

10.675 LECTURE 19

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1. TODAY

- Continuum Solvation
- Onsager
- PCM
- Embedding, ONIOM
- QM/MM

2. SOLVATION

Looking at the di-chloryl ethane in the gas phase (trans vs gauche positions)
In the gas phase, we take the trans configuration as 0 energy, but the gauche configuration as 1 kcal/mole.

In a solvent, both energies are essentially the same due to the solvents high dielectric constant.

What is $\Delta E^{elec,solv}$ (solvation energy)?

$$\Delta E^{elec,solv} = E^{elec,liq} - E^{elec,gas}$$

Onsager's reactions field method (JACS b8 (1936) 1486)

Essentially, the solvation sphere is embedded within a system of liquid of dielectric value ϵ

$H_{rf} = H_o + H_1$ where H_1 is the perturbation of the solvent

This is all done with gas phase calculations (HF; DFT, etc)

$$a_o^3 = \frac{3V_m}{4\pi N}$$

$H_1 = -\hat{\mu} \cdot \vec{R}$ where R is the "reaction field"

$$\vec{R} = g\vec{\mu}$$

$$g = \frac{2(\epsilon-1)}{(2\epsilon+1)a_o^3}$$

3. POLARIZED CONTINUUM METHOD - PCM

Jacobo Tomasi and coworkers

- 1) Choose \vec{R}
 - 2) Solve SCF Problem w/H
 - 3) Compute $\vec{R} = g\vec{\mu}$
- if $\vec{R}(3) \approx \vec{R}(1)$ then done

$\Delta E(\text{gauche-trans})$ for 1,2 dichloroethane (STP)

<i>Medium</i>	ϵ	<i>HF</i>	<i>MP₂</i>	<i>experimental</i>
<i>gas</i>	1	1.96	1.64	1.20
<i>organicsolvent</i>	4.3	0.83	0.54	0.69
<i>pureliquid</i>	10.1	0.49	0.26	0.31
<i>acetonitrile</i>	35.9	0.30	0.09	0.15

Assume solute has gas phase dipole moment μ but no charge. it's just polarizable.

Cavity is "polarizable" w/charge distribution on surface of the cavity

Treat the solute as a continuum charge distribution $\rho(\vec{r})$ in a cavity w/arbitrary shape.

Describe polarization of infinite dielectric by the creation of surfaces w/density

$\sigma(\vec{s})$

$v(r)$ electrostatic potential

$v_\rho(r) + v_\sigma(r)$ are from solute and surface respectively

Sole $\nabla^2 v(r) = 0$ and match the boundary conditions via $v(s)_- = v(s)_+$

$(\frac{\delta v(s)}{\delta n})_{s_-} = \epsilon(\frac{\delta v(s)}{\delta n})_{s_+}$

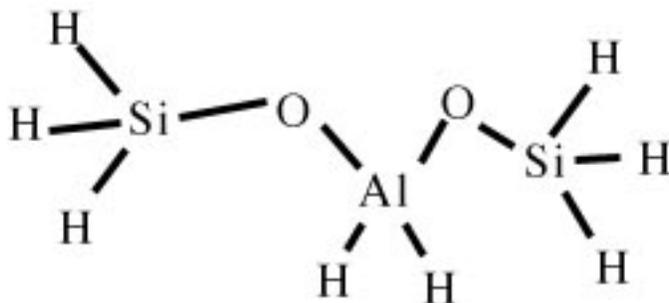
$\sigma(s) = -[\frac{\epsilon-1}{4\pi\epsilon}]E(s)_n = v_\sigma$ Where $E(s)_n$ is the electric field produced by the solute.

$H = H_o + v_\sigma$ Solve this self consistently

4. EMBEDDING OF CLUSTERS (SAUER & COWORKERS)

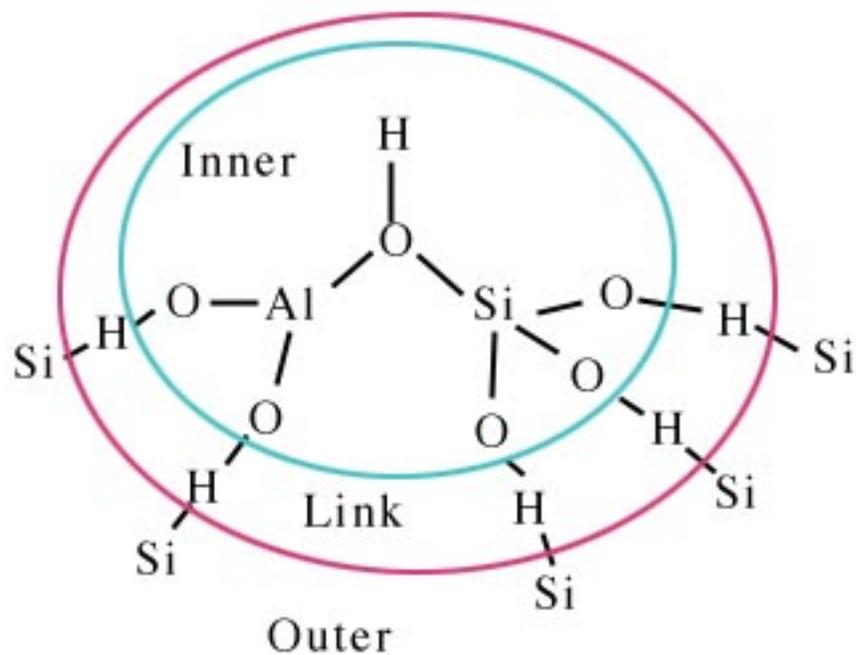
Faujssite = 144 Atoms

ZSM-5 = 288 Atoms



proton affinity vs cluster size

<i>NumShells</i>	<i>PA(HF)/STO - 36</i>	<i>HF(Mixed/Embedded)</i>
1	388.2	298.0
2	381.0	299.4
3	363	299.6
4	391	299.2



But, cannot treat breaking and formation of bonds. QM only for small systems
 Solution, combine the 2.

$$E(s) = E_{QM}(I) + E_{MM}(o) + E(I-O) \text{ interaction term using mm} \approx E_{MM}(I-O)$$

$$E_{MM}(I-O) + E_{MM}(O) = E_{MM}(s) - E_{MM}(I)$$

$$\Rightarrow E(s) = E_{QM}(I) + E_{MM}(s) - E_{MM}(I)$$

Now, let

$$E(s) = E_{QM}(c) + E_{MM}(O) + E_{MM}(I-O) - E_{MM}(I-O) - E_{QM}(L) - E_{QM}(I-L)$$

$$\text{but } E_{MM}(s) = E_{MM}(C) + E_{MM}(O) + E_{MM}(I-O) - E_{MM}(L) - E_{MM}(I_L)$$

$$E(s) = E_{QM}(C) + E_{MM}(s) - E_{MM}(C) + \Delta$$

$$\Delta = E_{MM}(L) - E_{QM}(L) + E_M(I-L) - E_{QM}(I-L)$$

$$\text{If } E_{MM} \approx E_{QM} \Rightarrow \Delta \cong 0$$

5. QM/MM

Type of method, "double link atom"

QM is in a certain region, the rest is standard MM.