

Lecture 16

Electrostatics, Part 1

n-body expansion; multipole moments

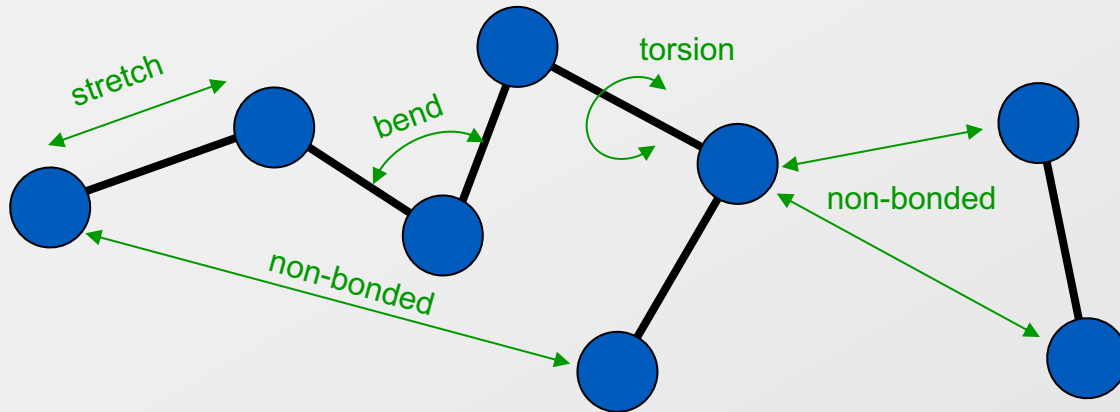
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CE 500 – Modeling Potential-Energy Surfaces

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



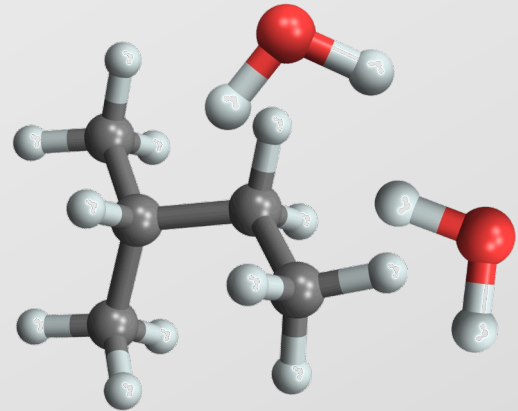
$$E_{\text{MM}} = \underbrace{E_{\text{str}} + E_{\text{bend}} + E_{\text{tors}} + E_{\text{cross}}}_{\text{bonded}} + \underbrace{E_{\text{vdW}} + E_{\text{el}}}_{\text{non-bonded}}$$

Intermolecular energy is treated as sums of 2-body, 3-body, 4-body, etc. interactions

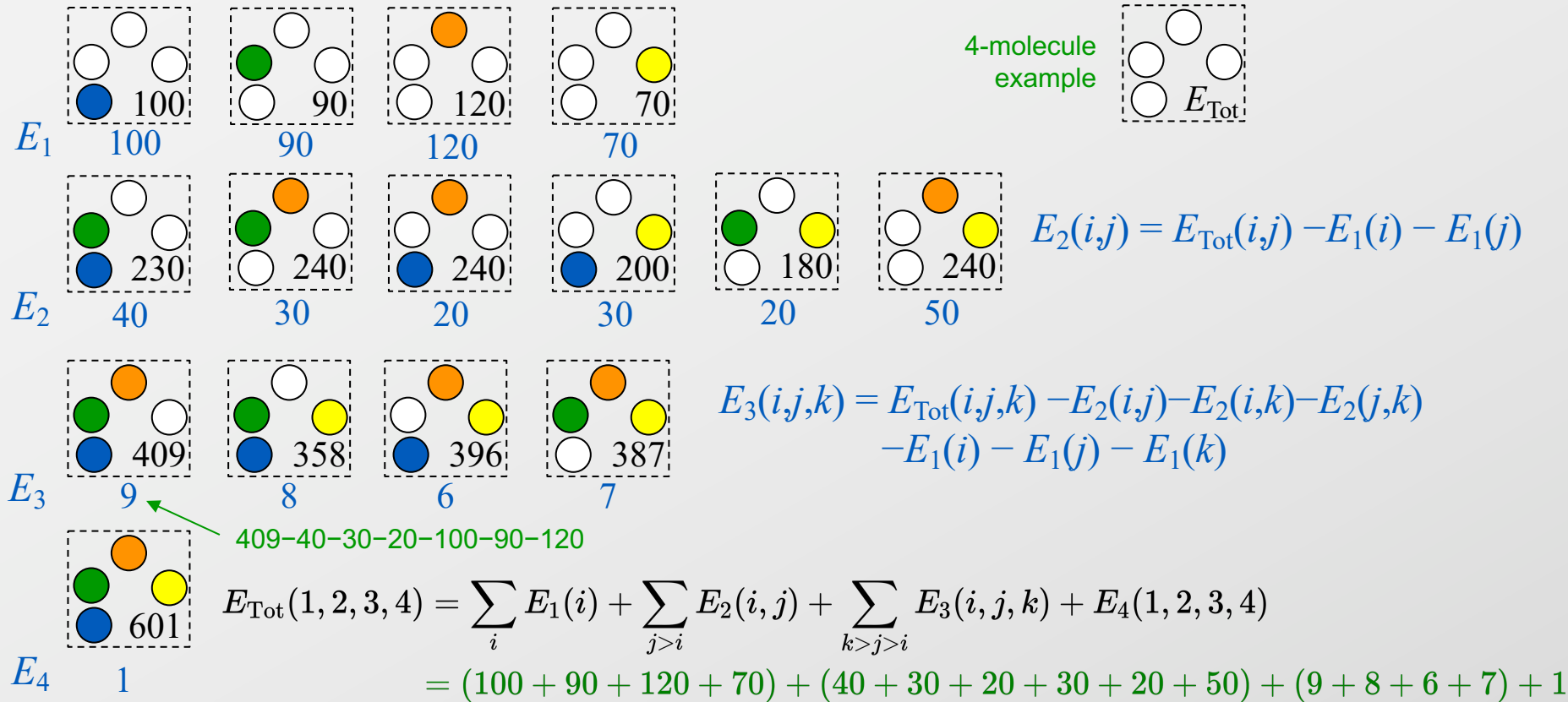
- Sums over molecules

$$E(\mathbf{r}^N) = \underbrace{\sum_i E_1(\mathbf{r}_i)}_{\text{Intramolecular, external fields}} + \underbrace{\sum_i \sum_{j>i} E_2(\mathbf{r}_i, \mathbf{r}_j)}_{\text{pairwise sum}} + \underbrace{\sum_i \sum_{j>i} \sum_{k>j} E_3(\mathbf{r}_i, \mathbf{r}_j, \mathbf{r}_k)}_{\text{sum over triplets}} + \dots$$


- Each term E_n for $n > 1$ is itself a sum over atom pairs (or larger groups, in principle) between molecules



Intermolecular energy is treated as sums of 2-body, 3-body, 4-body, etc. interactions



Use of pairwise-additivity is widespread, even though it accounts for only 80-90% of the energy

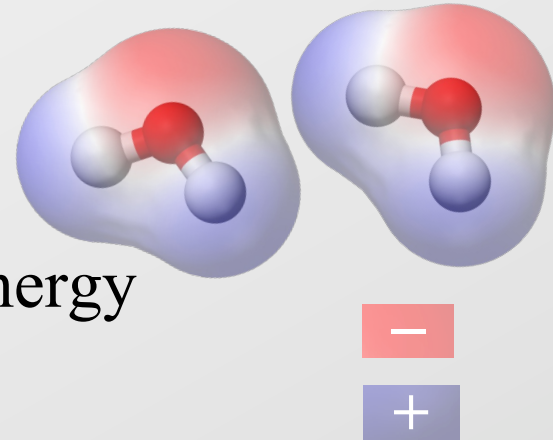
- Consequently, pair models that are fit to bulk properties do not describe true two-body interactions
 - Instead, they implicitly account for multibody effects
 - Models fit this way lose accuracy when applied at other densities
 - This is accepted because higher-order contributions are expensive to calculate
 - Also, many models focus on bio, hence only a narrow set of conditions
- 

liquid density; heat of
vaporization

Except at close separations, Coulomb forces govern non-bonded interactions

- Electron density about a molecule is not uniform
- This gives rise to regions of positive and negative charges
- The classical Coulomb integral gives the energy

$$E_{\text{Coul}} = \int \int \frac{\rho(1)\rho(2)}{r_{12}} d1d2$$



- In practice, the charge distributions are represented in approximate forms that simplify modeling and calculation

Placement of partial charges is a basic way to represent the electron density

- Point charges on different molecules interact via Coulomb's law

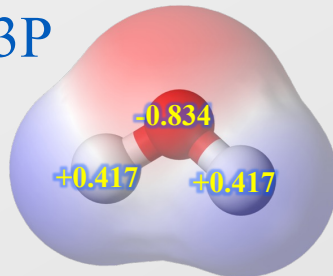
$$E_{\text{el}} = \sum_{i=1}^{N_A} \sum_{j=1}^{N_B} \frac{q_i q_j}{r_{ij}}$$

- Fit is underspecified, so there is an art to doing it effectively
- Charges may or may not coincide with atom centers
 - Example: two water models

TIP = "Transferable
Intermolecular Potential"

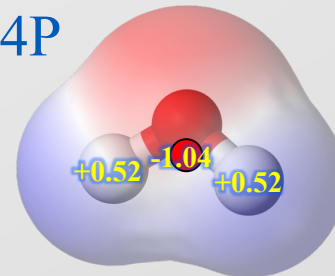
TIP3P

3 sites:
O - LJ and Coulomb
H, H - Coulomb only*



TIP4P

4 sites:
O - LJ only
M, H, H - Coulomb only



Many models for water have been proposed. It is difficult to get all properties accurately

Table 2.6 A selection of water models and associated properties.^{112, 113}

Model property	SPC/E	TIP3P	TIP4P	TIP4P/2005	TIP5P	BK3	AMOEBA	Exp.
T_m	215	146	232	252	274	250	261	273
ρ	0.994	0.98	0.988	0.993	0.979	0.997	1.000	0.997
ΔH_{vap}	49.3	42.0	44.6	50.2	43.8	45.8	43.5	44.0
C_p	88	79	84	88	121	92	88	75
ϵ	68	94	50	58	91	79	81	78

T_m : melting temperature (K), ρ : density at 298 °C (g/ml), ΔH_{vap} : heat of vaporization (kJ/mol), C_p : heat capacity (J/mol K), ϵ : dielectric constant.

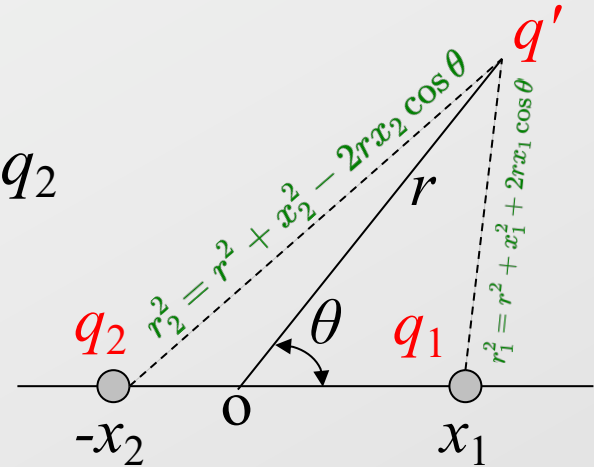
At large separations, details of the charge distribution are less important

- Consider a point charge q' some distance from a pair of charges q_1 and q_2

$$E_{\text{el}} = \frac{q'q_1}{(r^2 + x_1^2 + 2rx_1 \cos \theta)^{1/2}} + \frac{q'q_2}{(r^2 + x_2^2 - 2rx_2 \cos \theta)^{1/2}}$$

- Expand in series for $r \rightarrow \infty$

$$E_{\text{el}} = \frac{q'(q_1 + q_2)}{r} + \frac{q'(q_2x_2 - q_1x_1)}{r^2} \cos \theta + \frac{q'(q_1x_1^2 + q_2x_2^2)}{r^3} \frac{1}{4}(1 + 3 \cos 2\theta) + \mathcal{O}\left(\frac{1}{r}\right)^4$$



$$E_{\text{el}} = \frac{q_1}{\text{Sqrt}[r^2 + x_1^2 + 2 r x_1 \text{Cos}[t]]} + \frac{q_2}{\text{Sqrt}[r^2 + x_2^2 - 2 r x_2 \text{Cos}[t]]}$$

$$\frac{q_1}{\sqrt{r^2 + x_1^2 + 2 r x_1 \text{Cos}[t]}} + \frac{q_2}{\sqrt{r^2 + x_2^2 - 2 r x_2 \text{Cos}[t]}}$$

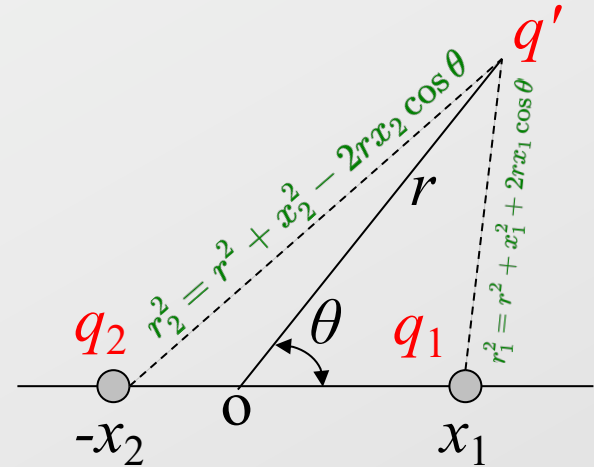
Series[Eel, {r, Infinity, 4}] // Simplify

$$\frac{q_1 + q_2}{r} + \frac{(-q_1 x_1 + q_2 x_2) \text{Cos}[t]}{r^2} + \frac{(q_1 x_1^2 + q_2 x_2^2) (1 + 3 \text{Cos}[2 t])}{4 r^3} - \frac{(q_1 x_1^3 - q_2 x_2^3) (3 \text{Cos}[t] + 5 \text{Cos}[3 t])}{8 r^4} + \mathcal{O}\left[\frac{1}{r}\right]^5$$

Multipole moments quantify the most important features of a charge distribution

$$E_{\text{el}} = \frac{\overset{\text{charge}}{q'}(q_1 + q_2)}{r} + \frac{\overset{\text{dipole}}{q'}(q_2 x_2 - q_1 x_1)}{r^2} \cos \theta + \frac{\overset{\text{quadrupole}}{q'}(q_1 x_1^2 + q_2 x_2^2)}{r^3} \frac{1}{4} (1 + 3 \cos 2\theta) + \mathcal{O}\left(\frac{1}{r}\right)^4$$

$$E_{\text{el}} = \frac{q'Q}{r} + \frac{q'\mu}{r^2} \cos \theta + \frac{q'\Theta}{r^3} \frac{1}{4} (1 + 3 \cos 2\theta) + \dots$$



- The electrostatic moments are
 - *Charge* $q = q_1 + q_2$
 - *Dipole* $\mu = q_2 x_2 - q_1 x_1$
 - *Quadrupole* $\Theta = q_1 x_1^2 + q_2 x_2^2$

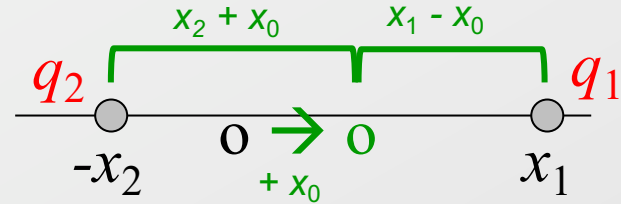
Next would be octupole

The first nonzero moment is independent of the origin

- Consider effect of shifting origin

no effect

$$q : q_1 + q_2 = q$$



If $q = 0$

$$\mu : q_2(x_2 + x_0) - q_1(x_1 - x_0) = \mu + (q_2 + q_1)x_0 = \mu$$

*If $q = 0$
and
 $\mu = 0$*

$$\begin{aligned} \Theta : & q_2(x_2 + x_0)^2 + q_1(x_1 - x_0)^2 \\ &= \Theta + 2x_0 \underbrace{(q_2x_2 - q_1x_1)}_{\mu} + x_0^2 \underbrace{(q_2 + q_1)}_q = \Theta \end{aligned}$$

More generally, the multipole moments are tensorial quantities

- Charge is a rank-0 tensor (scalar): $q = \sum_i q_i$

- Dipole moment is a rank-1 tensor (vector): $\boldsymbol{\mu} = \sum_i q_i \mathbf{r}_i$

$$\boldsymbol{\mu} = \left(\sum_i q_i x_i \quad \sum_i q_i y_i \quad \sum_i q_i z_i \right)$$

- Quadrupole moment is a rank-2 tensor: $\Theta = \sum_i q_i \mathbf{r}_i \mathbf{r}_i$

$$\Theta = \begin{pmatrix} \sum_i q_i x_i^2 & \sum_i q_i x_i y_i & \sum_i q_i x_i z_i \\ \sum_i q_i y_i x_i & \sum_i q_i y_i^2 & \sum_i q_i y_i z_i \\ \sum_i q_i z_i x_i & \sum_i q_i z_i y_i & \sum_i q_i z_i^2 \end{pmatrix}$$

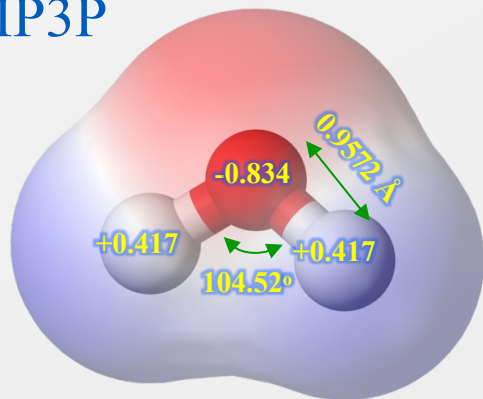
A traceless version is often preferred; also may diagonalize

$$Q = \frac{3}{2} \begin{pmatrix} \sum_i q_i (x_i^2 - \frac{1}{3} r_i^2) & \sum_i q_i x_i y_i & \sum_i q_i x_i z_i \\ \sum_i q_i y_i x_i & \sum_i q_i (y_i^2 - \frac{1}{3} r_i^2) & \sum_i q_i y_i z_i \\ \sum_i q_i z_i x_i & \sum_i q_i z_i y_i & \sum_i q_i (z_i^2 - \frac{1}{3} r_i^2) \end{pmatrix}$$

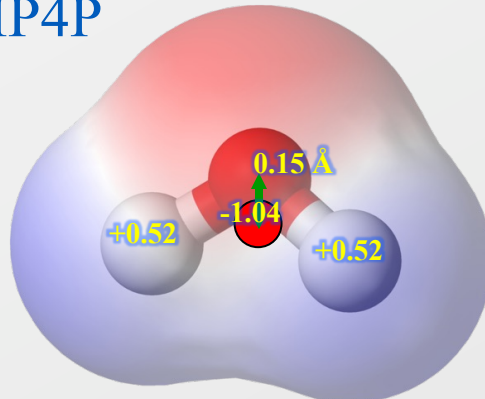
$$\begin{pmatrix} x_i \\ y_i \\ z_i \end{pmatrix} \begin{pmatrix} x_i & y_i & z_i \end{pmatrix}$$

Let's practice by computing the dipole and quadrupole moments of the TIPxP models

TIP3P



TIP4P



$$\boldsymbol{\mu} = \left(\sum_i q_i x_i \quad \sum_i q_i y_i \quad \sum_i q_i z_i \right)$$

$$\Theta = \begin{pmatrix} \sum_i q_i x_i^2 & \sum_i q_i x_i y_i & \sum_i q_i x_i z_i \\ \sum_i q_i y_i x_i & \sum_i q_i y_i^2 & \sum_i q_i y_i z_i \\ \sum_i q_i z_i x_i & \sum_i q_i z_i y_i & \sum_i q_i z_i^2 \end{pmatrix}$$

Use origin on oxygen atom

1 Coulomb-Å = 2.9979×10^{19} Debye (D)

1 Buckingham = 1 D-Å

$e = 1.602 \times 10^{-19}$ Coulombs

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/9qhqtq/alma9939265811804803
- C.G. Gray and K.E. Gubbins, *Theory of Molecular Fluids*, Vol. 1: Fundamentals (1984).
 - Detailed, comprehensive discussion of molecular electrostatics
 - Not required reading. Recommended for anyone needed to look at the topic in more detail.