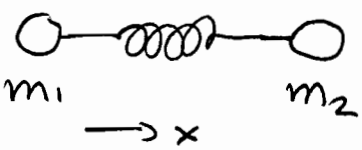
Classical Vibrations



$R = x_2 - x_1$ Force $= -k\cdot(R-R_e)$

$m_1 \frac{d^2x_1}{dt^2} = +k(R-R_e)$ ① (F in +x direction)

$m_2 \frac{d^2x_2}{dt^2} = -k(R-R_e)$ ② (F in −x direction)

$-① \times \frac{1}{m_1} + ② \times \frac{1}{m_2}$

$$\Rightarrow \frac{d^2R}{dt^2} = -\frac{k}{m_2}(R-R_e) - \frac{k}{m_1}(R-R_e) = -\frac{k}{\mu}(R-R_e) \quad ③$$

where $\frac{1}{\mu} = \frac{1}{m_1} + \frac{1}{m_2}$ ③ is a 2nd order O.D.E.

with solution $R = R_e + A\sin\left(\sqrt{\frac{k}{\mu}}\,t\right) + B\cos\left(\sqrt{\frac{k}{\mu}}\,t\right)$

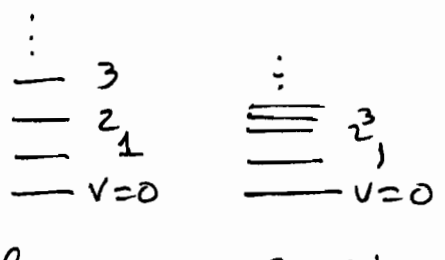
A, B constants depending on initial conditions

Frequency $\omega = \sqrt{k/\mu}$ E_{vib} can have any value

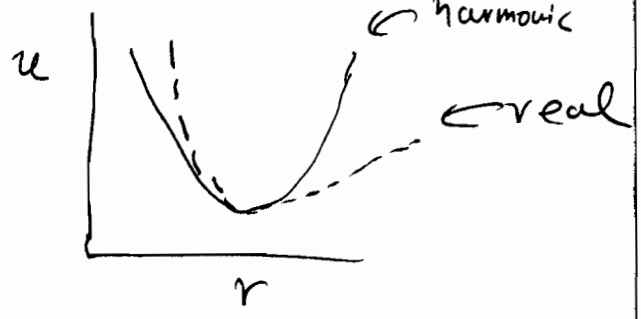
Real molecules obey Schrödinger's equation (see lecture 2 notes) and have quantized vibrations with energies (assuming harmonic vibrations)

$$E_{vib} = \frac{h}{2\pi}\sqrt{\frac{k}{\mu}}\left(v+\frac{1}{2}\right) \qquad v = 0, 1, 2, \ldots$$

These motions result in characteristic absorption lines:



harmonic experimental



Many-body vibrations

For two masses connected by a spring, we saw that the problem can be reduced to that of a single combined mass ($1/\mu = 1/m_1 + 1/m_2$) vibrating

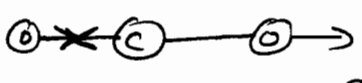
For N atoms $\rightarrow$ $3N$ cartesian coordinates

3 translational, 3 rotational $\}$ $3N-6$ vibrational degrees of freedom

(2 for linear molecules) ($3N-5$ for linear)

e.g., for CO_2 $O=C=O$ $3 \cdot 3 - 5 = 4$ "normal modes"

symmetric Stretch



asymmetric Stretch

bending in-plane

out-of-plane bending

These motions (classical) correspond to (quantum) adsorption lines from which the corresponding force constants can be obtained.

Molecular Mechanics

Application of classical mechanics to determination of molecular equilibrium structures and their vibrations (normal modes).

Origin in the 1970's, A.K.A "force field" methods

Bond Stretching

We have already talked about the harmonic approximation,

(A)—(B) $\quad U_{AB} = \frac{1}{2} k (R_{AB} - R_e)^2$

R_e: equilibrium bond length

k, R_e can be obtained from experimental values, or calculated from ab initio methods

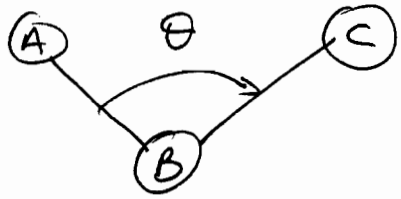
Other options: * $U_{AB} = D\left[1 - \exp\left[-\alpha(R_{AB} - R_e)\right]\right]^2$ (Morse Potential)

* Fixed bond lengths — consistent w/ lack of excitation of corresponding quantum vibrations at room temperature, eliminates need for small integration steps in molecular dynamics

* FENE potential $U_{AB} = -\frac{1}{2} k R_e^2 \ln\left[1 - \left(\frac{R_{AB} - \Delta}{R_e}\right)^2\right]$

Finite-Extensible-Network-Elasticity } $|R_{AB} - \Delta| \le R_e$, Δ is max extension

Bond Bending

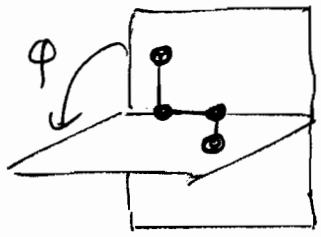


$u(\theta) = \frac{k}{2}(\theta - \theta_0)^2$

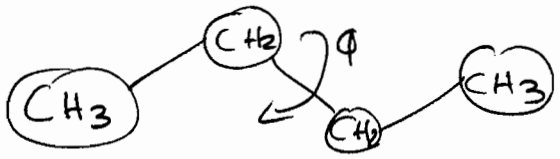
e.g. C–C–C $\quad \theta_0 = 109.47^\circ$

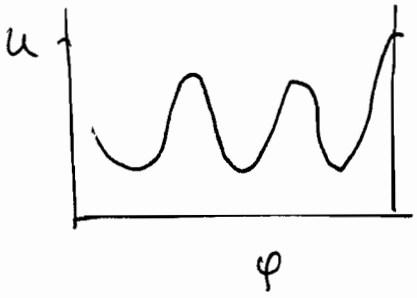
$k = 9.9$ cal/(mol deg)

Dihedral Motions (torsion)



e.g. C_4H_{10} (n-butane)

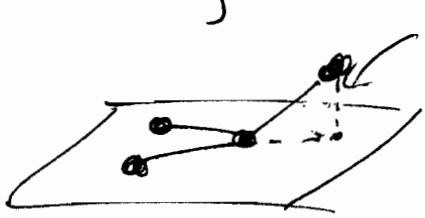




$$u(\varphi) = \sum_{n=0}^{N} C_n \cos(\varphi)^n$$

← typical energy function

Similar geometric terms for out-of-plane bending



$u = k q^2$

United Atoms versus Explicit H

Many force fields group together CH_3, CH_2 etc into "superatoms", saving computational costs

Some Common force fields

Internally consistent, optimized for specific properties, covering broader or narrower range of compounds

MM1,2,+ → Hydrocarbons
AMBER } biomolecules
OPLS } (also CHARMM)

UFF → solids
TRAPPE → Phase equil. data

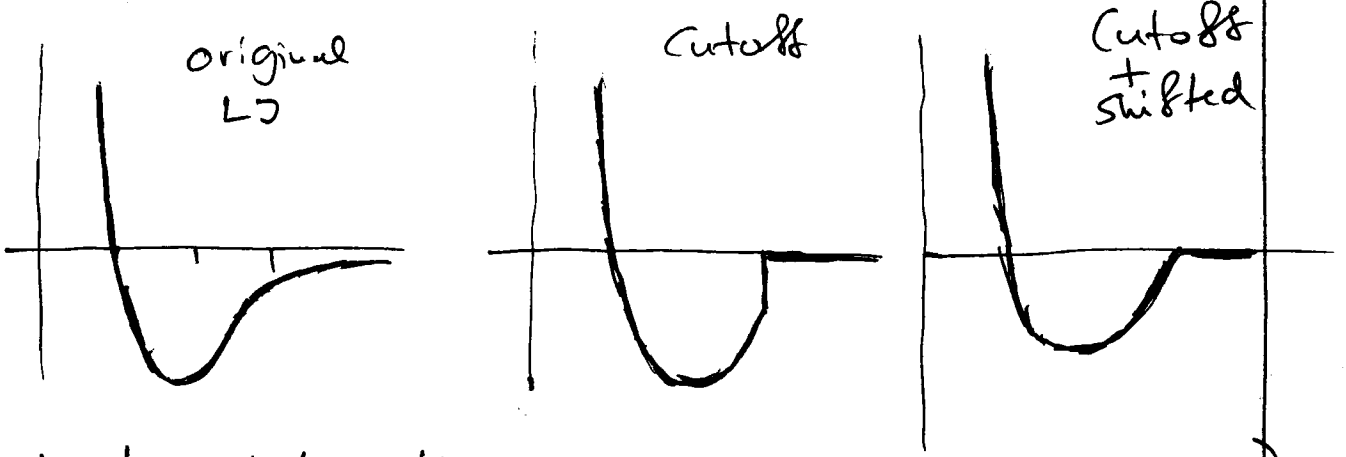
General form

$$U = \underbrace{\sum U_{AB}}_{\text{bond stretch}} + \underbrace{\sum U_{ABC}}_{\text{bond bend}} + \underbrace{\sum U_{ABCD}}_{\text{dihedral, out of plane}} + \underbrace{\sum U_{AB}}_{\text{non-bonded}} + \underbrace{\sum U_{AB}}_{\text{Coulomb}} \underbrace{\left[+ \sum U_{ABCDE\ldots} \right]}_{\text{multi-body interactions}}$$

dominate computational time

Potential Cutoffs

Non-bonded interactions frequently have a range that exceeds the box length -



(Coulombic interactions require special treatment - Las unphysical results can occur on cutoff.

To correct for "Long-Range" effects:

$$U_{LR} = \int_{R_c}^{\infty} 4\pi r^2 \rho U(r)\, dr$$

(does not work for Coulombic)