

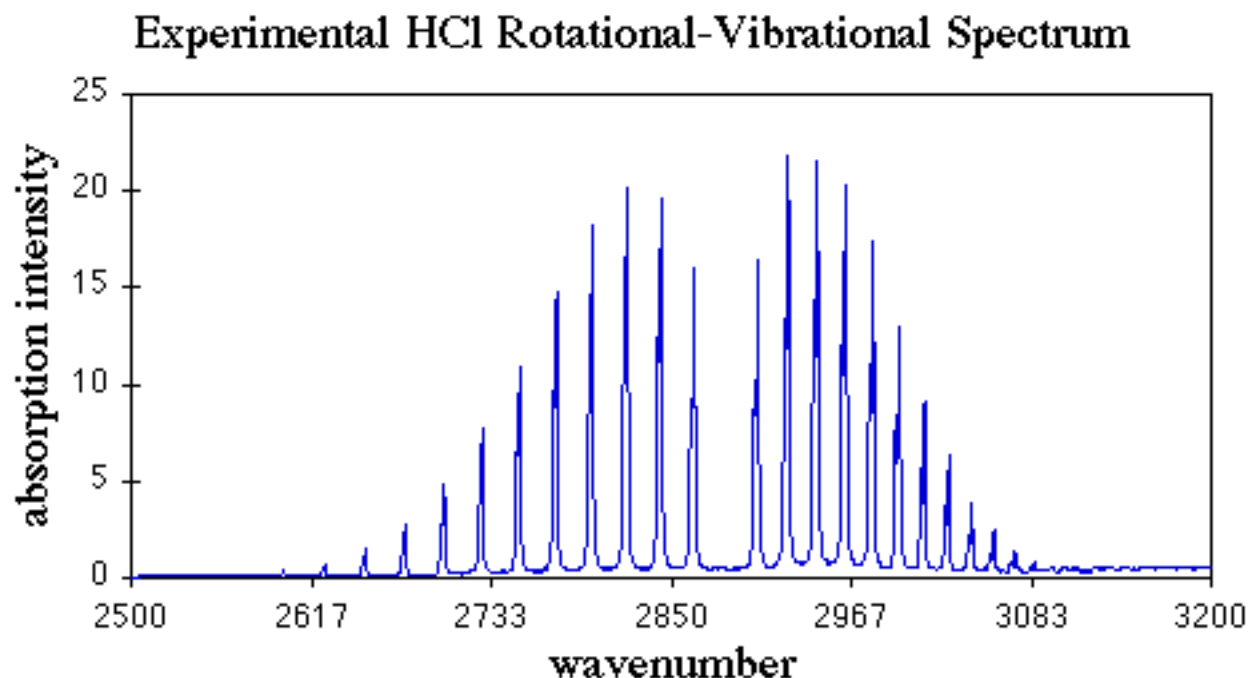
# The Potential Energy Surface (PES)

And the Basic Force Field  
Chem 4021/8021 Video II.iii

# Fundamental Points About Which to Be Thinking

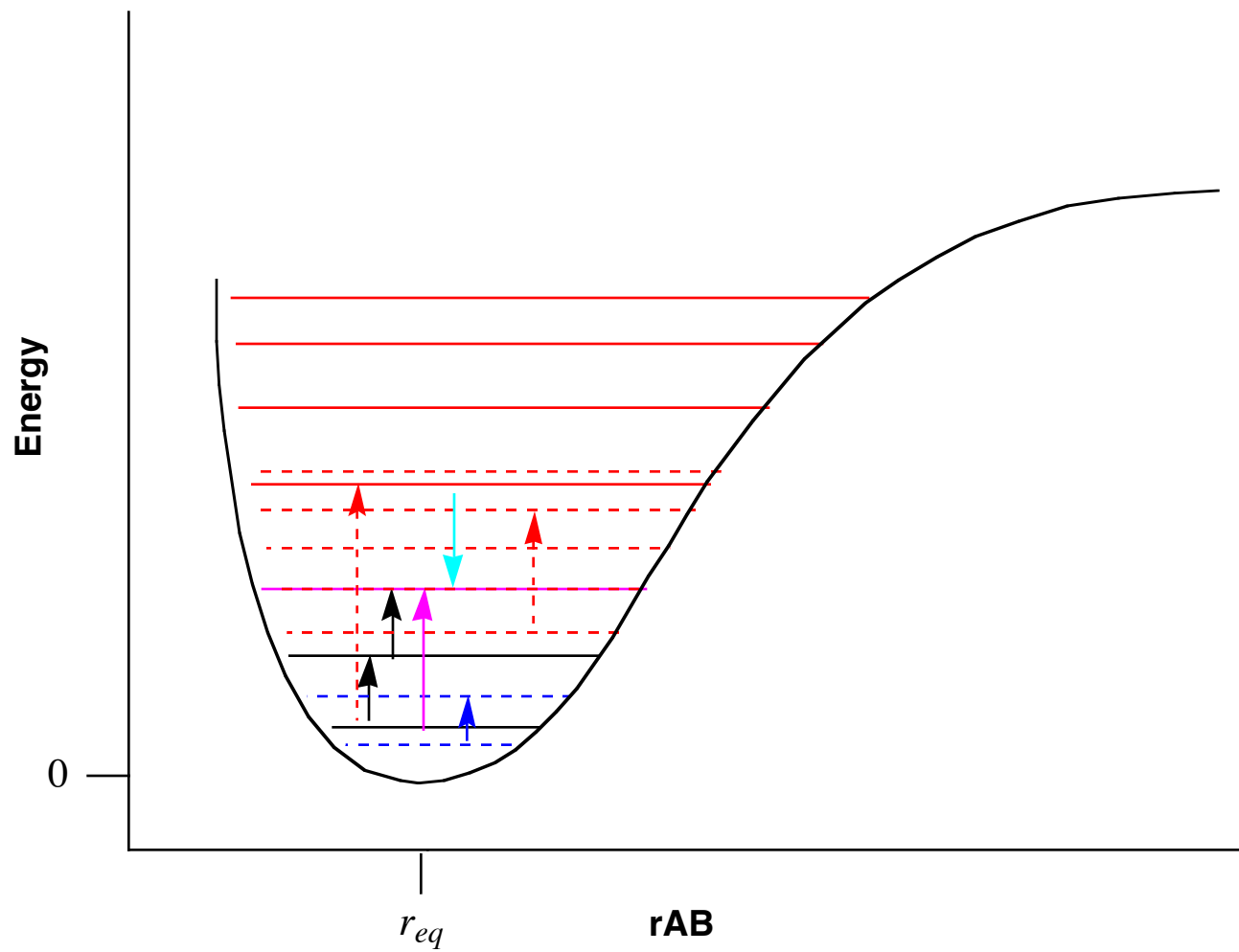
- It's clear the PES is useful, so how can I construct it for an arbitrary system (defined simply by the molecular formula)?
- It seems that for equilibrium and rate constants, I don't actually need to know the whole surface, only the energies of critical points (minima and saddle points)—is there a 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?

## An *Experimental* One-dimensional PES

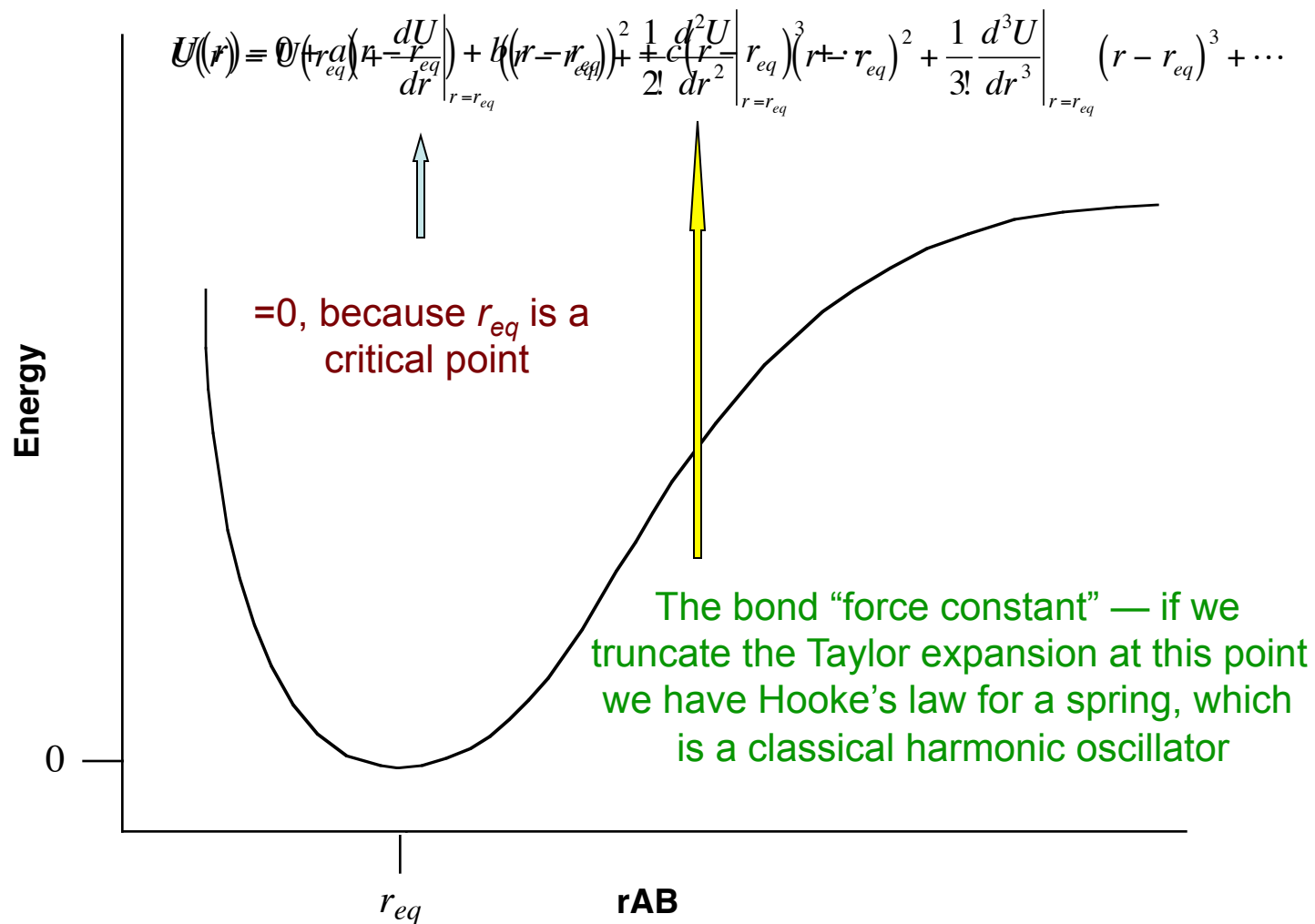


*Quantum mechanics tells us that vibrational energy levels are quantized, and that the energy separations between levels are dictated by the shape of the potential within which vibration takes place (i.e., the 1-D PES). By observing the allowed (above, with rotational information too) and forbidden (not shown) transitions of HCl and its isotopomers (which have different vibrational energy levels by virtue of having different reduced masses) the shape of the PES can be deduced over a large range.*

# In Practice



## How is This Curve Represented Mathematically?



*Simplest idea is a polynomial function expanded about  $r_{eq}$  (by the nature of the spectroscopy, we know most about the curve in the region of  $r_{eq}$ )*

# Thought Provocations

- Could a PES of arbitrarily high dimensionality be constructed as a sum of either independent or coupled analytic equations taking its coordinates as variables?
- What will be the best coordinates to use for that PES?
- How do the chosen coordinates relate to the manner in which the molecular geometry is described?
- What are the best functional forms (e.g., polynomial, Fourier, exponential, etc.) to use to construct various surfaces most efficiently?

# Mature Concepts in Physical Organic Chemistry

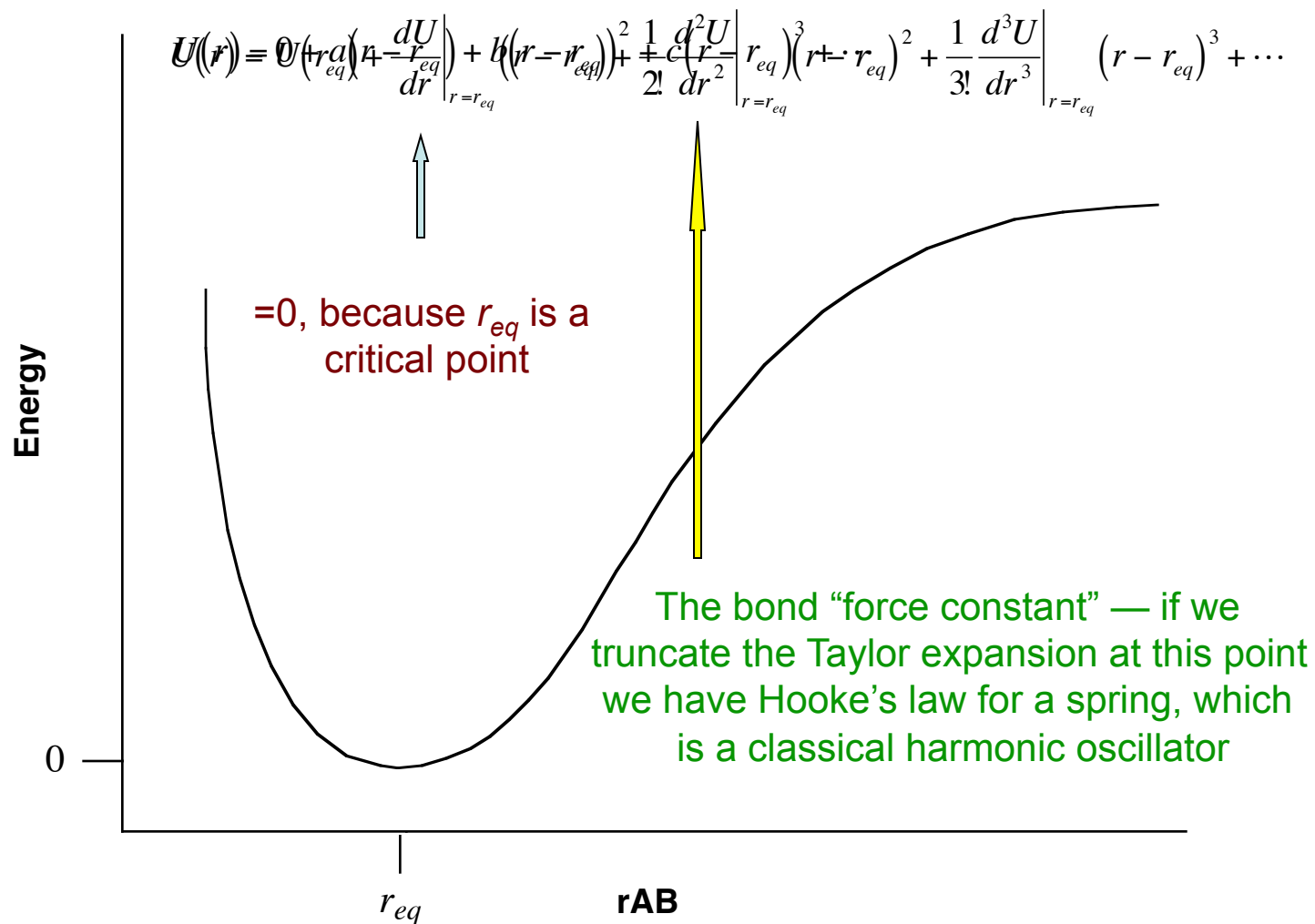
- “Strain” is a phenomenon associated with individual components of a molecular geometry being constrained by the overall geometry not to be able to adopt a common, “transferable”, ideal
- Strain comes in various flavors: bond, angle, and torsional, for example
- Ideal values of bond lengths, angles, and torsions, depend on more than just the atomic number, e.g., there are different “types” of the same atom
- A “force field” is defined by its atom types, its functions for computing strain, and the ideal constants that appear in those functions
- What are the implications of the above for a “complete” PES, e.g., for the PES fully defined for, say,  $C_5H_7NOS$ . How might you qualitatively describe the “character” of a “complete” PES?

# The Potential Energy Surface (PES)

And the Basic Force Field  
Chem 4021/8021 Video II.iv



# How is This Curve Represented Mathematically?

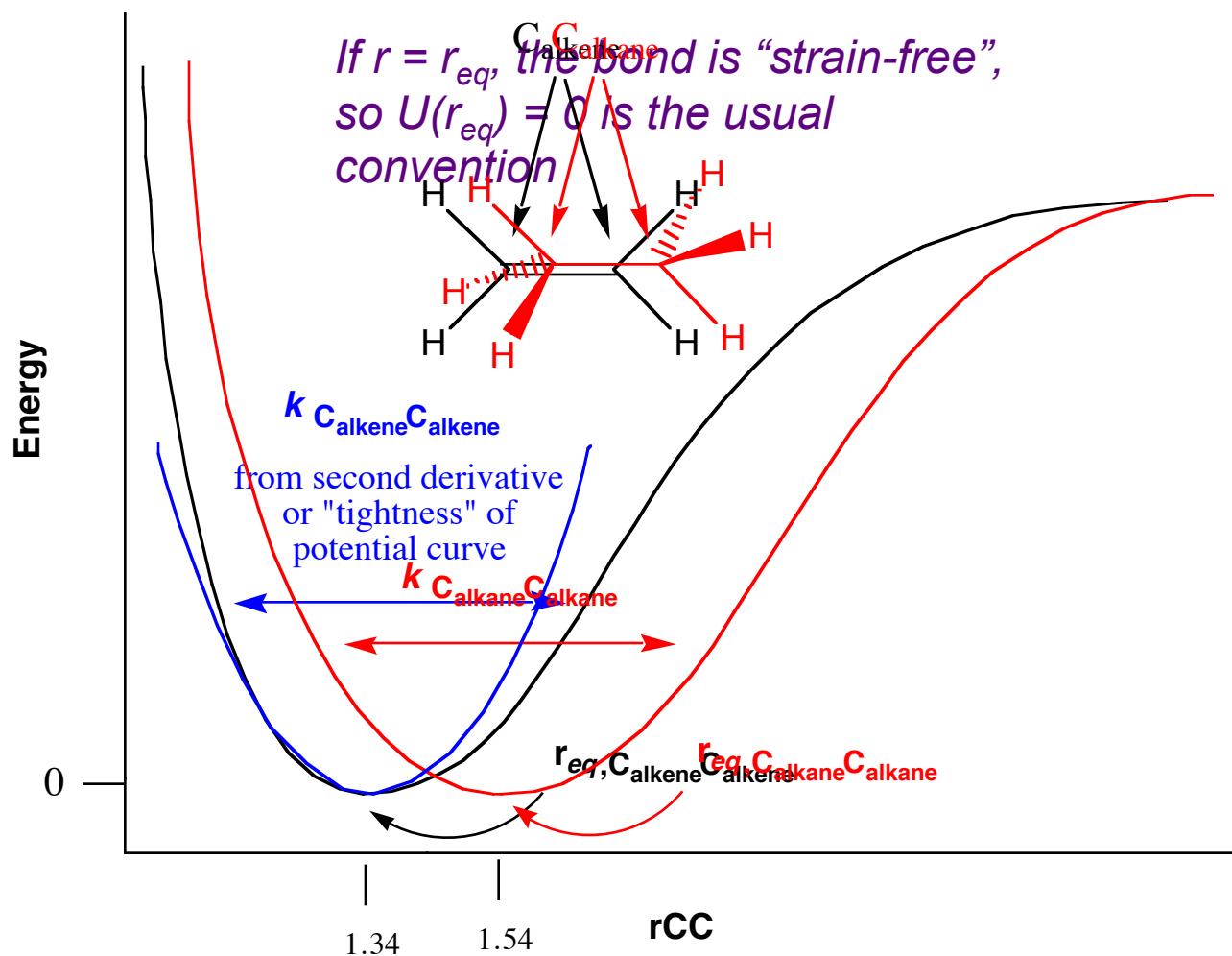


*Simplest idea is a polynomial function expanded about  $r_{eq}$  (by the nature of the spectroscopy, we know most about the curve in the region of  $r_{eq}$ )*

# Harmonic Bond Stretching for Different C Atom Types

$$U(r_{\text{C-alkene}}) = \frac{1}{2} k_{\text{C-alkene}} (r_{\text{C-alkene}} - r_{\text{eq,C-alkene}})^2$$

$$U(r_{\text{C-alkane}}) = \frac{1}{2} k_{\text{C-alkane}} (r_{\text{C-alkane}} - r_{\text{eq,C-alkane}})^2$$

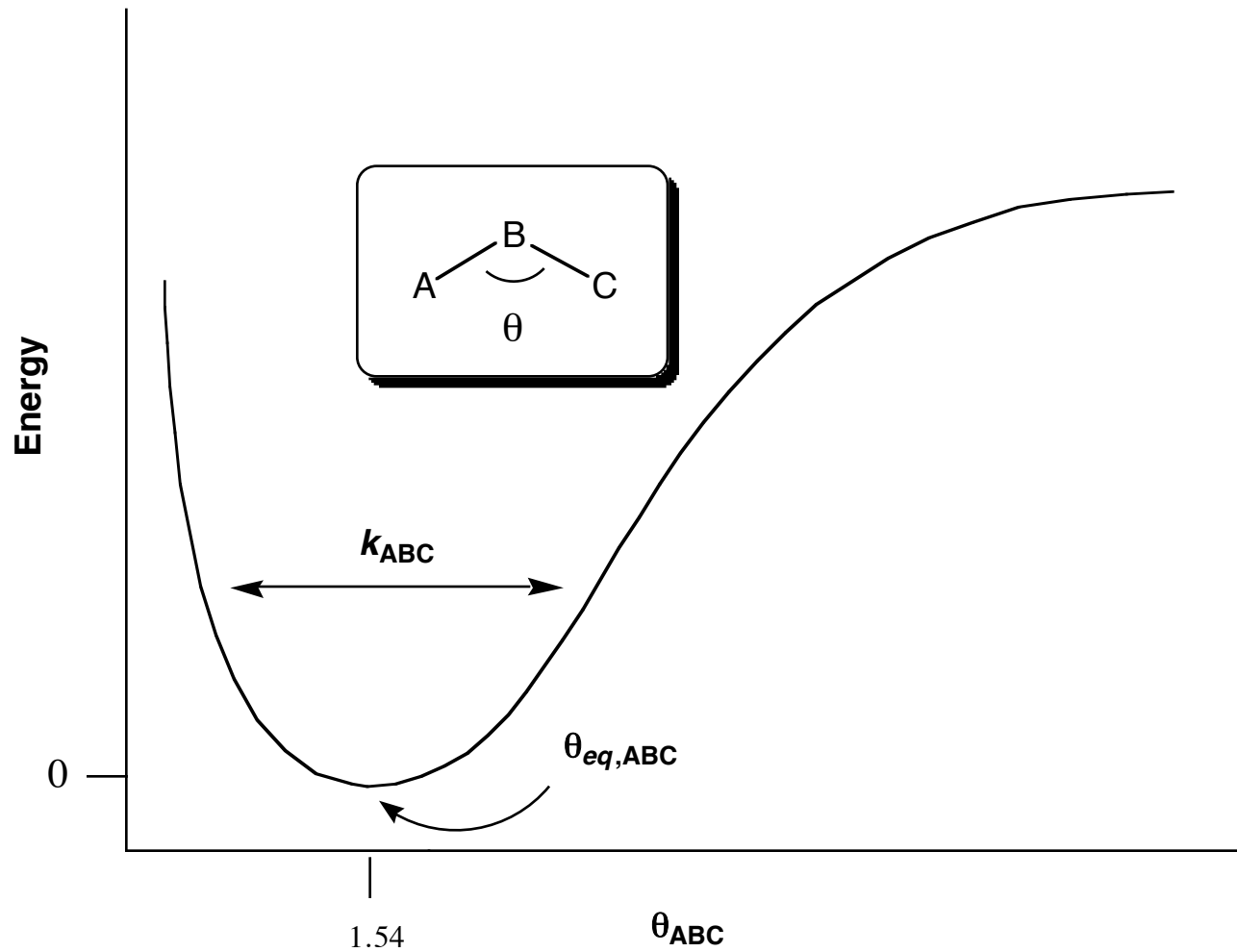


## From Whence the Constants, and How Many?

- The more atom types, the more sensitive the force field can be to chemical reality—organic force fields with 20+ carbon types are not unusual
- Every atom type, though, requires a definition of a force constant,  $k$ , and an equilibrium length,  $r_{eq}$ , between it and, in principle, *every other atom type defined so far*
- Number of bond stretch parameters goes up as  $N^2$  where  $N$  is the number of atom types...
- Assignment of parameters from experimental data (e.g., IR) or from high level QM calculations

# Angle Bending Can Also Be Taken to Be Harmonic

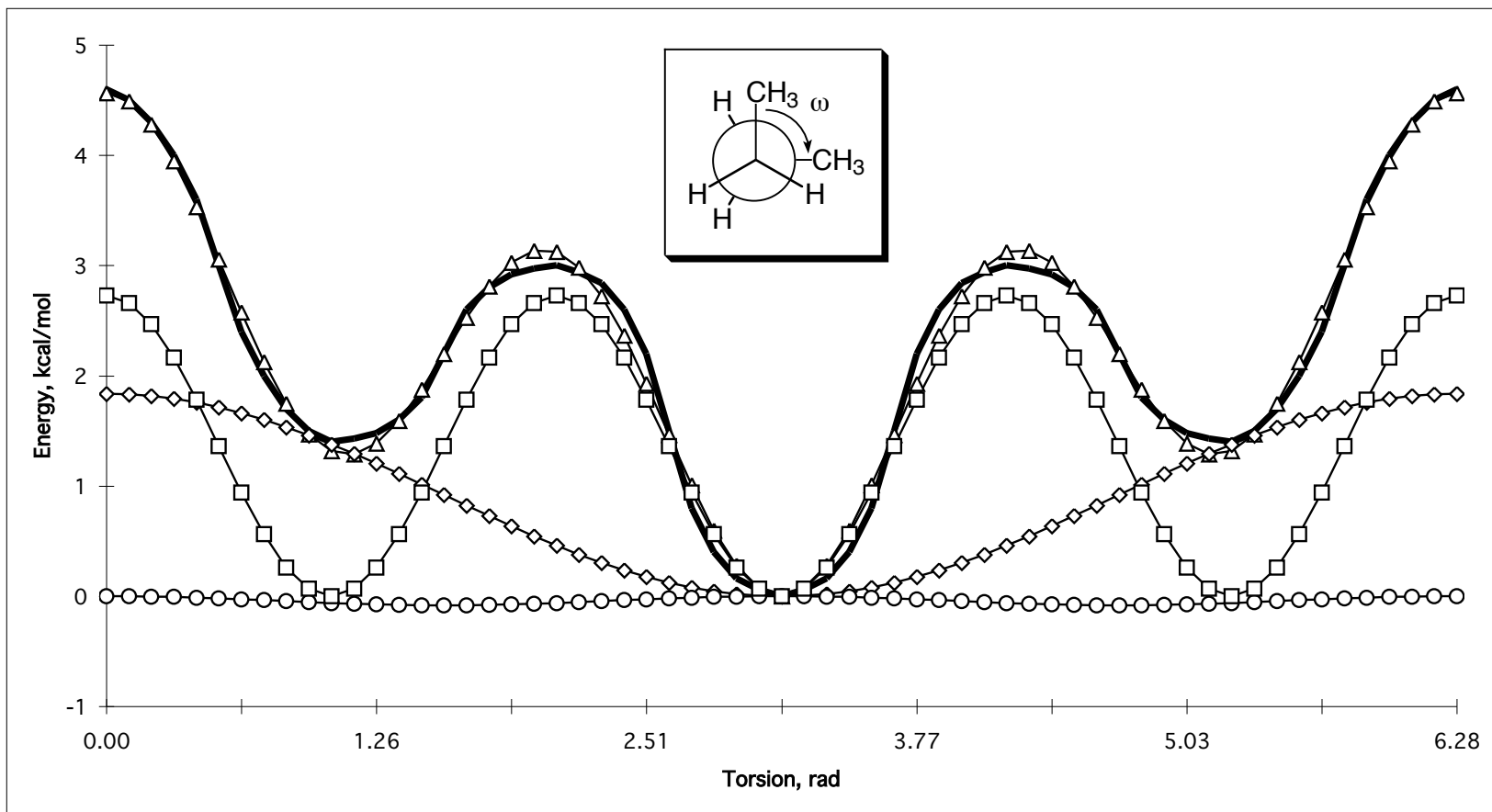
$$U(\theta_{ABC}) = \frac{1}{2} k_{ABC} (\theta_{ABC} - \theta_{ABC,eq})^2$$



*Note that the number of parameters now increases as  $N^3$  where  $N$  is the number of atom types...*

# Torsional Strain is a Periodic Function of Dihedral Angle

$$U(\omega_{ABCD}) = \frac{1}{2} \sum_{\{j\}_{ABCD}} V_{j,ABCD} \left[ 1 + (-1)^{j+1} \cos(j\omega_{ABCD} + \psi_{j,ABCD}) \right]$$



*Note that the number of parameters now increases as  $N^4$  where  $N$  is the number of atom types...*

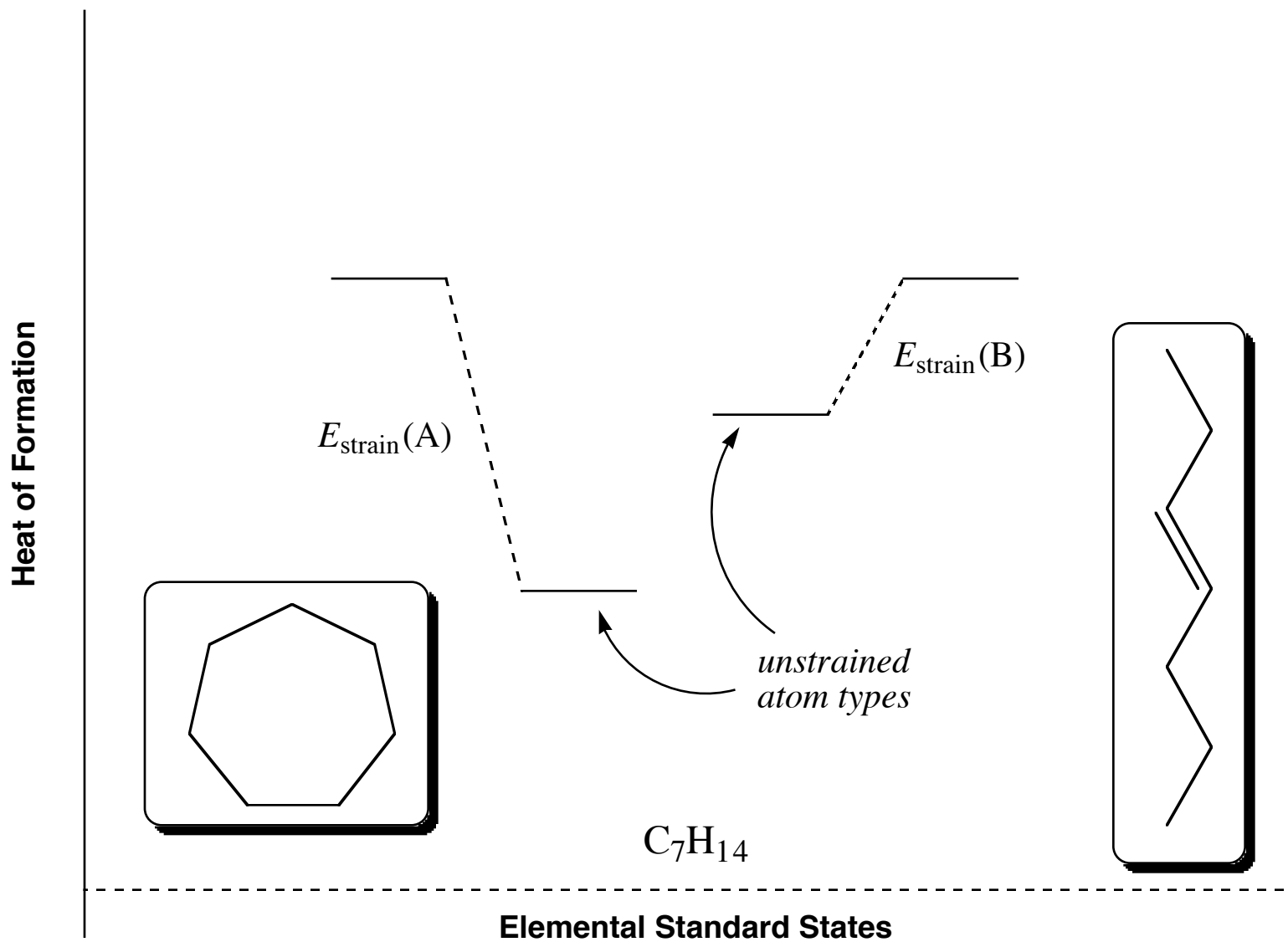
# Steps in Computation of Strain Energy

- Assign an atom type to all atoms
- Assign which atoms are bonded to which (either explicitly or with some algorithm, e.g., within van der Waals contact or closer)
- Look up all force constants, equilibrium values, phase angles, etc., for all bonds, angles, and torsions (decide what to do if any are missing...)
- Compute energy in a small fraction of a second on any decent computer

## Some Intermezzo Caveats

- Minimum for strain energy is zero
- That zero corresponds to a hypothetical molecule in which all of the atoms are in strain-free environments
- In order to compare the relative energies of two isomers directly, they must be composed of the same atom types—otherwise, they have different zeroes of energy
- When they have different atom types, a comparison requires that the enthalpies of formation of the different atom types be available (e.g., from group-equivalent analysis à la Benson)

# Example Comparison of Atomic Typomers

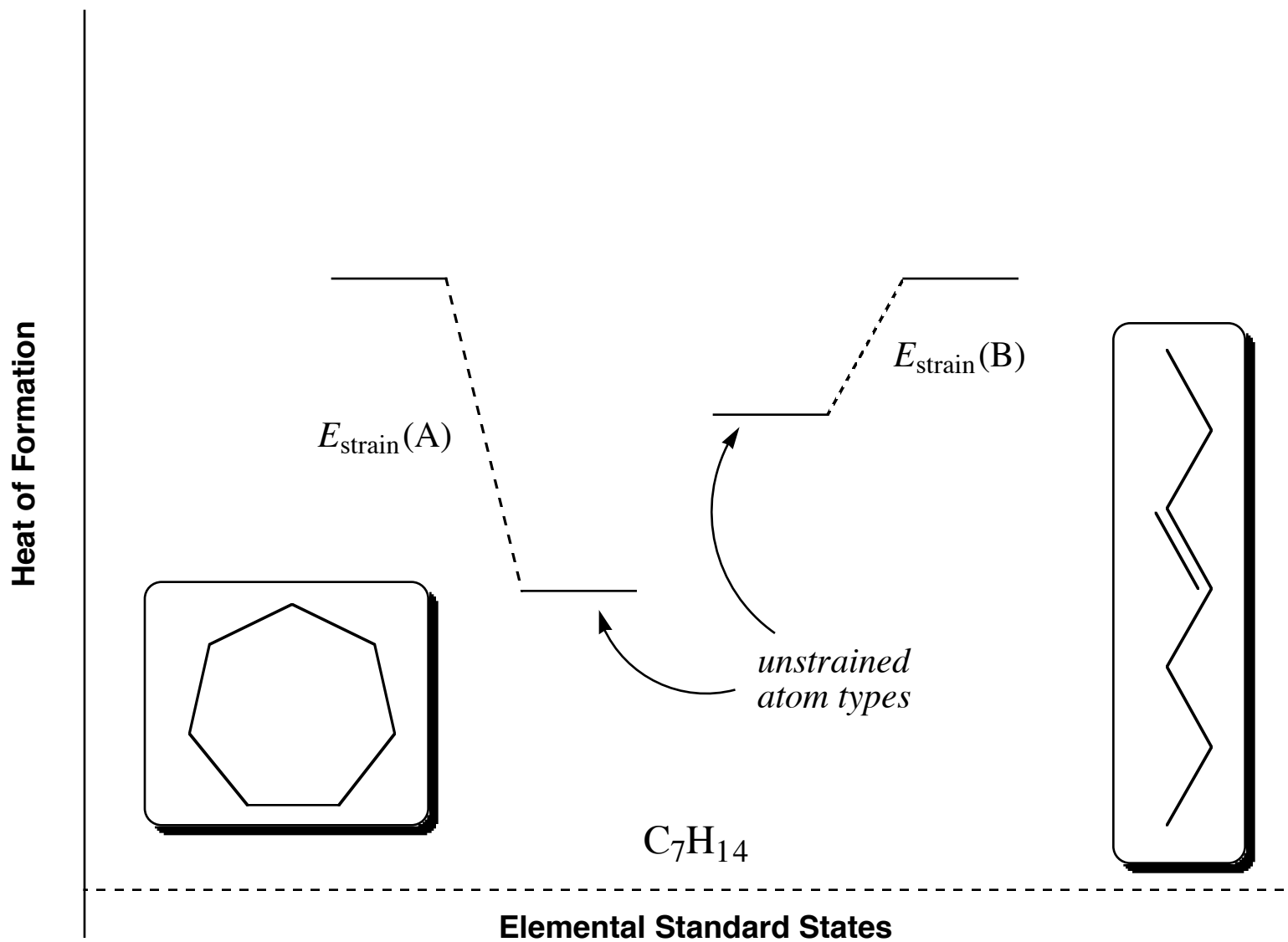




# The Potential Energy Surface (PES)

And the Basic Force Field  
Chem 4021/8021 Video II.v

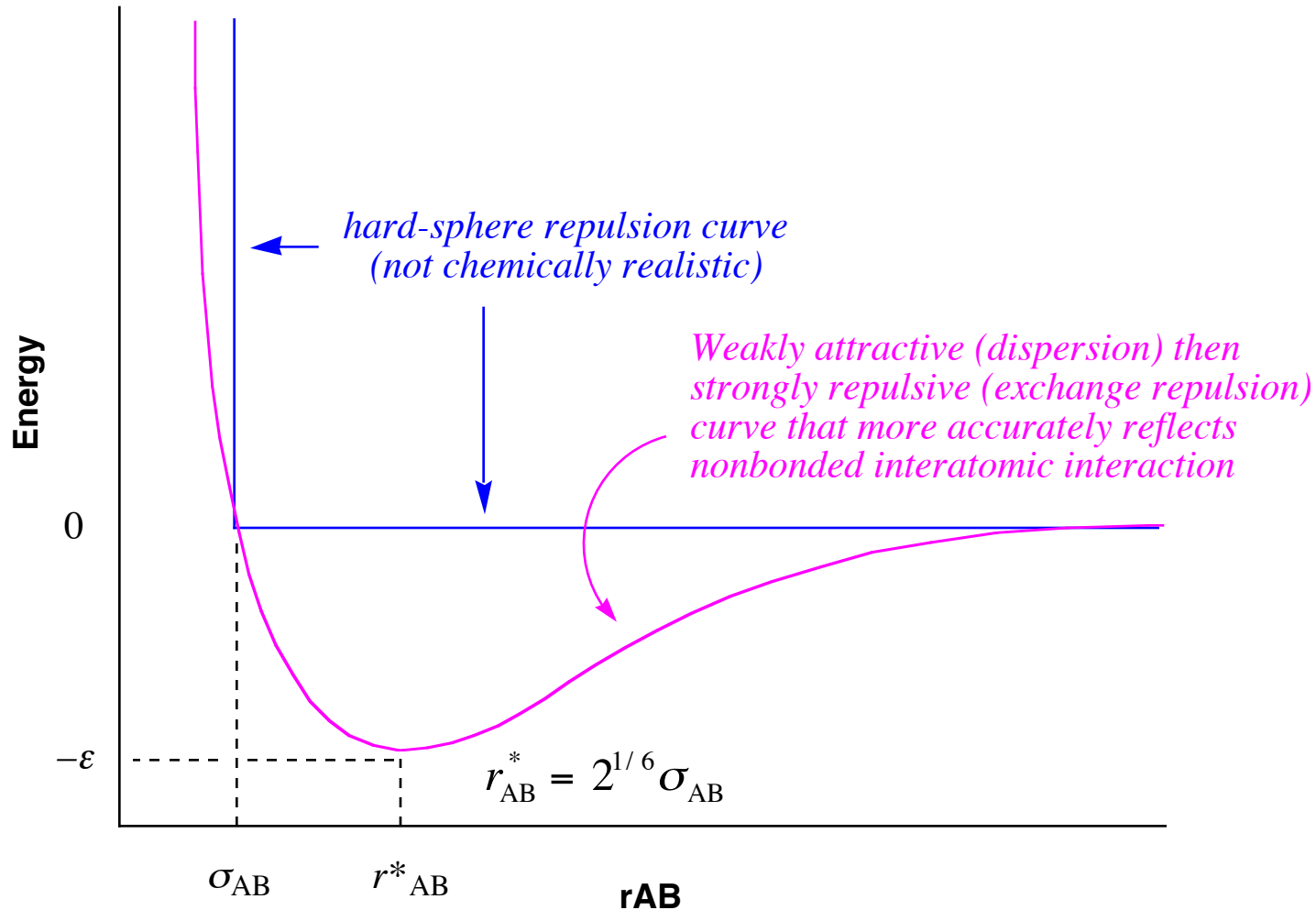
# Example Comparison of Atomic Typomers



# What About Interactions Between Nonbonded Atoms?

## Nonpolar Interaction

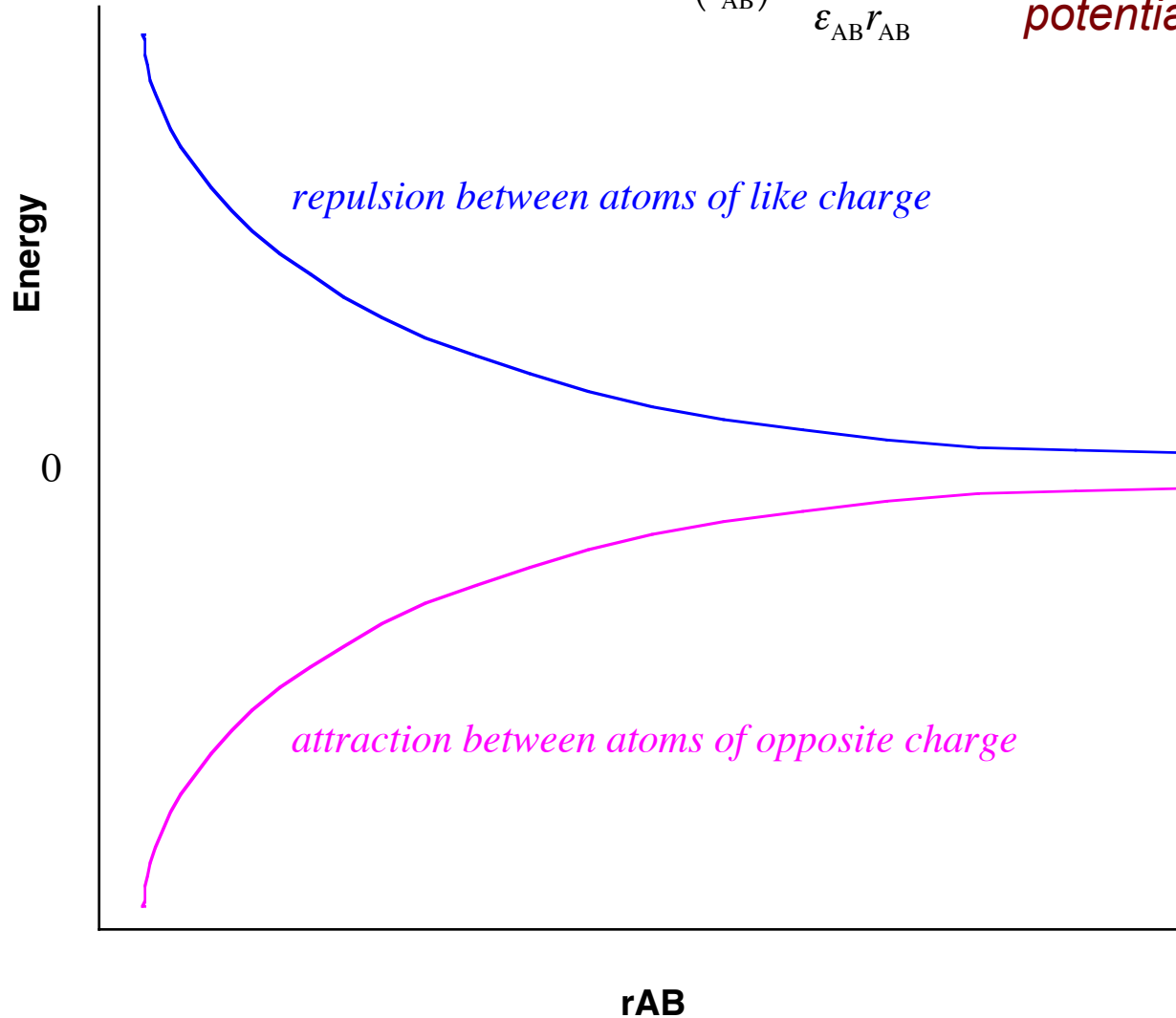
$$U(r_{AB}) = 4\epsilon_{AB} \left[ \left( \frac{\sigma_{AB}}{r_{AB}} \right)^{12} - \left( \frac{\sigma_{AB}}{r_{AB}} \right)^6 \right] \quad \text{Lennard-Jones potential}$$



# What About Interactions Between Nonbonded Atoms? Electrostatic Interactions

$$U(r_{AB}) = \frac{q_A q_B}{\epsilon_{AB} r_{AB}}$$

*Coulomb  
potential*



*repulsion between atoms of like charge*

*attraction between atoms of opposite charge*

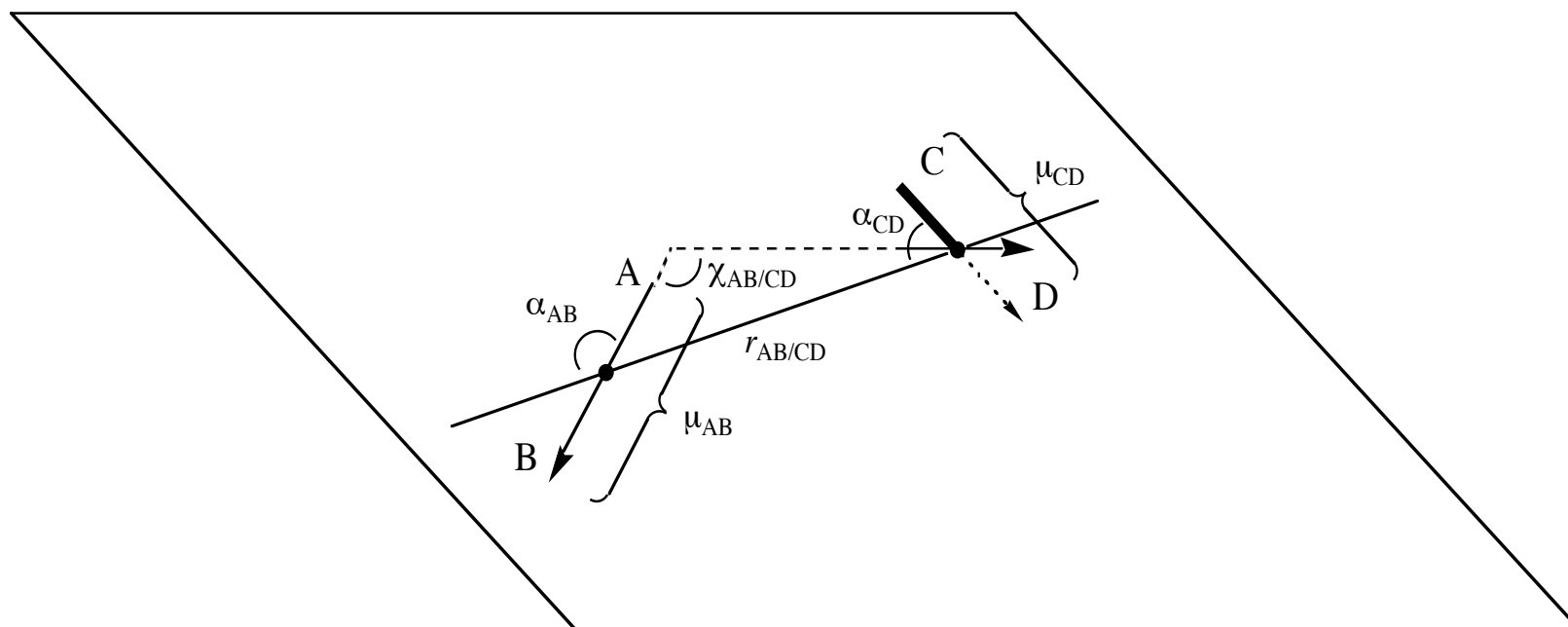
Note that partial charge becomes a new parameter for each atom type

The dielectric constant between two atoms,  $\epsilon_{AB}$ , is an atomic-pair parameter, and is rarely taken to be 1.0; it may be taken to depend on  $r_{AB}$

# Alternative Electrostatic Interaction Formalisms

$$U_{AB/CD} = \frac{\mu_{AB}\mu_{CD}}{\epsilon_{AB/CD}r_{AB/CD}^3} (\cos\chi_{AB/CD} - 3\cos\alpha_{AB}\cos\alpha_{CD})$$

*Dipole-dipole  
potential*

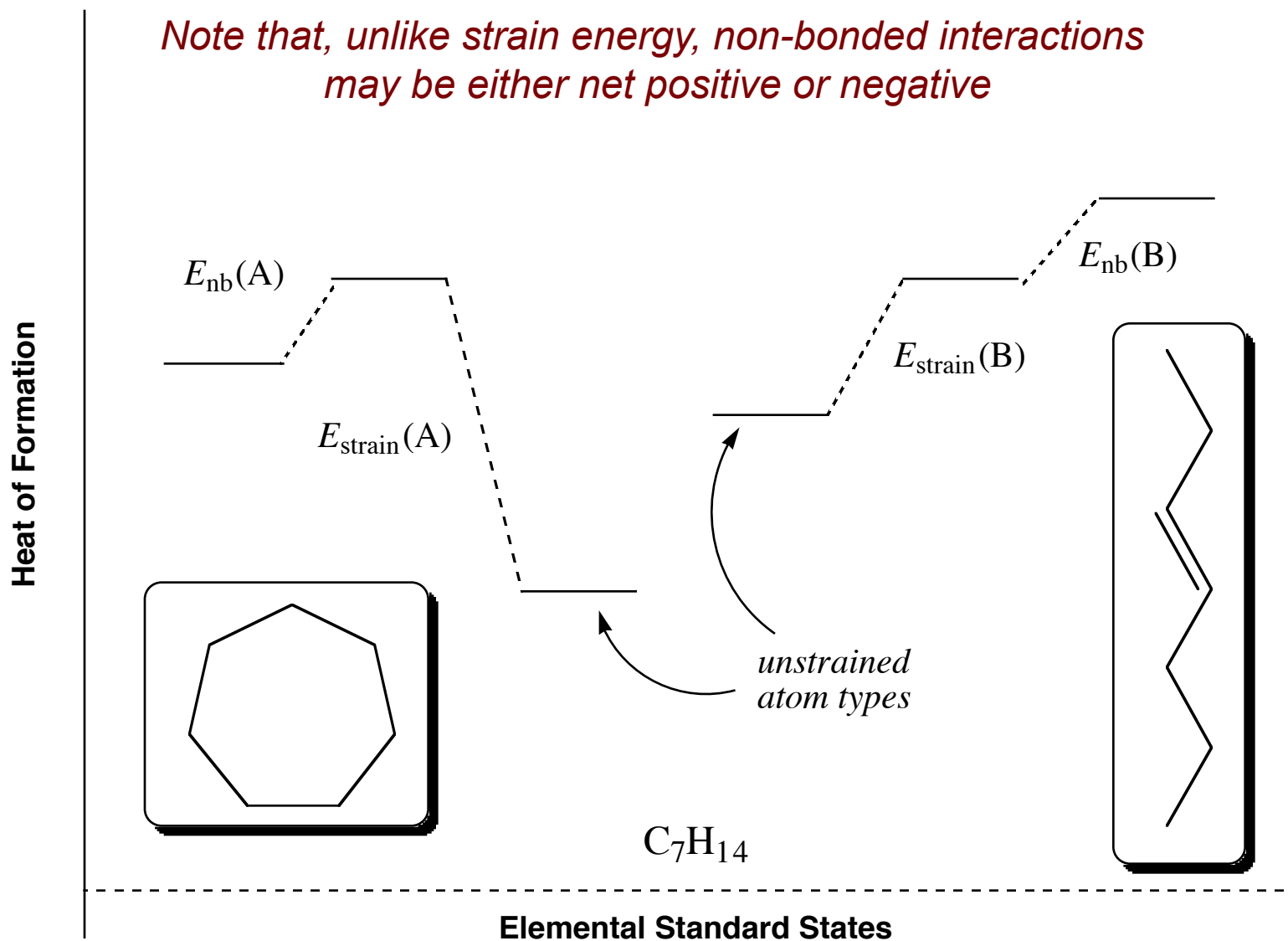


$$U(r_{XH}) = \frac{a'_{XH}}{r_{XH}^{12}} - \frac{b'_{XH}}{r_{XH}^{10}}$$

*Hydrogen-bonding  
potential*

# Force-field Energy vs. Strain Energy

*Note that, unlike strain energy, non-bonded interactions may be either net positive or negative*



# Finding Stationary Points

- Energies of arbitrary structures are less interesting than energies of stationary points
- Stationary points are defined by the first derivative of the energy with respect to motion along any coordinate (the “force” along that coordinate, in physics) being equal to zero
- With simple analytic equations for the energy as a function of coordinates, it is easy to compute the first derivatives for all coordinates
- Many applied mathematical algorithms are available for finding stationary points given energies, first derivatives, and possibly higher derivatives
- This defines “geometry optimization”

# Force-field Validation

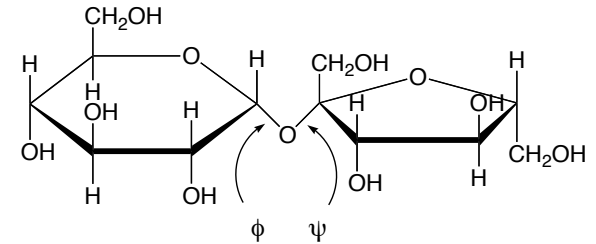
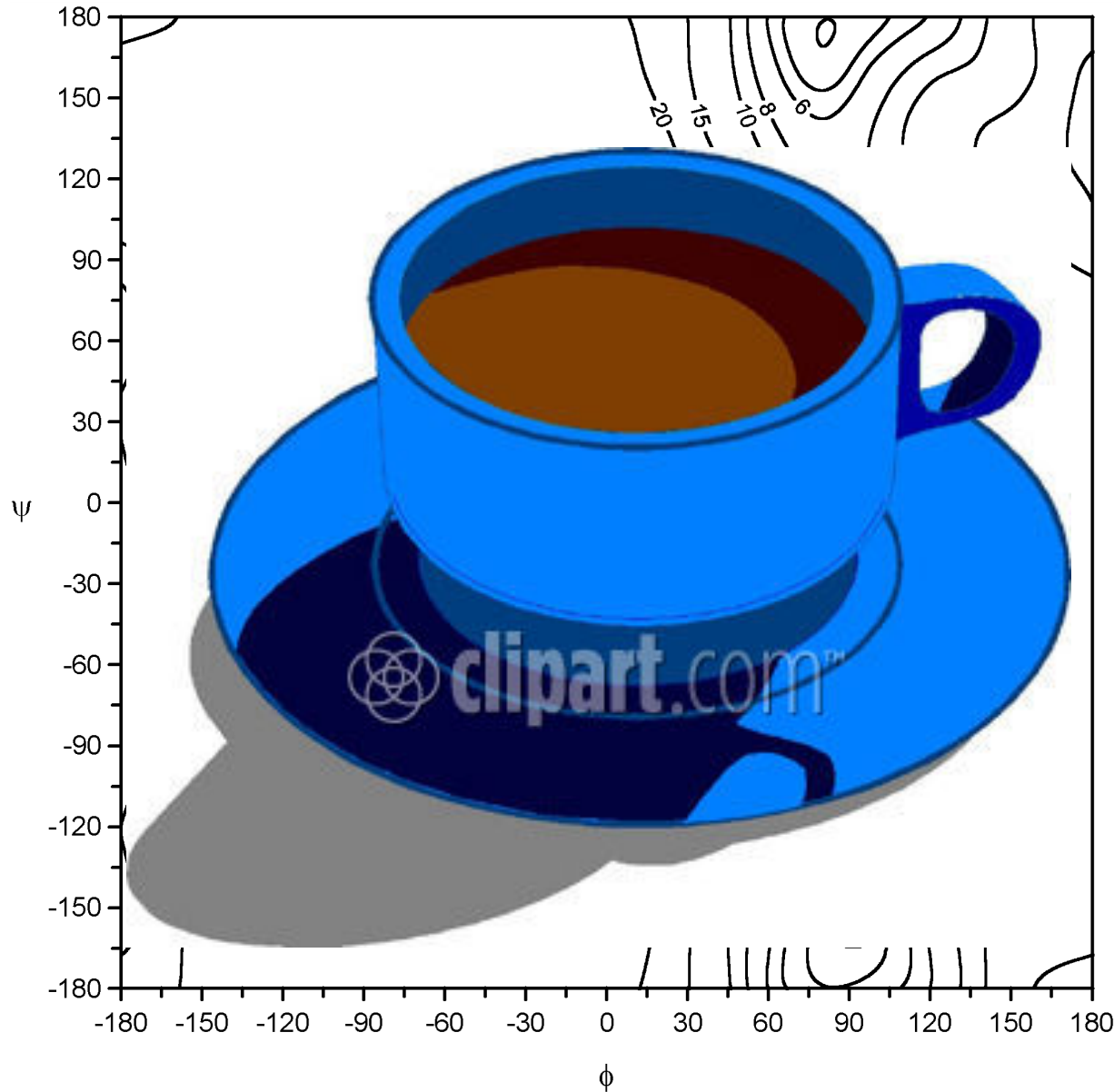
- Assemble a body of experimental data (typically structural and energetic in nature)
- Define an error function that balances what is tolerable for errors in bond lengths vs. isomer energies, for example
- Vary the parameters and functional forms of the force field to minimize the error function
- Lock all the parameters and functional forms into stone, give that set a name (e.g., “MM3”) and give it to the world; try to keep it stable!!!!
- The value of chemical intuition should not be discounted throughout this process



# Final Food for Thought

- Selection of a force field should be made based on how similar one's own molecule is to those used to parameterize the force field
- Within the harmonic approximation, force fields necessarily do better *near* minima than they do *far away from* minima
- Once bonds are defined, *they cannot break* in a harmonic force field, *nor can new ones form*; force fields are bad for reactions, good for structures and energies
- If you start with a bad guess structure, there is no guarantee that the nearest minimum will be a chemically meaningful one
- All of the issues above can be dealt with if they become problematic, and this drives force-field design

# Food for Thought: Sucrose



There are 11 rotatable bonds about which every possible conformation was considered in developing this relaxed PES with MM3 (that's Chemistry formally Quiz  $3^{11}$  energies per point on the substance surface does one)