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Micro-solvation model and its applications

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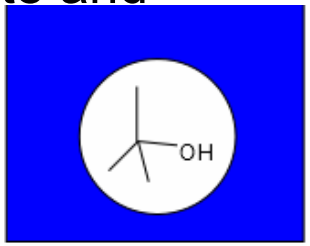
Group meeting

07/09/2018

Solvent effect

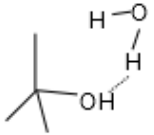
Solvent effect describes the interaction between solvent and solute.

① “Long range interaction”: electronic effect between polarized solute and solvent.



Implicit solvent

② “Short range interaction”: direct intermolecular interaction, especially molecules with H bonds.



Explicit solvent

Free energy of solvation directly describes the **solvent effect.**

$$\Delta G_{sol} = G_{sol} - G_{gas}$$

Solvent model --- continuum model

General idea: The solvent is taken as a homogeneous polarized continuum model.

$\Delta G_{sol} = G_{cav}+G_{dis}+G_{rep}+G_{ele}+G_{tm}$

G_{cav}: cavity formation energy (system energy ↑)

G_{dis}: dispersion energy

G_{rep}: repulsion energy

G_{ele}: electrostatic energy (system energy ↓)

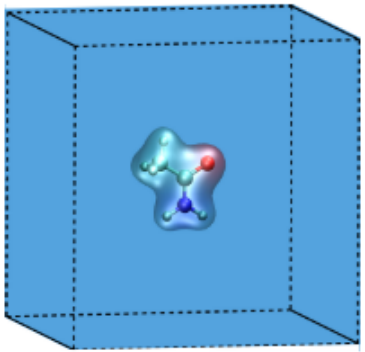
G_{tm} : thermal fluctuation (system energy ↓)

Advantages: cheap (fewer atoms)

Drawbacks: no “short range interaction” included

Mostly used methods: COSMO → PCM → SMD

Implicit solvent model



“Long range interaction”

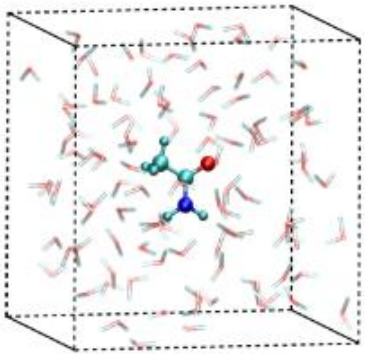
Neerav Kharche , Workshop on “Theory and Computation for Interface Science and Catalysis: Fundamentals, Research and Hands on Engagement using VASP” Nov. 3 – 7, 2014

J. Tomasi, B. Mennucci, R. Cammi, Chem. Rev. 2005, 105, 2999−3093

Solvent model --- micro-solvation model

explicit solvent model

General idea: Using specific solvent molecules to interact with solutes.



Advantages: closest to the reality

Drawbacks: time consuming, difficult to deal with bond breaking situation.

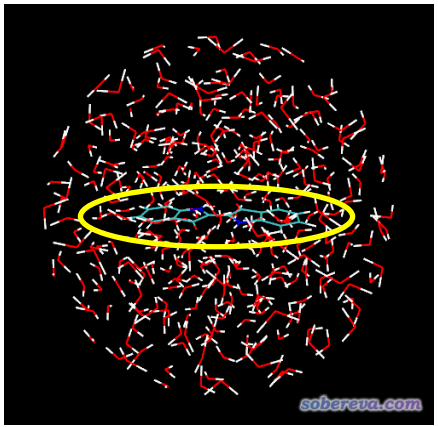
"Short range interaction"

Mostly used in: MD, MM, MC methods.

How to use micro-solvation model

The relatively strict way of adding solvent shell:

1. Surround solutes with solvent molecules, running molecular dynamics;
2. Pick some frames evenly time interval;
3. Select the range where solvent molecules around the solute, and make sure the solute has no exposed surface;
4. Optimize the cluster we select using DFT.



We can obtain the solute surrounded by a shell of solvent molecules, according to different time interval, we can have different structures of the solvent shell.

How to use micro-solvation model

The relatively simple way of adding solvent shell:

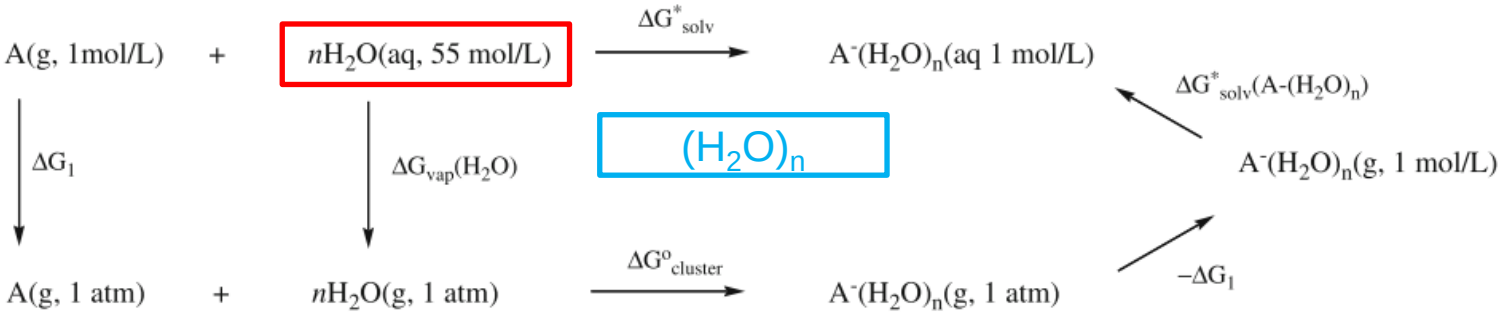
1. Using Packmol to generate water shell ;
2. Using UFF to optimize the structure roughly and quickly;
3. Choose proper water shell (VMD);
4. Using empirical method (such as PM6) to optimized .
5. Delete some unimportant waters.
5. Optimize the whole system under DFT level.

http://sobereva.com/406

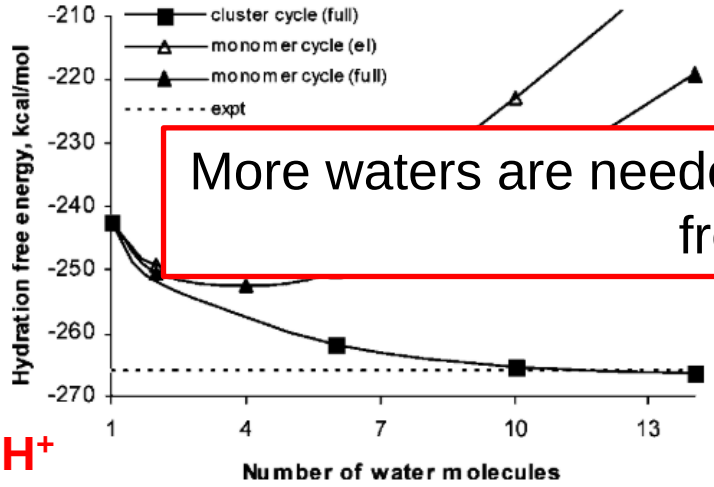
Application of micro-solvation --- solvation free energy

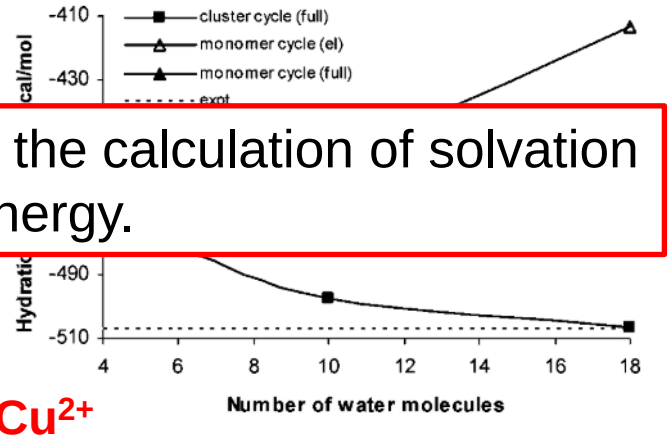
Monomer

cluster



COSMO/B3LYP/6-311G++G(d,p) level (full) +cavity formation energy. (ele) Only consider the electrostatic contribution from COSMO.





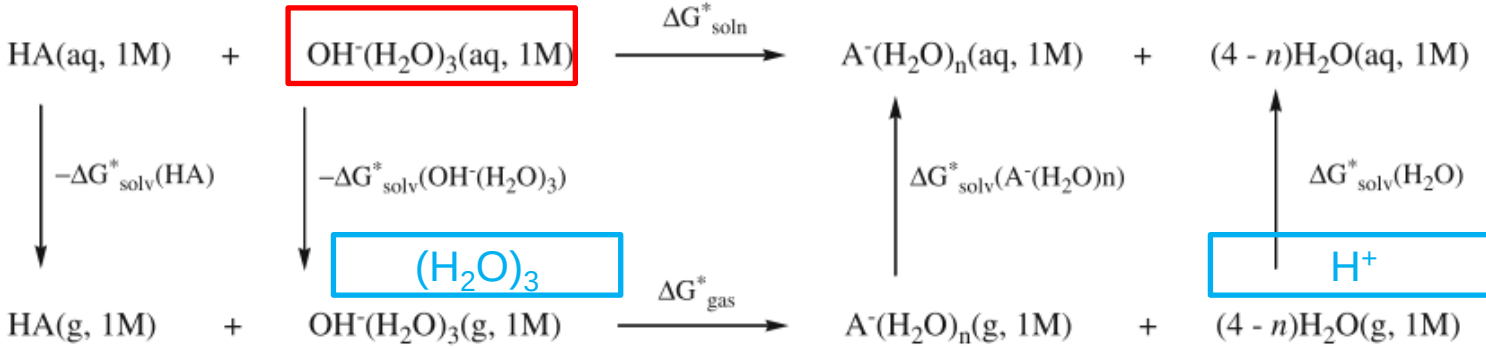
More waters are needed in the calculation of solvation free energy.

V. S. Bryantsev, M. S. Diallo, W. A. Goddard III, J. Phys. Chem. B 2008, 112, 9709–9719

Application of micro-solvation --- pK_a calculation

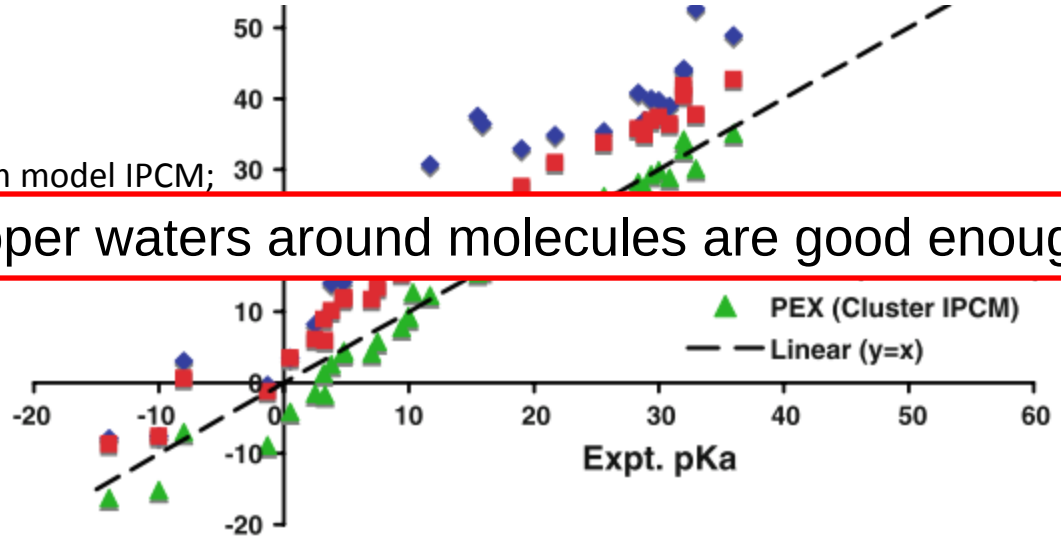
Proton exchange
Cluster-continuum

Cluster
Cluster-continuum



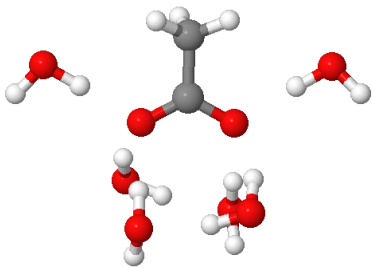
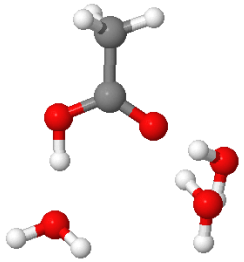
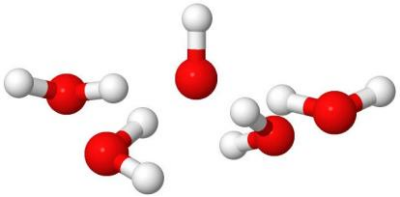
Pure IPCM: Only use the polarized continuum model IPCM;
Cluster IPCM: microsolva
PEX: proton exchange

Several proper waters around molecules are good enough.



J. Ho, M. L. Coot, Theor Chem Acc (2010) 125:3–21

How to use micro-solvation model in DFT

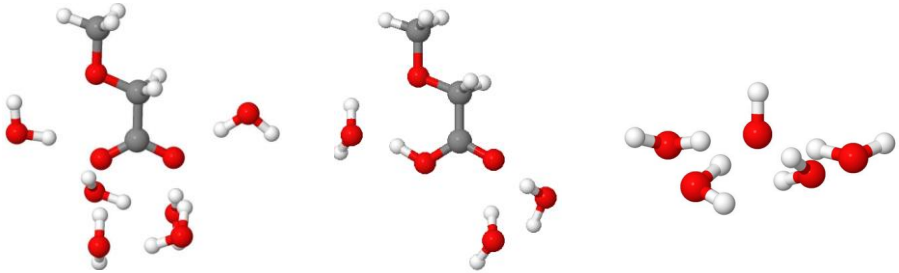
Room temperature	ΔG_{DFT} (PCM)/eV	ΔG_{DFT}/eV	ΔG_{Exp}/eV (pka=3.69)
$CH_3COOH + OH^- \rightarrow CH_3COO^- + H_2O$	-1.33	-0.69	-0.653

1. Including entropy correction: $S_{aq} = 0.54 \times S_{gas} + 2.86 \times 10^{-4}$ (eV·K^{-1})
2. We took experimental data 69.95 J/(mol·K) of water entropy considering water acts both as the role of solvent and product.

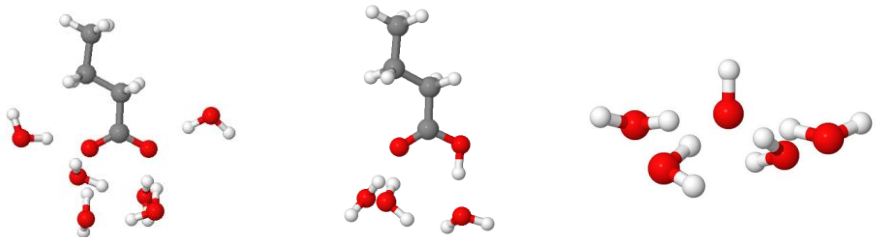
Building as many H bonds as possible in the functional group where the reaction occurs.

M. Namazian, S. Halvani, J. Chem. Thermodynamics, 2006, 38, 1495-1502
D. H. Wertz, J. Am. Chem. Soc. 1980, 102, 5316–5322

How to use micro-solvation model in DFT



Room temperature	ΔG_{DFT} (PCM)/eV	ΔG_{DFT}/eV	ΔG_{Exp}/eV (pka=3.69)
AECOOH + OH^- → AECOO^- + H_2O	-1.52	-0.55	-0.72



Room temperature	ΔG_{DFT} (PCM)/eV	ΔG_{DFT}/eV	ΔG_{Exp}/eV (pka=3.69)
BuCOOH + OH^- → BuCOO^- + H_2O	-1.28	-0.47	-0.649

M. Namazian, S. Halvani, J. Chem. Thermodynamics, 2006, 38, 1495-1502

Summary

1. Time and resources permitted, a strict micro-sovlation can be done with the help of MD;
2. In the calculation of solvation free energy, more solvent molecules give more accurate result;
3. In the pKa calculation, only the reactive functional group is needed to be surrounded by solvent molecules;
4. The combination of explicit and implicit method is needed in thermodynamic calculation.

Thanks for your attention!