

# Chapter 2 - Molecular Mechanics

## 2.1 History and Fundamental Assumptions

- Vibrational spectroscopy measures the E separations b/w different v.b. levels, which are quantized. ( $v=0 \rightarrow v=1$ )  
ground  $\rightarrow$  excited
- E for the excitation fall usually falls under the IR region of optical spectrum.
- The spacings between the various v.b. E levels depend on the potential E associated with bond stretching.
- Vib PE  $\Rightarrow$   $U(r_{AB}) = \frac{1}{2} k_{AB} (r_{AB} - r_{AB,eq})^2$   
k is second derivative of U, which is also a "force constant"  
 $\rightarrow$  Therefore, this whole equation is Hooke's law
- "Translatability"  $\Rightarrow$  force constants and equilibrium bond lengths are largely the same from one molecule to the next.

## 2.2. Potential E Functional Forms

### 2.2.1 Bond Stretching

Hooke's law  $\rightarrow$  only accurate when the bond stretching is close to reg. As bond gets more stretched, Hooke's law predicts that the E

becomes infinitely positive, which is not chemically realistic. To account for such inaccuracy, we include terms in the Taylor expansion

$$U(r_{AB}) = \frac{1}{2} [k_{AB} + k_{AB}^{(3)}(r_{AB} - r_{AB, eq})] (r_{AB} - r_{AB, eq})^2$$

Inclusion of cubic term

Complication of this equation is that it converges to  $\infty$  with  $r$  bond length - lowest possible  $E$  for a molecule described by the equation above, corresponds to all bonds being dissociated.

Then, add quartic term,

$$U(r_{AB}) = \frac{1}{2} [k_{AB} + k_{AB}^{(3)}(r_{AB} - r_{AB, eq}) + k_{AB}^{(4)}(r_{AB} - r_{AB, eq})^2] (r_{AB} - r_{AB, eq})^2$$

thus used in organic force field

Morse  $\oplus$  Taylor, considered together, result:

$$U(r_{AB}) = D_{AB} \left\{ 1 - [1 - \alpha_{AB}^3(r_{AB} - r_{AB, eq}) + \frac{1}{2} \alpha_{AB}^2 (r_{AB} - r_{AB, eq})^2 - \frac{1}{6} \alpha_{AB}^3 (r_{AB} - r_{AB, eq})^3] \right\}^2$$

## 2.2.2. Valence & bending

Typical force field function for 2 strain E:

$$U(\theta_{ABC}) = \frac{1}{2} [k_{ABc} + k_{ABC}^{(3)} (\theta_{ABC} - \theta_{ABC, eq}) + k_{ABC}^{(6)} (\theta_{ABC} - \theta_{ABC, eq})^2 + \dots] (\theta_{ABC} - \theta_{ABC, eq})$$

$\theta \Rightarrow$  valence & b/w bonds AB and BC

ABC  $\rightarrow$  force constants (now not dependent on 3 atoms)

- generic force field continues the expansion to the sextic term

) Issues: - doesn't show what happens as the bond  $\theta$  becomes linear,  $\theta = \pi$   
- possible to have multiple equilibrium values.

## 2.2.3 Torsions

- Torsional / dihedral  $\chi$  associated w/ four atoms connected in a sequence ABCD.
- Torsional  $\chi$  is defined as the  $\pm$  b/w bonds AB and CD when they are projected into the plane bisecting the BC bond.
- $\chi$  is  $\oplus$  if one rotates the bond in front of the bisecting plane.
- torsion  $\chi$  is periodic, and torsional PE also periodic

$$U(\omega_{ABCD}) = \frac{1}{2} \sum_{\{j\}_{ABCD}} V_j,_{ABCD} [1 + (-1)^{j+1} \cos(j\omega_{ABCD} + \Psi_j,_{ABCD})]$$

Torsional PE

make the function in brackets 0  
for all j when  $\omega = \pi$

- force field parameters are not orthogonal, so optimized values can be skewed by coupling with other parameters

- Inorganic shapes force field uses the following equations to compute & bending E.

$$U(\theta_{ABC}) = \sum_{\{j\}_{ABC}} k_{j,ABC}^{\text{Founer}} [1 + \cos(j\theta_{ABC} + \psi)]$$

$$k_{j,ABC}^{\text{Founer}} = \frac{2k_{ABC}}{j^2}$$

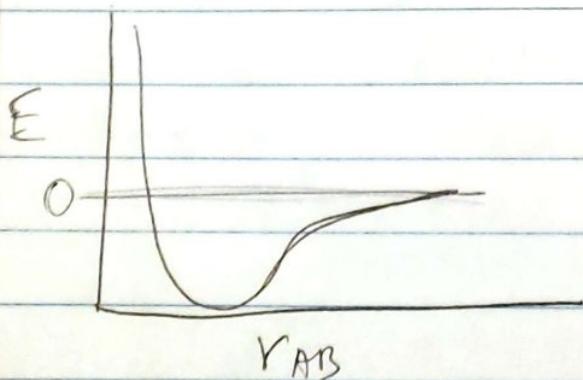
#### 2.2.4 Van der Waals Interactions

- isolated atoms are spherically symmetric, lacking any electric multipole moments.

- when there are no dissipative forces,

$$F_q = -\frac{\partial U}{\partial q} \Rightarrow q \text{ is coordinate direction}$$

U is PE  
F is force



$\Rightarrow$  This curve doesn't accurately describe reality.

- 2 atoms simultaneously develop electrical moments that are oriented so as to be mutually attractive. The force associated with this

is called "London" force.

- Equation to show dispersion and repulsion Es:

$$U(r_{AB}) = \frac{a_{AB}}{r_{AB}^{12}} - \frac{b_{AB}}{r_{AB}^6}$$

a, b are constants specific to atoms A and B

$$r_{AB} = \sqrt{(x_A - x_B)^2 + (y_A - y_B)^2 + (z_A - z_B)^2}$$

internal coordinate

Lennard Jones potential:

$$U(r_{AB}) = 4\epsilon A \left[ \left( \frac{\sigma_{AB}}{r_{AB}} \right)^{12} - \left( \frac{\sigma_{AB}}{r_{AB}} \right)^6 \right] \Rightarrow \epsilon \text{ and } \sigma \text{ are constants}$$

$\sigma$  has units of length

Rest equation is when  $U=0$  and we differentiate the equation above w.r.t.  $r_{AB}$ :

$$\frac{dU(r_{AB})}{dr_{AB}} = \frac{4\epsilon A}{r_{AB}} \left[ -12 \left( \frac{\sigma_{AB}}{r_{AB}} \right)^{13} + 6 \left( \frac{\sigma_{AB}}{r_{AB}} \right)^7 \right]$$

## 2.2.5 Electrostatic Interactions

Classical electrostatics asserts the E of interaction:  $U_{AB} = M^A \cdot V^B$

$M^A \Rightarrow$  ordered vector of the multipole moments of A

$V^B \Rightarrow$  ordered row vector of the electrical potentials deriving from the multipole moments of B,

- both expansion centre around the center of

mass of the molecules.

w/ the description numbers,  $\chi$ , of torsional linkage

(Interaction E b/w atoms A and B:

$$U_{AB} = \frac{q_A q_B}{r_{AB} r_{AB}}$$

## 2.3 Force-field and Thermodynamics

- E of 0 is obtained when the bond length or  $\chi$  adopts its equilibrium value.
- "strain free" molecule is one in which every coordinate adopts its equilibrium value.

! 2 different molecules cannot be meaningfully compared unless the zero of E is identical.

- H<sub>f</sub> can be computed as the sum of the heats of formation of all of the atom types plus the strain E.
- possibility of a negative force-field E is not a complication
- typical force-field E calculation will report:
  - strain E; - force-field E; - H<sub>f</sub>.
- energetic comparisons are necessarily limited to conformers, or other isomers that can be formed without any change in atom types.

## 2.4 Geometry Optimization

Finding minimum E structures is key to describing equilibrium b/c real molecules vibrate constantly

Normally about start equilibrium structures.

- priority in force-field development is to adopt reasonably simple functional forms so as to facilitate geometry optimization

### 2.4.1. Optimization Algorithms

- we want to move not in the direction of a single coordinate, but rather in direction of the greatest downward slope in E wrt. all coordinates. This direction is opposite of gradient vector  $\mathbf{g}$ :

$$\mathbf{g}(\mathbf{q}) = \begin{bmatrix} \frac{\partial U}{\partial q_1} \\ \frac{\partial U}{\partial q_2} \\ \frac{\partial U}{\partial q_3} \\ \vdots \\ \frac{\partial U}{\partial q_n} \end{bmatrix}$$

$n$ -dimensional coordinate vector

( $n = 3N - 6$ ,  $N$  is # of atoms)  $\Rightarrow$  if internal coordinates

( $n = 3N$ )  $\Rightarrow$  if Cartesian coordinates

- need at least 1 additional E. calculation for each DOF.

- If we have atom A, and we take partial derivative of E w.r.t. x coordinate.

$$\frac{\partial U}{\partial x_A} = \sum_{i \text{ bonded to } A} \frac{\partial U}{\partial r_{Ai}} \frac{\partial r_{Ai}}{\partial x_A}$$

} only bonds + H have A at terminus enough to be affected.

$$\frac{\partial U}{\partial r_{Ai}} = \frac{1}{2} [2k_A + 3k_{Ai}^{(3)}(r_{Ai} - r_{Ai,ep}) + 4k_{Ai}^{(4)}(r_{Ai} - r_{Ai,ep})^2]$$

$$(r_{Ai} - r_{Ai,ep})$$

Taylor expansion in arbitrary coordinates in matrix notation:

$$U(g^{(k+1)}) = U(g^{(k)}) + (g^{(k+1)} - g^{(k)})f^{(k)} + \frac{1}{2}(g^{(k+1)} - g^{(k)})^T H^{(k)} (g^{(k+1)} - g^{(k)})$$

Hessian matrix

## 2.4.2. Optimization aspects specific to Force Fields

- Force fields have issues, mostly in scaling behavior that the speed of a force-field calculation exhibits wrt increasing system size.
- We need to handle reactive processes:
  - define a new atom type and parameters to make/break bonds
  - compute the same E regardless of if the atomic connectivity is of the reactant or product
  - mix up force-field representation of the molecule with a QM representation

## 2.5. Menagerie of Modern Force Fields

### 2.5.1. Available Force Fields

- inter alia  $\Rightarrow$  different hydrogen bonding parameters
- issue of sloppiness in referring to the force field.
- Table 2.1 has names of active force fields that scientists use today. However, there's ~~is~~ a lot of confusion existing.

### 2.5.2 Validation

The process of testing the ability of a force field for molecules other than those over which it was parameterized is known as "validation".

- pick the most effective force field that was used prior \* (consider optimizing it later).

## Chapter 3 Simulation of Molecular Ensembles

### 3.1 Relationship B/w MM & real systems

- On-potential vibrational effects dictate that, even if OK, the molecule probabilistically samples a range of different structures
- after passing through equilibrium, the magnitude of free momentum begins to decrease, until the ball returns to the same point in phase

- space from where it began.
- Vast majorities of the techniques measure averages or ensemble averages or most typically both.  $\Rightarrow$  We want computational techniques capable of accurately reproducing these aspects of molecular behaviour.
- MC  $\Rightarrow$  Monte Carlo technique
- MD  $\Rightarrow$  molecular dynamics technique

### 3.2 Phase Space and Trajectories

-  $6-N$  dimensional space defined by these coordinates is called the "phase space" of the system. At any instant time, the system occupies one point in phase space

$$X = (x_1, y_1, z_1, p_{x1}, p_{y1}, p_{z1}, x_2, y_2, z_2, p_{x2}, p_{y2}, p_{z2}, \dots)$$

- Note, as we know from quantum mechanics, you cannot know position and momentum in the same time
- Definition of phase space point:  $X = (q, p)$

#### 3.2.1 Properties as Ensemble Averages

Phase state encompasses every possible state of a system

$$\langle A \rangle = \iint A(q, p) P(q, p) dq dp \Rightarrow \langle A \rangle \rightarrow \text{average property}$$

partition function  
 $P(q,p) = Q^{-1} e^{-E(q,p)/k_B T}$   
 ↓  
 probability of being at a particular phase point.  
 $Q = \int \int e^{-E(q,p)/k_B T} dq dp$  serves the function of  
 normalization constant  
 for  $P$ .

- Key to making the evaluation more tractable is to recognize that phase space is for the most part, a wasteland.
- What is needed in the equations down in the section above is some prescription for picking important points.)  
 That's what MC method is trying to do.

### 2.3.2 Properties as Time Averages of Trajectories

phase

- If we start at "reasonable" point, it's E conserving evolution over time seems likely to sample relevant regions of phase space

$$\langle A \rangle = \frac{1}{M} \sum_{i=1}^M A(t_i)$$

M is # of times property is sampled

If we do sampling continuously, the equation becomes:

$$\langle A \rangle = \lim_{t \rightarrow \infty} \frac{1}{t} \int_{t_0}^{t_0+t} A(\tau) d\tau$$



Was proved that equations:

$$\langle A \rangle = \iint A(q, p) P(q, p) dp dq$$

are equivalent to each other.

### 3.3 Molecular Dynamics

Phase point determines the location of the next phase point in the absence of outside forces acting upon the system.

#### 3.3.1 Harmonic Oscillator Trajectories

After passing equilibrium, the magnitude of the momentum begins to decrease until the ball returns to the same point in phase space from where it began

$$v = \frac{p}{m}$$

$$p(t_2) = p(t_1) + m \int_{t_1}^{t_2} a(t) dt$$

relationship b/w 2 momentum vectors

$$q(t_2) = q(t_1) + \int_{t_1}^{t_2} \frac{p(t)}{m} dt$$

relationship b/w 2 positions.

These 2 last equations make Newton's second law:  $\ddot{x} = \frac{F}{m}$

### 3.3.3. Practical Issues in Propagation

- Approximate past equations as Euler's, w/ the exact limit of  $\Delta t \rightarrow 0$ , we are offered a way of simulating a phase space trajectory.

$$q(t + \Delta t) = q(t) + \frac{p(t)}{m} \Delta t$$

$$p(t + \Delta t) = p(t) + m\alpha(t) \Delta t$$

Their relationship is  $\dot{\tau}(t) = \frac{1}{(3N-n)k_B} \sum_{i=1}^N \frac{|p_i(t)|^2}{m_i}$

# of atoms  
↓  
# of conserved degrees