

# Lecture 3

## CH-4114

### Molecular Simulation

**"Everything that living things do can be understood in terms of the jiggings and wiggings of atoms."**

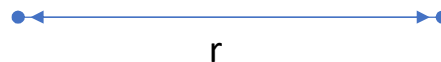
**- Richard P. Feynman**

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## Different Potential Energy Forms

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



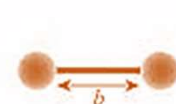
$$V(r^N) = \sum_{\text{vdW}} 4\epsilon_{AB} \left[ \left( \frac{\sigma_{AB}}{r_{AB}} \right)^{12} - \left( \frac{\sigma_{AB}}{r_{AB}} \right)^6 \right]$$



$$V(r^N) = \sum_{\text{bond}} V_{AB} + \sum_{\text{angle}} V_{ABC} + \sum_{\text{dihedral}} V_{ABCD} + \sum_{\text{non-bonded}} V_{AB}$$

$$= \sum_{\text{bond}} \frac{1}{2} K_{AB} (r_{AB} - r_{AB}^{eq})^2 + \sum_{\text{angle}} \frac{1}{2} K_{ABC} (\theta_{ABC} - \theta_{ABC}^{eq})^2$$

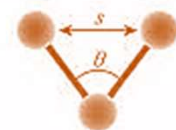
$$+ \sum_{\text{improper}} \frac{1}{2} K_{ABCD} (\phi - \phi_0)^2 + \sum_{\text{coulomb}} \frac{1}{4\pi\epsilon_0} \frac{q_A q_B}{r_{AB}} + \sum_{\text{vdW}} 4\epsilon_{AB} \left[ \left( \frac{\sigma_{AB}}{r_{AB}} \right)^{12} - \left( \frac{\sigma_{AB}}{r_{AB}} \right)^6 \right]$$



Bond stretching



Proper dihedral torsion



Angle bending



Improper dihedral torsion

# 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

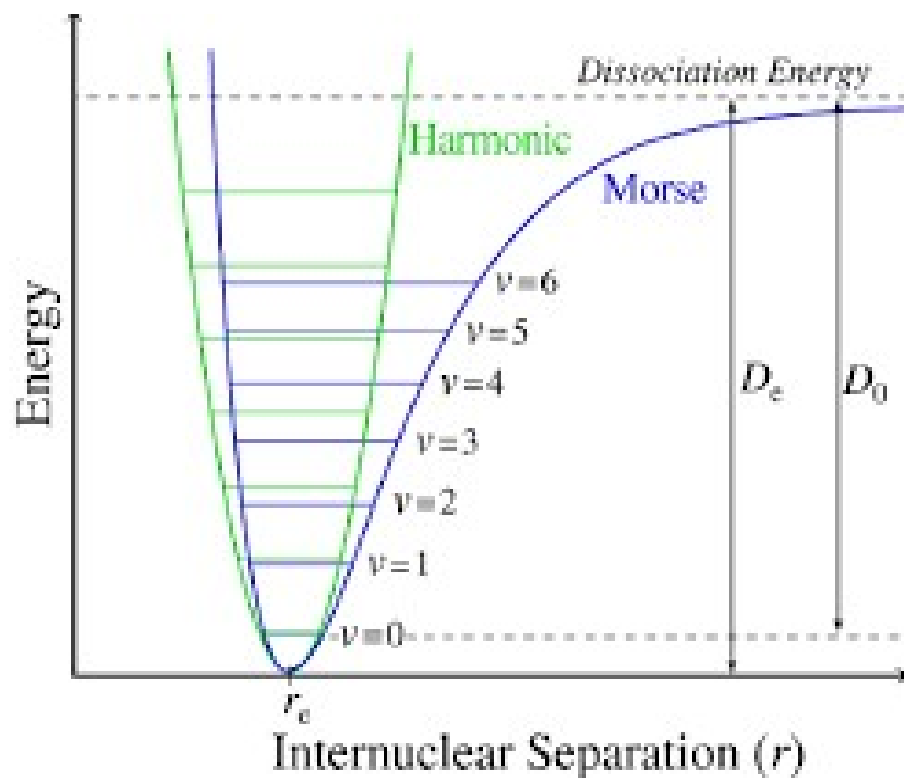
$a$  = width of potential well

$d_0$  = 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

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

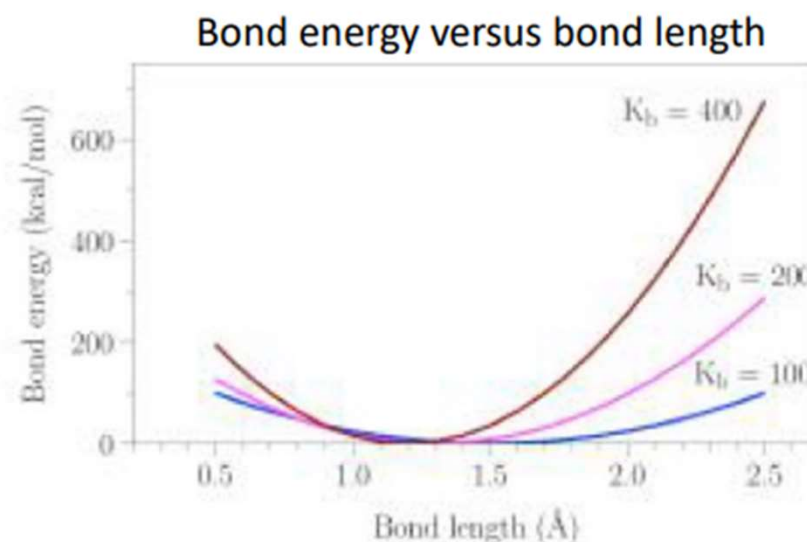
- $k$  obtained from vibrational spectra
- $d_0$  obtained from X-ray crystallography
- Hard degree of freedom
- Often constrained in MD

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

If  $\delta d = .2 \text{ Å}$  for carbonyl

$$V_{\text{bond}} = 11.4 \text{ kcal/mol}$$

Chemical type	$K_{\text{bond}}$	$d_0$
C-C	100 kcal/mole/Å <sup>2</sup>	1.5 Å
C=C	200 kcal/mole/Å <sup>2</sup>	1.3 Å
C≡C	400 kcal/mole/Å <sup>2</sup>	1.2 Å

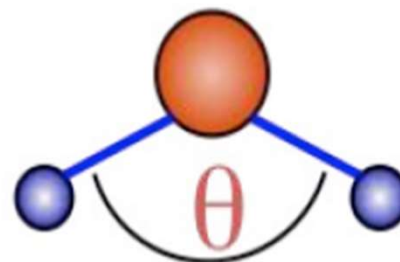
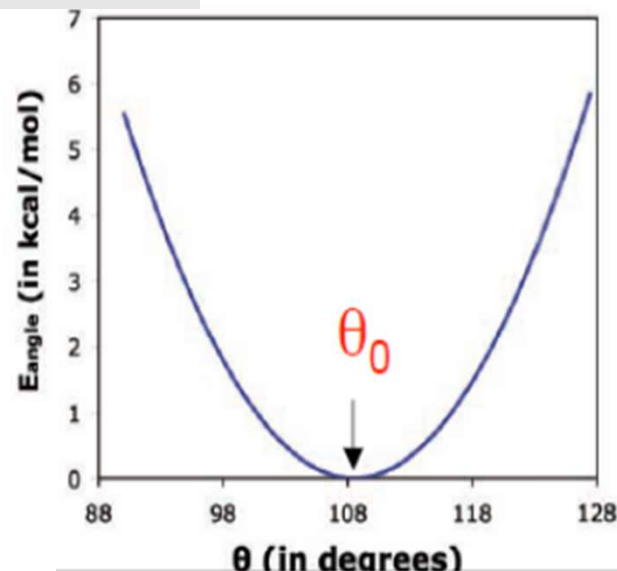


## Angle Bending

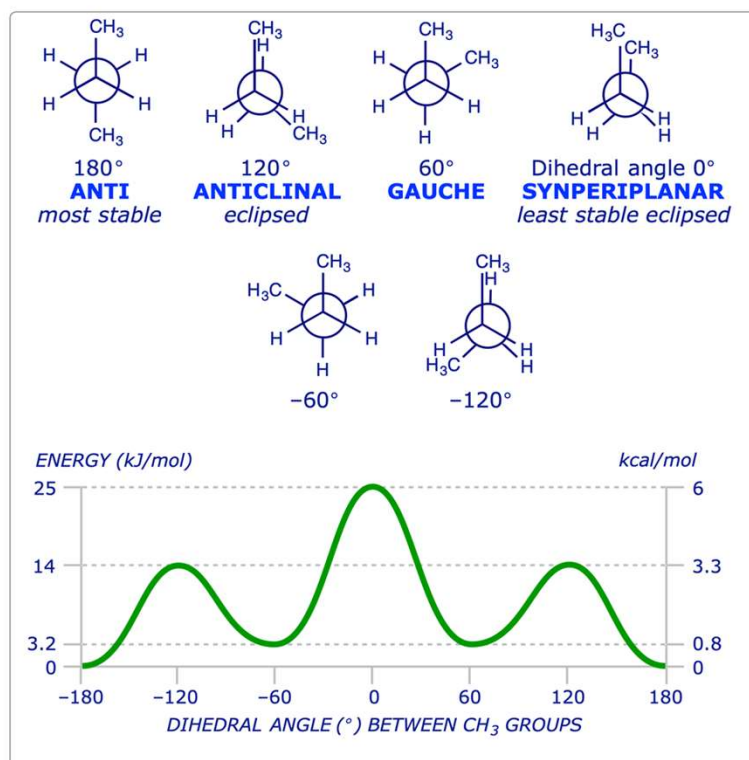
- Hooke's Law in angle coordinates

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

- Equilibrium Angle  $\theta_0$  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  $k_{\theta}$  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



*synperiplanar*-Butane has **two** different types of strain:

## **TORSIONAL STRAIN**

Three eclipsed pairs of bonds (total cost about 12 kJ/mol)

## **STERIC STRAIN**

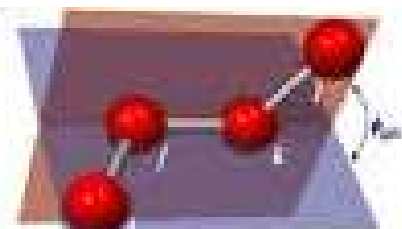
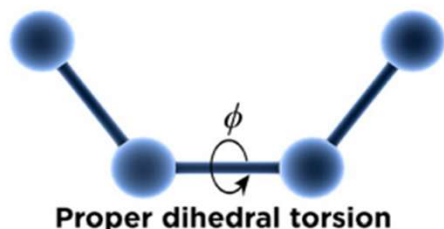
Eclipsed [CH<sub>3</sub>-CH<sub>3</sub>] (costs about 13 kJ/mol)

*Gauche* is less stable than *anti* :

## **STERIC STRAIN**

Gauche [CH<sub>3</sub>-CH<sub>3</sub>] costs 3.2 kJ/mol

## Torsion Angle



### Fourier expansion

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

$\phi$ : Dihedral (torsion) angle,

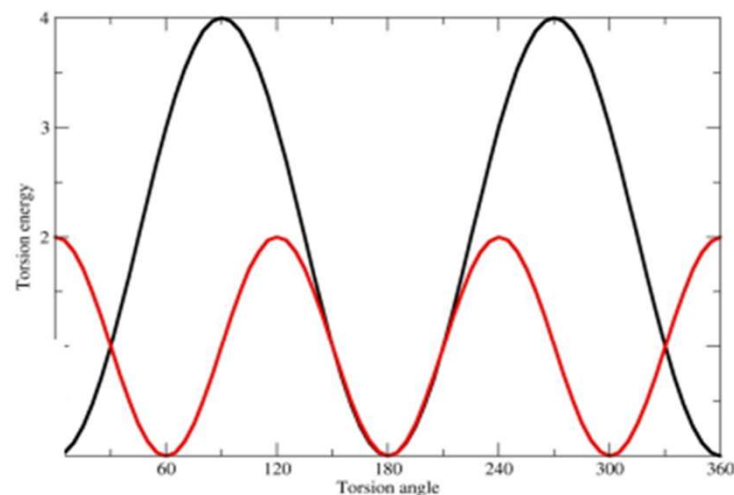
$V_n$ : Amplitude (barrier height) of the  $n$ th term,

$n$ : Periodicity (how many times the potential repeats in  $360^\circ$ ),

$\gamma_n$ : Phase offset (usually  $0^\circ$  or  $180^\circ$ , depending on convention).

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

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



Torsional potentials are periodic functions of the angle  $\phi$  (e.g., every  $120^\circ$ ,  $180^\circ$ ).

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  $-180^\circ$  to  $+180^\circ$ ?

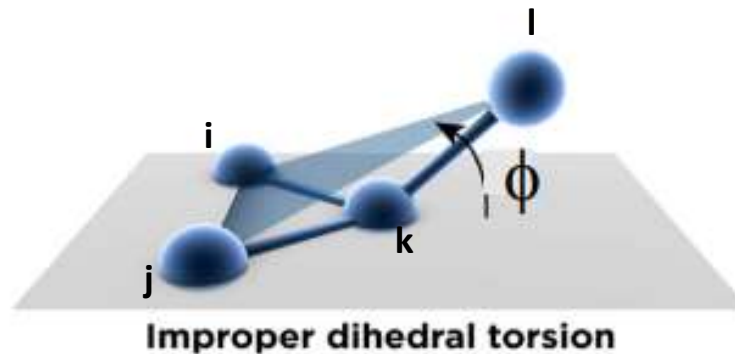
- Describe out of plane motion
- This is often important to maintain planar structure.

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

