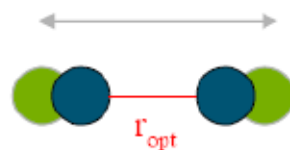
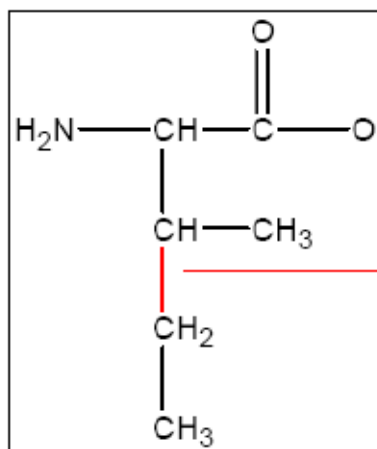
$E \sim \mathbf{f}$ (atomic positions)

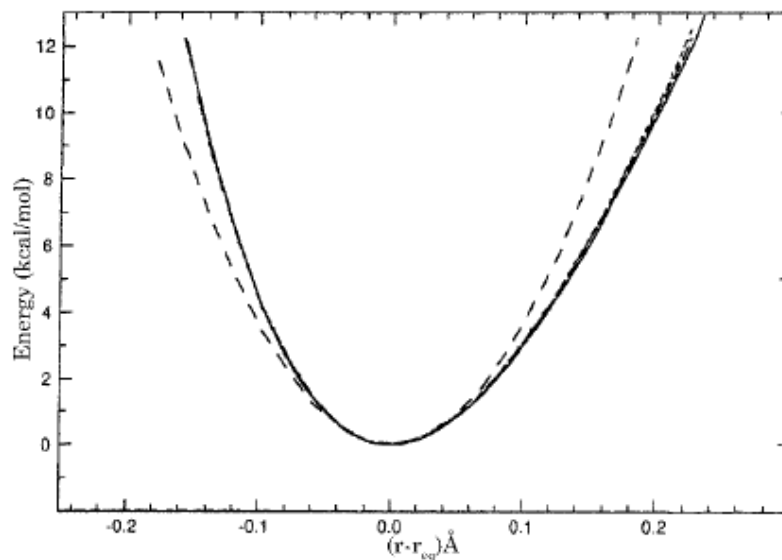
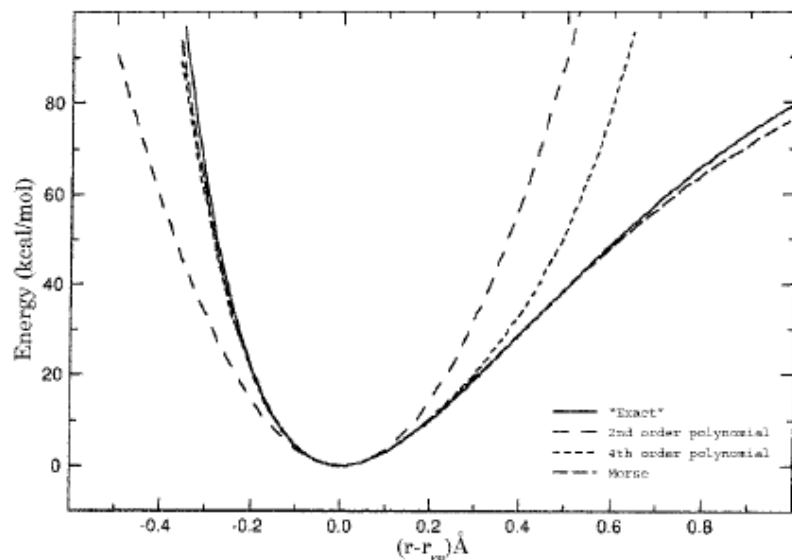
E_{bonded}

$$E = E_{\text{stretch}} + E_{\text{bend}} + E_{\text{torsion}} + E_{\text{impropers}} + E_{\text{electrostatic}} + E_{\text{vanderWaals}}$$

$E_{\text{non-bonded}}$

Bonds





Morse potential

$$E_{\text{stretching}} = D_e \cdot \{1 - \exp[-a(r - r_o)]\}^2$$

Harmonic potential (Hooke)

$$E_{\text{stretching}} = \sum_{1,2 \text{ pairs}} K_r (r - r_o)^2$$

*ca. 100 to 500
kCal/mol/Å²*

• Morse potential requires 3 parameters so computationally expensive and difficult to parameterize.

• Harmonic potential is usually good enough since most bonds remain within +/- 0.1 Angstroms of “optimum”.

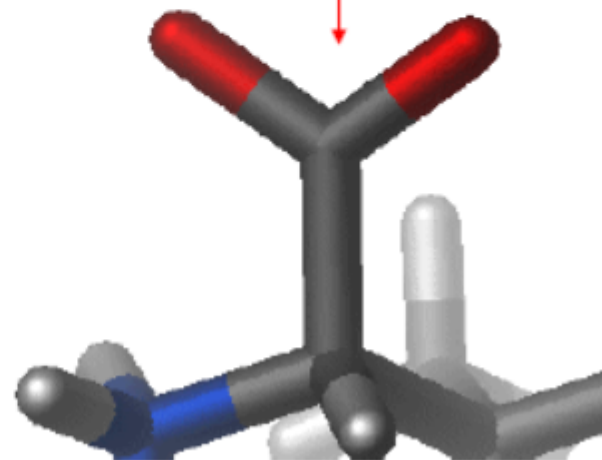
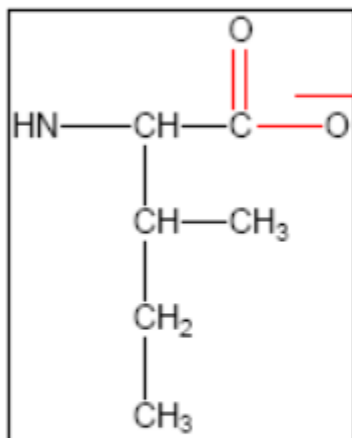
Angles

$$E_{\text{bending}} = \sum_{1,2 \text{ pairs}} K_{\theta} (\theta - \theta_0)^2$$

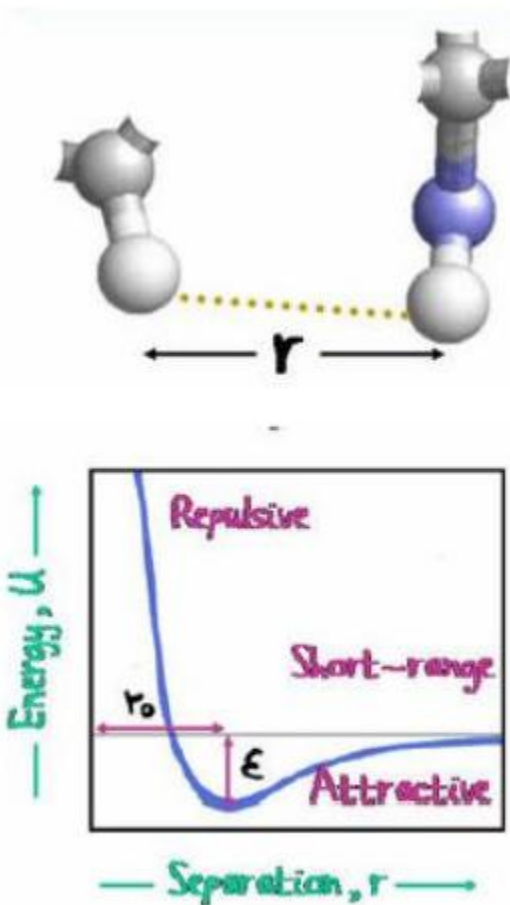


less energy is required to distort an angle than to stretch or compress a bond;

lower K_{θ} values: e.g. $10^{-3} \text{ kcal.mol}^{-1}.\text{deg}^{-2}$



Non bonded interactions (van der Waals)



Lennard-Jones potential

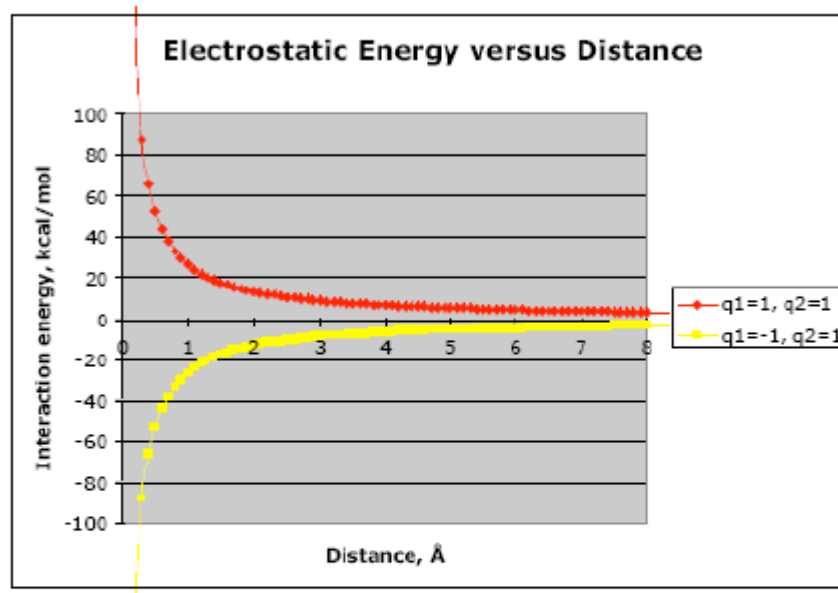
$$E_{vdW} = \sum_{nonbondedpairs} \epsilon \cdot \left[\left(\frac{r_0}{r} \right)^{12} - 2 \cdot \left(\frac{r_0}{r} \right)^6 \right]$$

$$E_{vdW} = \sum_{nonbondedpairs} \left[\left(\frac{A}{r^{12}} \right) - 2 \cdot \left(\frac{C}{r^6} \right) \right]$$

Electrostatics

Coulomb potential

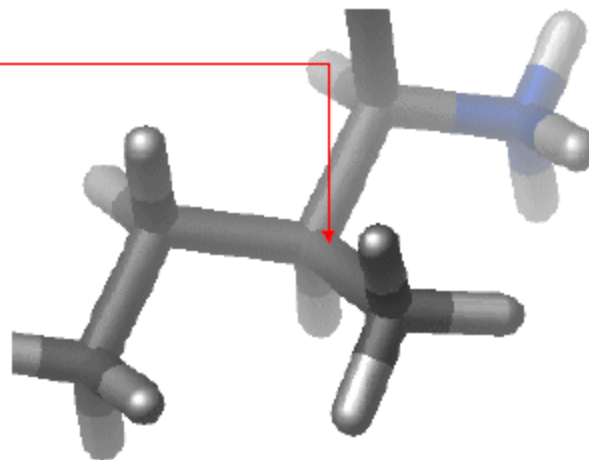
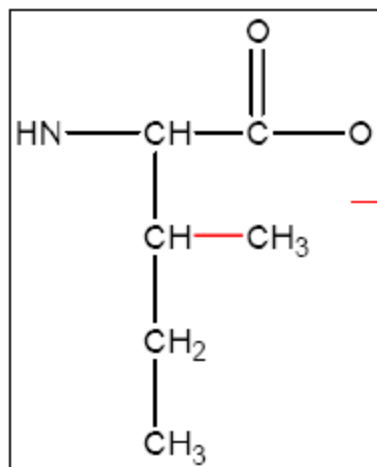
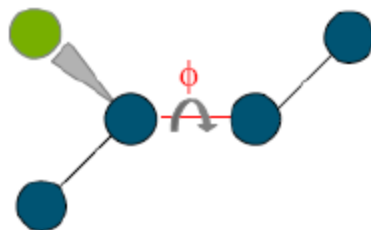
$$E_{vdW} = \sum_{nonbonded\ pairs} \frac{q_i \cdot q_j}{\epsilon \cdot r}$$



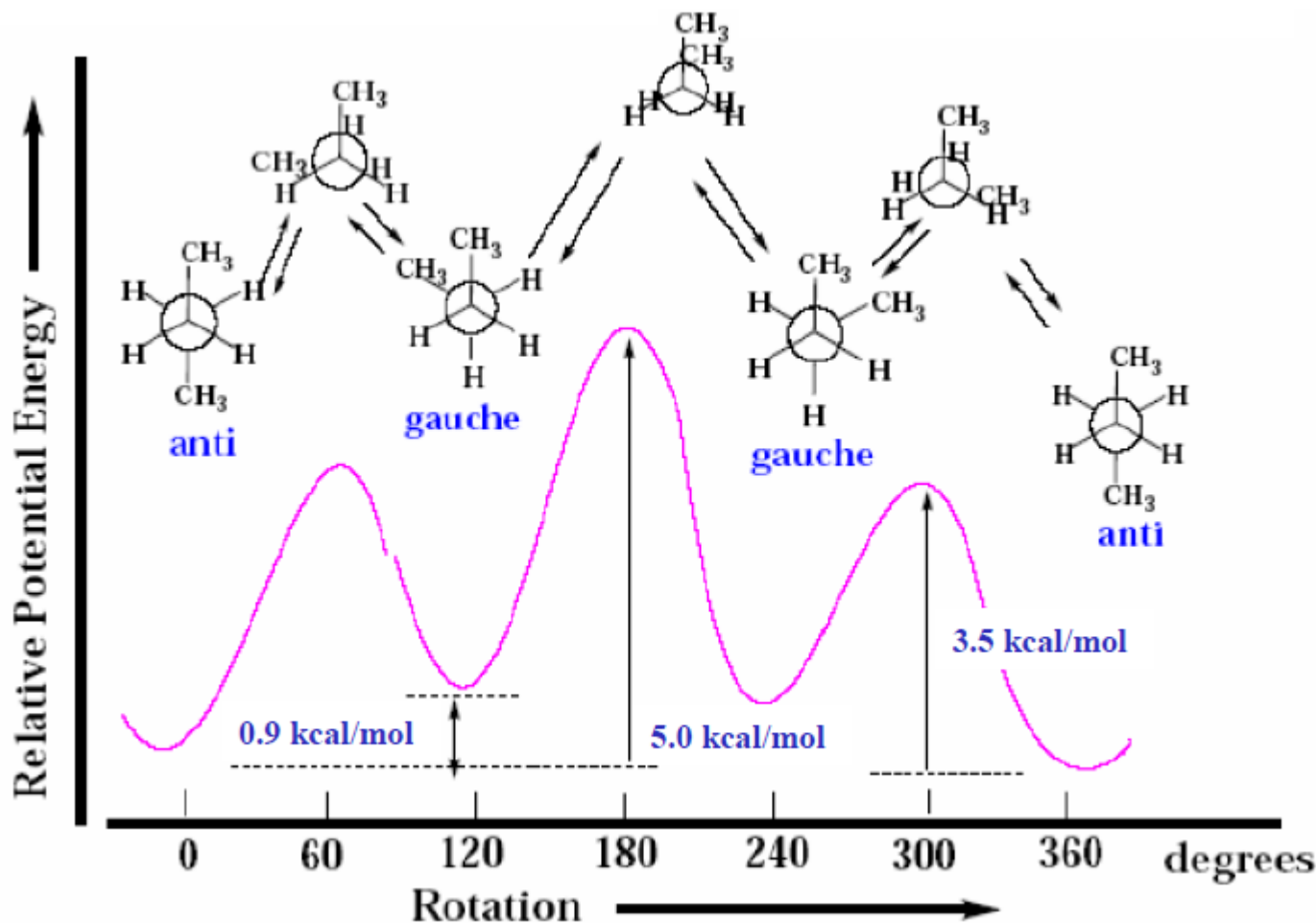
- point charge model
- no dipole-induced effects

Dihedrals

$$E_{\text{torsion}} = \sum_{1,4 \text{ pairs}} K_{\phi} (1 - \cos(n\phi - \delta))$$



Example of a PES slice: n-butane



An example from my lab

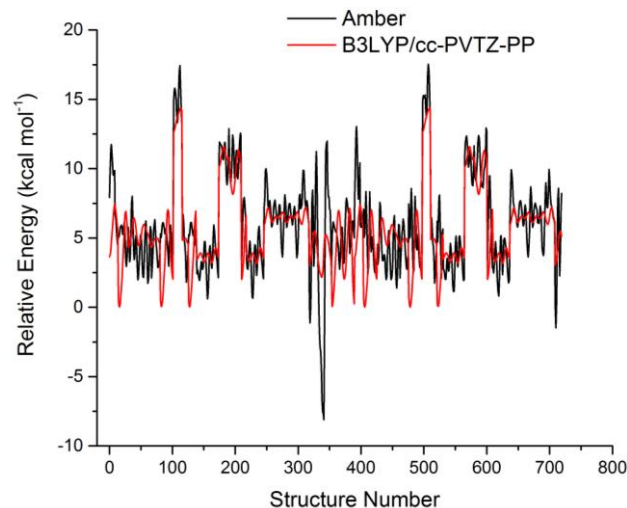
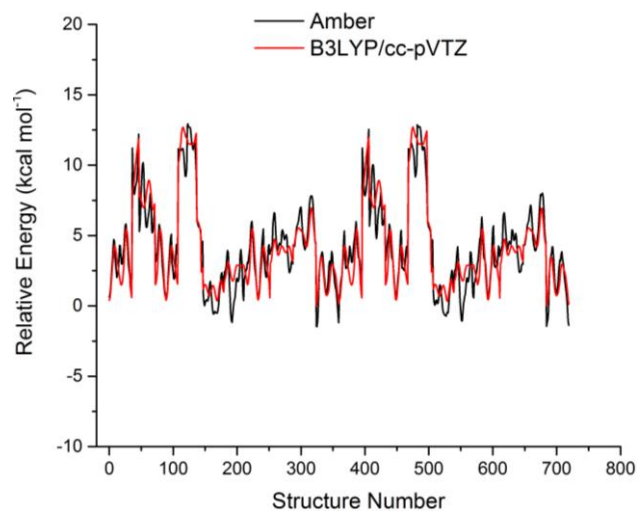
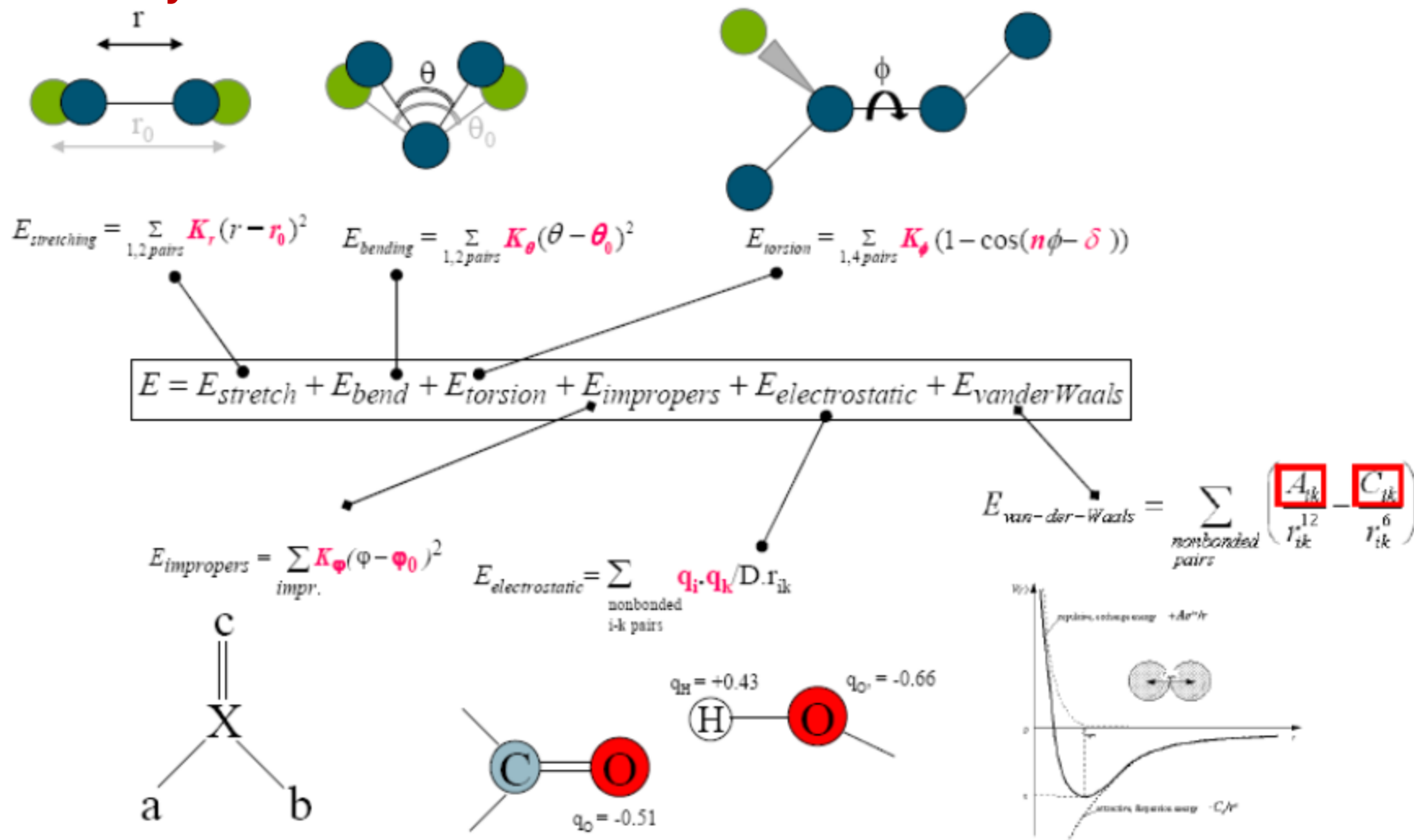


Figure S1 Fitting obtained with Paramfit of energies of the structures generated with dihedral scans for Sec (left) and Tec (right).

Summary



Human resources department



"Oh, not a computer, Caldwell —
we're replacing you with a
computer *simulation*."