

# Lecture 15

## Force Fields

Midterm exam review; intramolecular energy models

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*CE 500 – Modeling Potential-Energy Surfaces*

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# Force fields represent the PES using simple empirical functions of nuclear coordinates

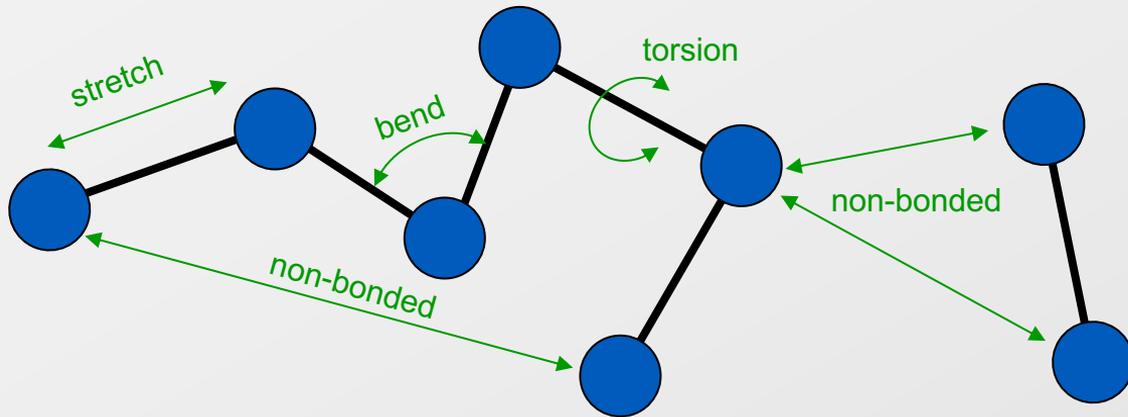
Also called “molecular mechanics”

- Large computational expense of electronic energy limits time and length scales accessible by first-principles methods
- Force fields can compute the energy very quickly, but more approximately
  - Parameterized using first-principles and/or experimental data
    - Many forms and parameterizations have been proposed
  - Bonding information must be specified *a priori*
  - Still, force-field models face limits on system size and length of time
    - Millions of atoms and microseconds of time are range that can be attained
    - Most simulations are much smaller and/or shorter

# A variety of simplifications are used to trade off accuracy, complexity, and speed

- Pairwise-additive energy
- Rigid molecules
  - fast intramolecular motions slow down MD calculations
- Ignore hydrogen atoms
  - united atom representation
- Ignore polarization
  - expensive  $n$ -body effect
- Ignore electrostatics
- Treat whole molecule as one big atom
  - maybe anisotropic
- Model vdW forces via discontinuous potentials
- Ignore all attraction
  - Hard spheres or other shapes
- Model space as a lattice
  - especially useful for polymer molecules

# Molecular-mechanics energy is written as a sum of bonded and nonbonded terms



$$E_{\text{MM}} = \underbrace{E_{\text{str}} + E_{\text{bend}} + E_{\text{tors}} + E_{\text{cross}}}_{\text{bonded}} + \underbrace{E_{\text{vdW}} + E_{\text{el}}}_{\text{non-bonded}}$$

# Transferable potentials depend on functional groups, not entire molecule

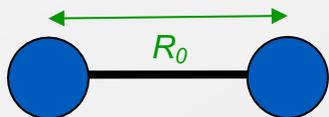
- Atom types are defined
  - Elemental identity (C, O, N, etc.)
  - Type of chemical bonds it has
- Force-field parameters are keyed to atom type
- This allows force fields to be built for arbitrary molecules
  - In contrast, using bespoke parameters for each molecule would make the whole approach unworkable
- Models will vary in how they define atom types and groups

Table 2.1 MM2(91) atom types. (partial list)

Type	Symbol	Description	Type	Symbol	Description
1	C	sp <sup>3</sup> -carbon	28	H	Enol or amide
2	C	sp <sup>2</sup> -carbon, alkene	48	H	Ammonium
3	C	sp <sup>2</sup> -carbon, carbonyl, imine	36	D	Deuterium
4	C	sp-carbon	20	lp	Lone pair
22	C	sp <sup>3</sup> -carbon, cyclopropane	15	S	Sulfide (R <sub>2</sub> S)
29	C·	Radical	16	S <sup>+</sup>	Sulfonium (R <sub>3</sub> S <sup>+</sup> )
30	C <sup>+</sup>	Carbocation	17	S	Sulfoxide (R <sub>2</sub> SO)
38	C	sp <sup>2</sup> -carbon, cyclopropene	18	S	Sulfone (R <sub>2</sub> SO <sub>2</sub> )
50	C	sp <sup>2</sup> -carbon, aromatic	42	S	sp <sup>2</sup> -sulfur, thiophene
56	C	sp <sup>3</sup> -carbon, cyclobutane	11	F	Fluoride

F. Jensen

# Bond stretching is usually modeled using a 2-body harmonic potential



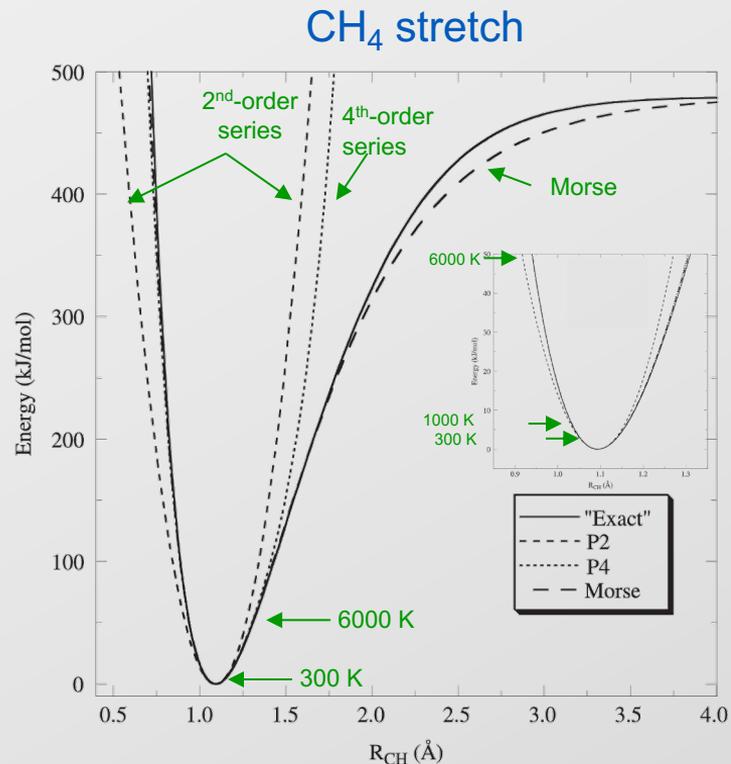
- Taylor series about minimum-energy pair separation

$$E_{\text{str}}(R) = \cancel{E(0)} + \cancel{E'} \times (R - R_0) + \frac{1}{2} E'' \times (R - R_0)^2 + \dots$$
$$\approx k(R - R_0)^2$$

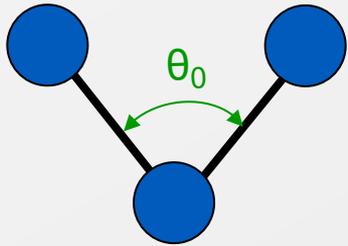
– 2 parameters

- Morse potential allows dissociation

$$E_{\text{Morse}}(R) = D \left( 1 - e^{-\alpha(R-R_0)^2} \right)$$



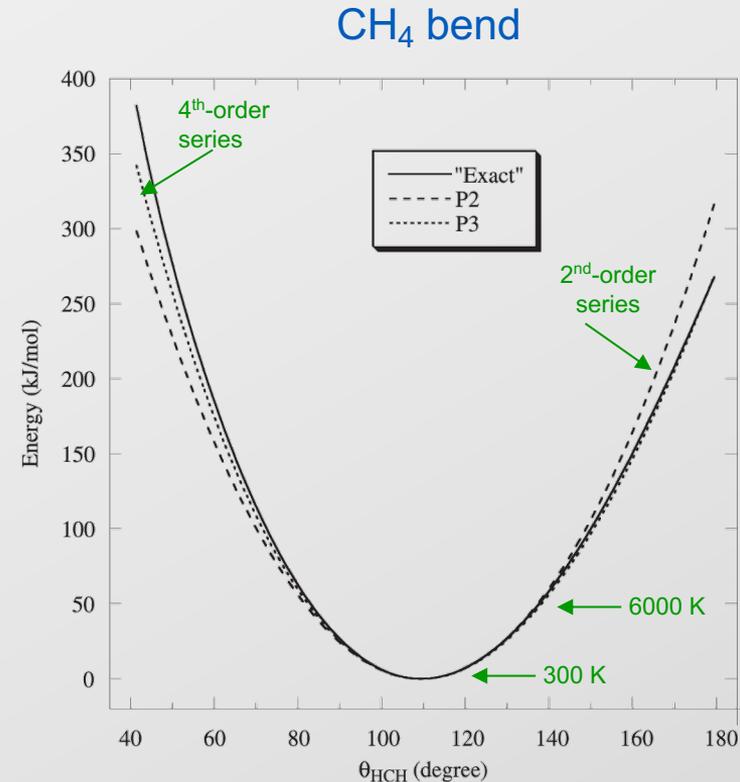
# Bond bending is usually modeled using a 3-body harmonic potential



- Taylor series about minimum-energy angle

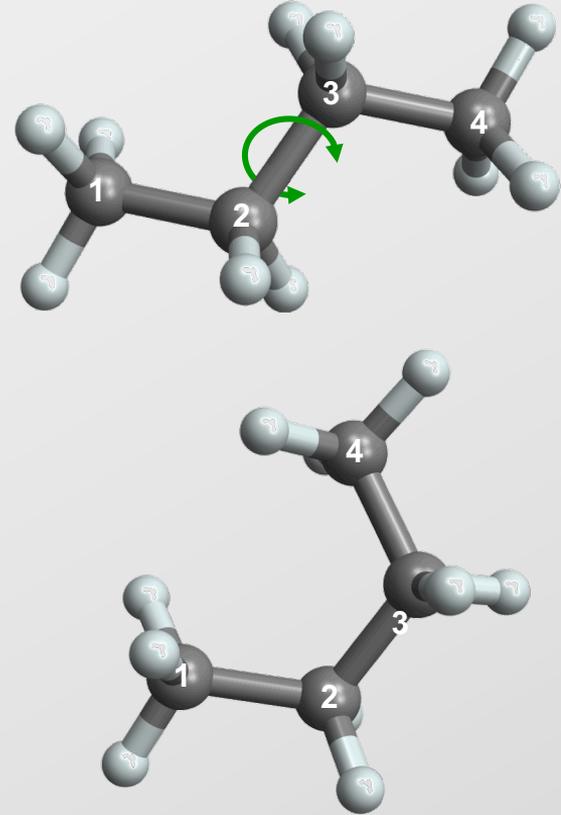
$$E_{\text{bend}}(\theta) = k(\theta - \theta_0)^2$$

- 2 parameters



# The 4-body torsion potential uses a Fourier sum to obey the symmetry of the rotation

- New features
  - Rotational barrier from both non-bonded and torsional energy
  - Torsional energy is periodic
  - Rotation energy much lower than stretch/bend
- Fourier form  $E_{\text{tors}}(\omega) = \sum_{n=1} V_n \cos(n\omega)$ 
  - Select  $n$  consistent with symmetry
    - E.g., only  $n = 3, (6, 9, \dots)$  for ethane
    - Typically only  $n = 1, 2,$  and/or  $3$  are used

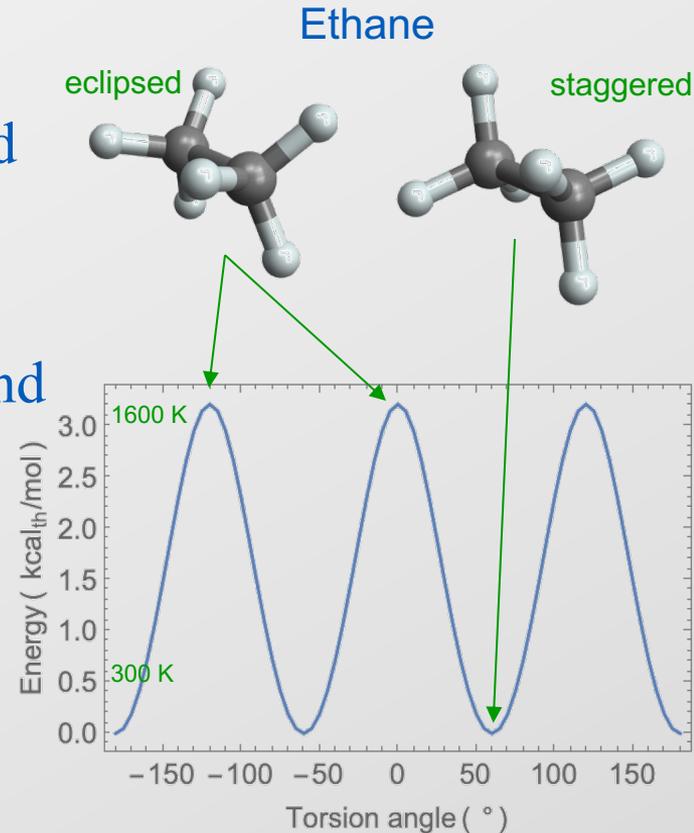


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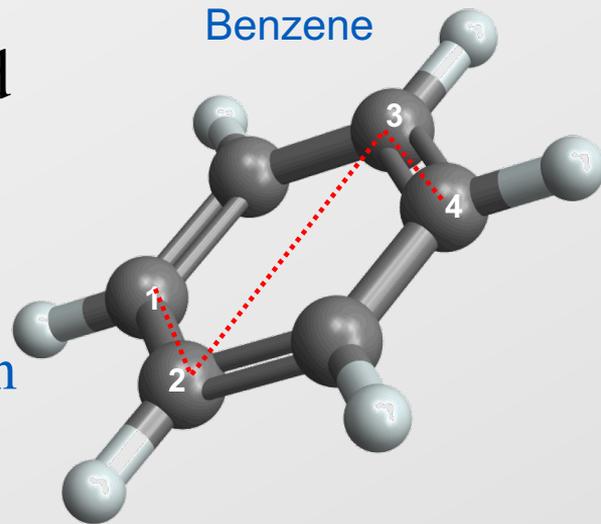
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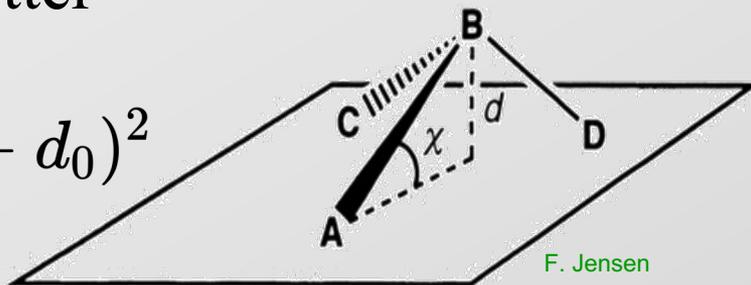


# Out-of-plane 4-atom bending energy can be treated in several ways

- Keeps atoms in or out of plane, as needed
- Improper torsion
  - Defines an artificial torsion angle
  - Not most effective, but popular because it can re-use torsion potential for this purpose
- Geometry-oriented potentials are better

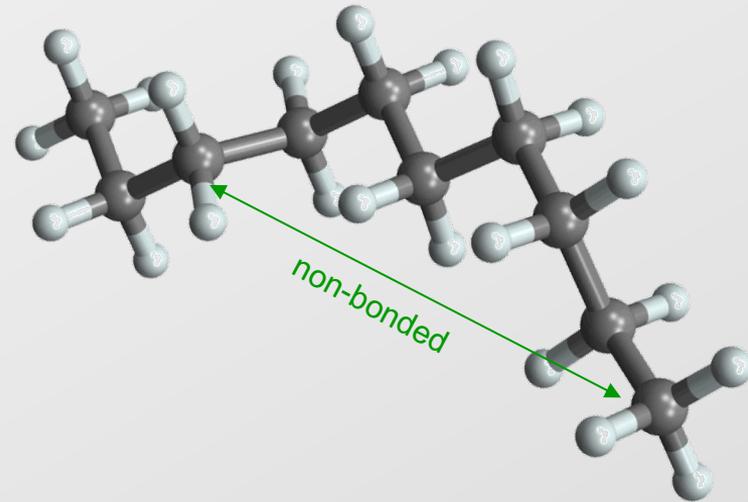


$$E_{\text{oop}} = k(\chi - \chi_0)^2 \quad \text{or} \quad E_{\text{oop}} = k(d - d_0)^2$$



# Non-bonded interactions apply to atoms that are in same molecule but not near each other

- These have the same general forms as for atoms on different molecules
- Most force fields apply these interactions to atoms separated by three bonds or more
  - Sometimes 1,4 interactions are scaled down by some amount (0.5 – 1.0)
  - Thus, in A–B–C–D sequence, A and D will interact with both torsion and attenuated non-bonded interactions



# Suggested Reading/Viewing

- Frank Jensen, *Introduction to Computational Chemistry*, 3rd ed., Wiley (2017). Chapter 2.

Available online via UB library:

- [https://search.lib.buffalo.edu/permalink/01SUNY\\_BUF/9qhqtp/alma9939265811804803](https://search.lib.buffalo.edu/permalink/01SUNY_BUF/9qhqtp/alma9939265811804803)