



Lecture 3

CH-4114

Molecular Simulation

"Everything that living things do can be understood in terms of the jigglings and wiggles of atoms."

- Richard P. Feynman

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Different Potential Energy Forms

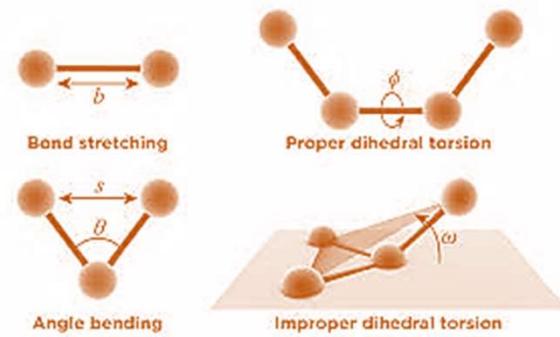
$$V(r^N) = \sum_{coulomb} \frac{1}{4\pi\epsilon_0} \frac{q_A q_B}{r_{AB}}$$



$$V(r^N) = \sum_{vdW} 4\epsilon_{AB} \left[\left(\frac{\sigma_{AB}}{r_{AB}} \right)^{12} - \left(\frac{\sigma_{AB}}{r_{AB}} \right)^6 \right]$$



$$\begin{aligned} V(r^N) &= \sum_{bond} V_{AB} + \sum_{angle} V_{ABC} + \sum_{dihedral} V_{ABCD} + \sum_{non-bonded} V_{AB} \\ &= \sum_{bond} \frac{1}{2} K_{AB} (r_{AB} - r_{AB}^{eq})^2 + \sum_{angle} \frac{1}{2} K_{ABC} (\theta_{ABC} - \theta_{ABC}^{eq})^2 \\ &\quad + \sum_{improper} \frac{1}{2} K_{ABCD} (\phi - \phi_0)^2 + \sum_{coulomb} \frac{1}{4\pi\epsilon_0} \frac{q_A q_B}{r_{AB}} + \sum_{vdW} 4\epsilon_{AB} \left[\left(\frac{\sigma_{AB}}{r_{AB}} \right)^{12} - \left(\frac{\sigma_{AB}}{r_{AB}} \right)^6 \right] \end{aligned}$$



Bond Stretching

Morse Potential

$$V_{\text{bond}} = D_e \left[1 - e^{-a(d-d_0)} \right]^2$$

D_e = depth of potential energy minimum

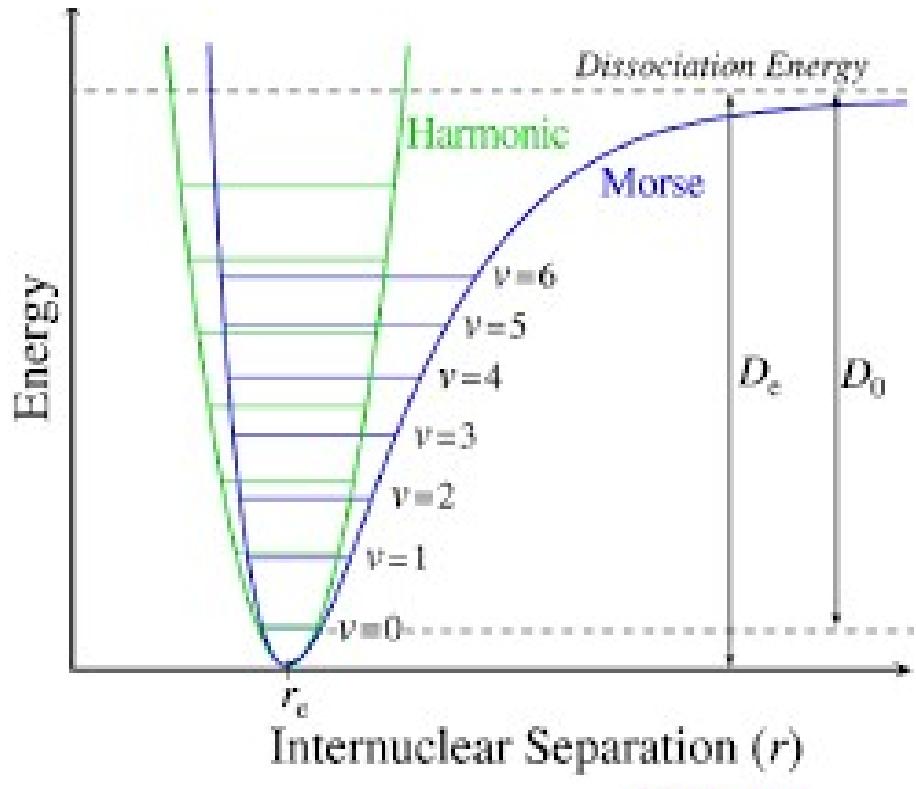
a = width of potential well

d_0 = equilibrium bond length

Hooke's law

$$V_{\text{bond}} = \frac{k}{2} (d - d_0)^2$$

- harmonic approximation
- non dissociative
- reasonable for small displacements



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Bond Stretching Parameters

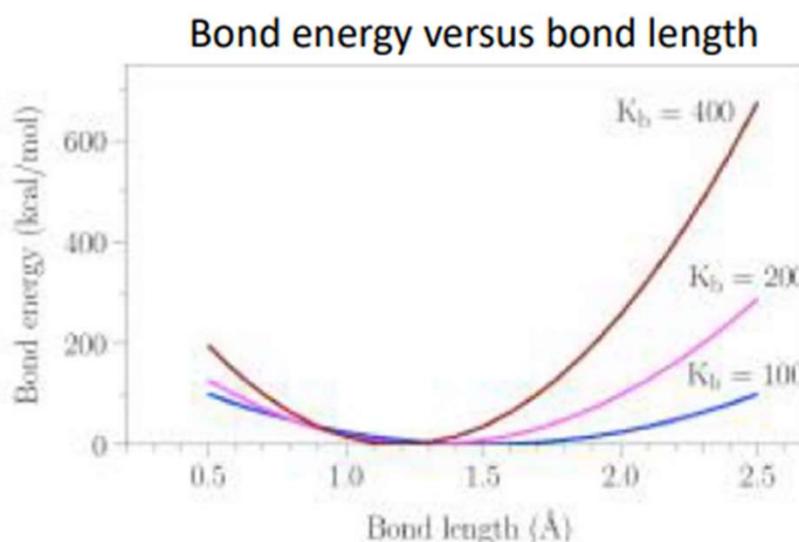
$$V_{\text{bond}} = \frac{k}{2} (d - d_0)^2$$

- k obtained from vibrational spectra
- d_0 obtained from X-ray crystallography
- Hard degree of freedom
- Often constrained in MD

$$k (\text{C=O}) = 570 \text{ kcal/mol/ \AA}^2$$

If $\delta d = .2 \text{ \AA}$ for carbonyl
 $V_{\text{bond}} = 11.4 \text{ kcal/mol}$

Chemical type	K_{bond}	d_0
C-C	100 kcal/mole/\AA ²	1.5 \AA
C=C	200 kcal/mole/\AA ²	1.3 \AA
C=C	400 kcal/mole/\AA ²	1.2 \AA



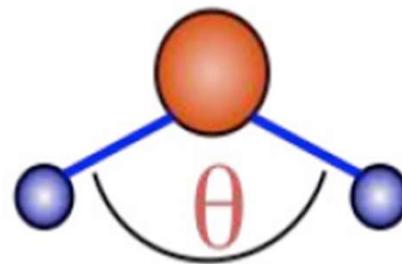
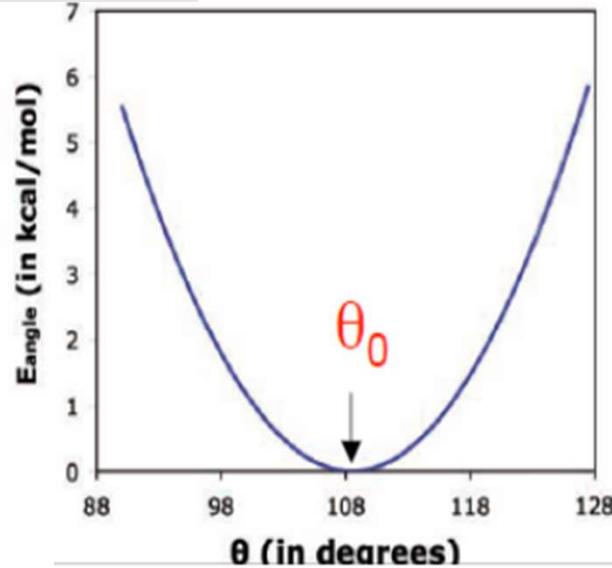
Angle Bending

- Hooke's Law in angle coordinates

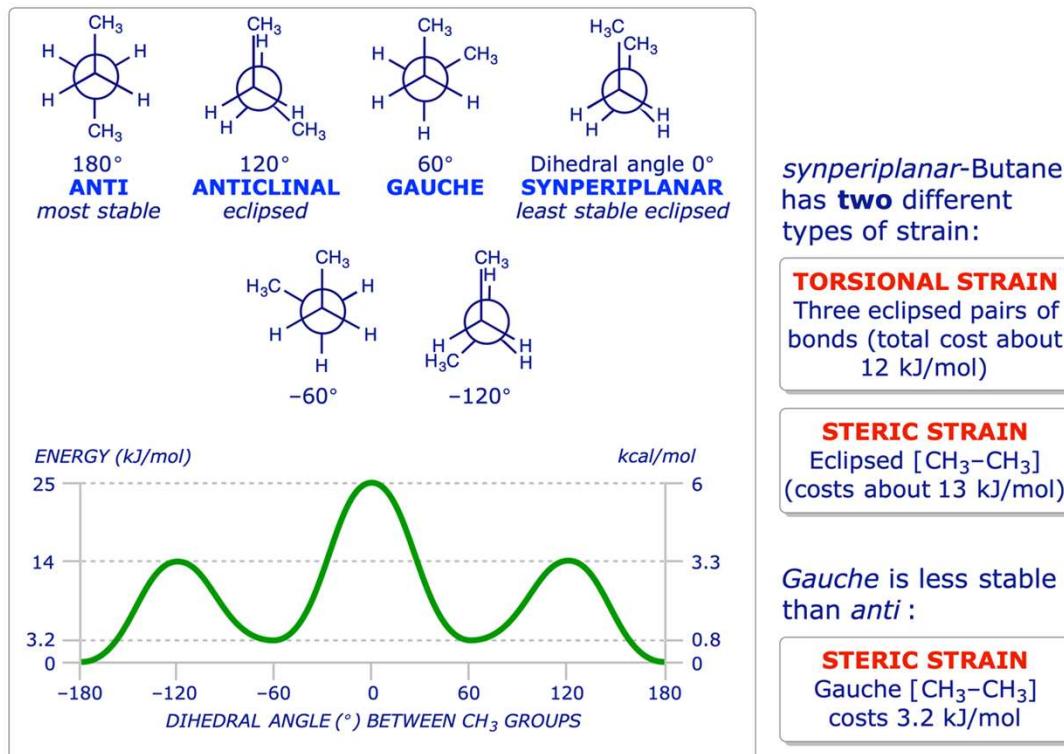
$$V_{\text{angle}} = \frac{k_\theta}{2} (\theta - \theta_0)^2$$

➤ Equilibrium Angle θ_0 usually obtained from:
(i) X-ray crystallography (solid-state structures),
(ii) Gas-phase electron diffraction,
(iii) Microwave spectroscopy (high precision for small molecules).

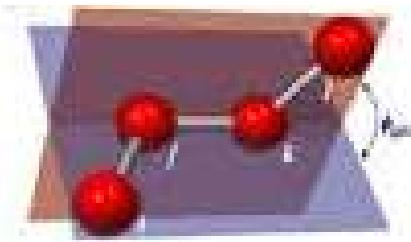
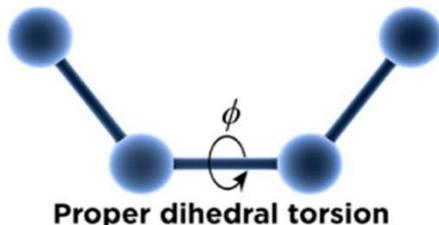
➤ Force Constant k_θ is obtained from vibrational Spectroscopy (IR/Raman):
(i) The vibrational frequencies of bending modes (i.e., changes in bond angles) are related to $k\theta$.
(ii) Normal mode analysis on experimental spectra helps extract bending force constants.
(iii) Quantum Chemistry (Ab Initio Calculations)



Stereochemistry & Understanding of Dihedral/Torsion Potential

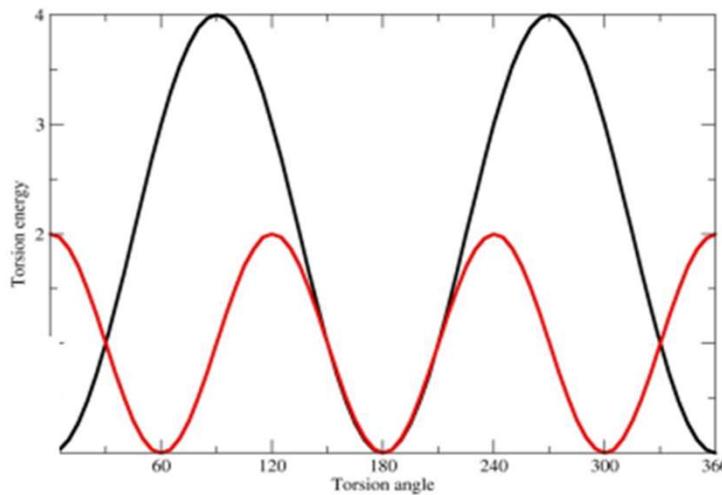


Torsion Angle



Black: $V_n=4; n=2; \gamma=180$

Red: $V_n=2; n=3; \gamma=0$



Fourier expansion

$$V_{\text{torsion}} = \sum \frac{V_n}{2} [1 + \cos(n\phi - \gamma_n)]$$

ϕ : Dihedral (torsion) angle,

V_n : Amplitude (barrier height) of the n th term,

n : Periodicity (how many times the potential repeats in 360°),

γ_n : Phase offset (usually 0° or 180° , depending on convention).

Torsional potentials are periodic functions of the angle ϕ (e.g., every 120° , 180°).

Different molecules have different rotational barriers depending on the hybridization and steric of atoms involved.

The cosine terms model barrier heights and periodicity of rotation about a bond.

Torsion Angle

Revive your programming skill:

Homework:

Given the torsion parameters $n_list = [1, 2, 3]$, $Vn_list = [0.20, 0.50, 1.20]$, and $gamma_list = [180^\circ, 0^\circ, 0^\circ]$, can you write a Python script to compute and plot the Fourier torsion potential $V(\phi)$ over the range -180° to $+180^\circ$?

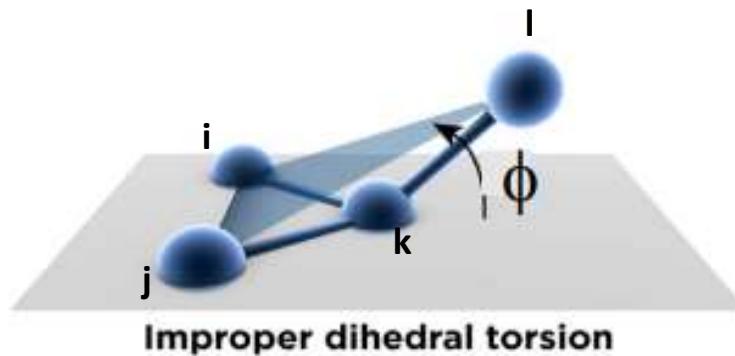
- Describe out of plane motion
- This is often important to maintain planar structure.

Examples:

Peptide bond

Benzene

$$V_{\text{improper}} = \sum \frac{k_{ijkl}}{2} (\phi_{ijkl} - \phi_0)^2$$



Summary on potential accounting for relevant degrees of simple molecules

