METHODS FOR TREATING SOLVENT EFFECTS AND INTERMOLECULAR FORCES

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OUTLINE

• Solvation Methods
  – Explicit vs. implicit methods

• Explicit Methods
  – TIP3P, TIP4P
  – SPC, SPC/E

• EFP Method for Solvation
  – Summary of EFP1 method for water
  – Sample input files
  – Monte Carlo method
  – Example applications

• Generalized EFP Method (EFP2)
SOLVATION MODELS: CONTINUUM

- Mostly based on Onsager reaction field model
- Computationally efficient
- Sensitive to cavity size and shape
- Do not account for explicit solute-solvent interactions
SOLVATION MODELS: EXPLICIT

- Solvent molecules described using potentials
  - Empirical potentials: lots of fitted parameters
  - *Ab initio* potentials: computationally expensive
- Include explicit solute-solvent interactions
- Configurational sampling necessary: computationally demanding
Multi-Layered Approach to Solvation

Ab Initio Solute

Continuum

MM
TIP3P, TIP4P

- Jorgensen *etal*, *JCP*, 79, 926 (1983)
- Basically simple Lennard-Jones model

\[ \varepsilon_{mn} = \sum_i \sum_j \left[ \frac{q_i q_j}{r_{ij}} \right] + \frac{A}{R^{12}} - \frac{C}{R^6} \]

- \( \varepsilon_{mn} \) = interaction energy between waters m,n
- \( q_O < 0 = -2q_H \), A, C fitted to bulk properties
- Rigid molecules
- TIP4P adds a 4th center inside O toward Hs
- Very popular model; doesn’t get OO radial distribution function right: misses 2nd peak
DISCRETE/EXPLICIT MODELS

• SPC (Simple Point Charge), SPC/E
  – Berendsen *etal*, JPC, 91, 6269 (1987)
  – SPC:
    \[ \varepsilon_{mn} = \sum_i^m \sum_j^n [q_i q_j / r_{ij}] + A / R^{12} - C / R^6 \]
  – SPC same as TIP, but fitted to MD simulations of density and vaporization energy
  – Rigid molecules
  – Gets OO radial distribution function right
  – Accounts for polarizability/induction
SPC/E RDF

Curve: SPC/E
Points: exptl
General Effective Fragment Potential

§ *Discrete* solvation method

§ Fragment potential is one electron contribution to the *QM* Hamiltonian if QM part is present

§ Potentials are obtained by separate *QM* calculations depend on properties of *isolated* molecules can be systematically improved

§ Internally frozen geometries
GOALS

• Develop general approach to accurately describe intermolecular interactions
  – Solvent effects on
    • Ions and molecules
    • Chemical reaction mechanisms
    • Spectral shifts
  – Liquid behavior
  – Liquid-gas, liquid-surface interface
  – Van der Waals interactions
  – Polymer interactions
  – Enzyme interactions

• Incorporate all important physics
  – No parameter fits

• Efficient
STICKY FEET
Densely packed bundles of hairlike setae (right, 50 μm long) cover the pads of a gecko’s feet. The tips of the setae branch out into hundreds of smaller projections, known as spatulae (above, each tip is 200 nm across). These structures help geckos hang onto walls and ceilings via van der Waals interactions.

GECKO TAPE
Scientists have used diverse materials to make “gecko tapes” that mimic the lizard’s remarkable feet. Polymide gecko tape from Andre Geim’s lab at the University of Manchester, in England, is made from a mold created by a lithographic process (above right, each projection is 2 μm long). Ali Dhinojwala at Ohio’s University of Akron prepared a gecko tape made of columns of carbon nanotubes that has four times the sticking power of gecko feet (left, each column is 100 μm wide).
System is divided into

- an *ab initio* region for the “solute” and
- a *fragment* region for the solvent molecules.

\[ E = E_{ab\ initio} + E_{interaction} \]
In the most general implementation EFP should include all relevant energy contributions:

\[ E_{\text{interaction}} = E_{\text{coulomb}} + E_{\text{polarization}} + E_{\text{exch. rep.}} + E_{\text{dispersion}} + E_{\text{charge transfer}} + E_{\text{higher order terms}} \]
Interaction energy consists of: *electrostatic*, *polarization* and *exchange repulsion/charge transfer term*

$$E_{interaction} = E_{coulomb} + E_{polarization} + E_{exchange \ repulsion/charge \ transfer}$$

$$E_{interaction} = \sum_{k=1}^{K} V_{k}^{Elec}(\mu,s) + \sum_{l=1}^{L} V_{l}^{Pol}(\mu,s) + \sum_{m=1}^{M} V_{m}^{Rep}(\mu,s)$$

- Distributed Multipolar expansion
- LMO polarizability expansion
- Fit to Functional Form
Coulomb/Electrostatic Term

\[ V_k^{\text{Elec}}(\mu, s) = \frac{q_k(\mu)q_s}{r_{sk}} - \sum_a \mu_a^k(\mu)F_a(r_{sk}) - \frac{1}{3} \sum_{a,b} \Theta_{ab}^k(\mu)F_{ab}(r_{sk}) - \frac{1}{15} \sum_{a,b,c} \Omega_{abc}^k(\mu)F_{abc}(r_{sk}) \]

where \( q, \mu, \Theta \) and \( \Omega \) are the charge, dipole, quadrupole and octopole, respectively.

\( F_a, F_{ab} \) and \( F_{abc} \) are the solute electric field, field gradient and field hessian.

This DMA is a classical point multipole approach: what if fragments approach each other or solute too closely?:

Classical treatment is then too repulsive: multiply entire expression by damping term to account for overlapping charge densities:

\[ V_k^{\text{Elec}}(\mu, s) \rightarrow (1 - \beta_k(\mu)e^{-\alpha_k(\mu)r_{sk}^2})V_k^{\text{Elec}}(\mu, s) \]

All calculations done once for a given solvent molecule; e.g., water.
Polarization/Induction Term

\[ V_{l}^{Pol}(\mu) = -\sum_{a,b} F_{a}(r_{l})\alpha_{ab}^{l}(\mu)\langle F_{b}(r_{l}) \rangle \]

\[ \alpha_{xy}^{l} = \lim_{F_{y} \to 0} \frac{\mu_{x}^{l}(F_{y}) - \mu_{x}^{l}(0)}{F_{y}} \]

Polarizability is treated as a distributed tensor with each tensor located at the centroid of a localized orbital.

For water, there are five such LMOs, two O-H bond orbitals, two lone pairs, one inner shell.

F is the field due to the \textit{ab initio} part of the system.

\( \alpha_{xy}^{l} \) is a component of the polarizability of the fragment molecule in the lth localized orbital.

Iterated to self-consistency.

Polarization damping important, especially for polar or ionic species.
Exchange Repulsion/Charge Transfer Terms

Fragment-\textit{ab initio} interaction:

\[ V_{m}^{\text{Re}\, p}(\mu, s) = \sum_{j}^{J} \beta_{m,j}(\mu) e^{-\alpha_{m,j}(\mu)r_{m,s}^2} \]

Gaussian functions centered at atom centers and center of mass: J=2, M=4 for water.

Fitted to a set of dimer calculations: several values of R(O-O) for each orientation. Total of 192 points on dimer surface. Fitted to minimize:

\[ \Delta = \sum_{p}^{P} \omega_{p} \left[ \left\langle \Psi \left| \sum_{m}^{M} V_{m}^{\text{Re}\, p} \right| \Psi \right\rangle_{p} - E_{\text{rem}}^{(ab)}(P) \right]^{2} \]

\( \omega_{p} \) is a weighting factor, usually = 1.0; \( \Psi = \text{ab initio} \) wavefunction
Fragment-fragment interaction: similar, except a single exponential function is fitted to the 192 points.

Analytic gradients (first derivatives) have been derived and coded for all terms. So, one can perform geometry optimizations, transition state searches, dynamics
MENSHTUKIN REACTION: SIMON WEBB

- N. Menshutkin, *Z. Phys. Chem.*, **1890**, 5, 589; 6, 41

- $R_3N + RX \rightarrow R_4N^+X^-$

- Reaction rate increases with polarity of solvent

- How does EFP method do?
PREVIOUS CALCS

• M. Sola et al
  – \( \text{NH}_3 + \text{CH}_3\text{Br} \)
  – Two \textit{ab initio} RHF/3-21G waters
  – Continuum model for solvent
  – Free energy of activation = 8.3 kcal/mol

• J. Gao et al
  – QM/MM (AM1/TIP3P) study of \( \text{NH}_3 + \text{CH}_3\text{Cl} \)
  – Free energy of activation = 26.3

• J. Rivail et al
  – Continuum study of \( \text{NH}_3 + \text{CH}_3\text{Cl} \)
  – Free Energy of activation \( \approx 23 \) kcal/mol
EXPERIMENTAL RESULTS

- K. Okamoto et al.
  - $\text{NH}_3 + \text{CH}_3\text{I}$
  - Free energy of activation = 23.5 kcal/mol
- Nothing known for $\text{NH}_3 + \text{CH}_3\text{Br}$
COMPUTATIONAL METHODS

• NH₃ + CH₃Br (GAMESS)
• Solute treated with \textit{ab initio} methods
• Solvent treated with both \textit{ab initio} & EFP
• Geometries: RHF or MP2
• Basis set: VDZP + diffuse sp on Br
MEP FOR 2 WATERS

![Graph showing MEP for 2 waters with reaction coordinate (amu$^{1/2}$bohr) and relative energy (kcal/mol).]

- **2 EFP water molecules MEP**
- **all ab initio MEP**
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( ) = Direct
HIGHER-LEVELS OF EFP1

• DFT-based EFP (Ivana Adamovic)
  – Same general approach
  – Based on B3LYP
  – Adds some level of correlation

• MP2-based EFP (Jie Song)
  – Same general approach
  – Separate fits for exchange repulsion+CT, dispersion
  – More effective correlation, especially at long range
  – EFP-EFP done, EFP-QM in progress
SOLVENT-INDUCED UV SHIFTS: SOOHAENG YOO

• How well can EFP represent the effect of solvent on UV shifts?
  – Test case is acetone (CH$_3$C=O), n-$\rightarrow$$\pi^*$
    • Experimental data is available
  – Solute described by
    • DFT for ground state
    • Time-dependent DFT (TDDFT) for excited states
    • B3LYP functional
  – Solvent represented by EFP1/DFT
  – QM/MM (DFT/EFP) MD ground state simulations
  – Spectrum obtained from average of snapshots
Acetone (in the gas phase)

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Basis Set: DH(d,p) B3LYP DFT
Acetone + EFP1

HOMO

LUMO

All DFT: 4.481 eV; DFT/EFP: 4.461 eV
Acetone + 100 EFP1

- Optimized Snapshot
- Snapshot During MD (T=300K)
Simulated Spectrum for $n-\pi^*$

**Acetone + 100 EFP1**

(T=300K) $\langle \omega \rangle = 4.63$ eV

Using 200 MD configurations (T=300K)
Basis Set: DH(d,p)
B3LYP DFT
Experimental blueshift: 0.19~0.21 eV
GAMESS (TDDFT/EFP1): 0.21 eV
Water hexamer isomers

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- basis set: DH(d,p)

- units: kcal/mol
# Water hexamer isomers

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## Water hexamer isomers

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- basis set: DH(d,p)

- units: kcal/mol
Initial structure: 62 waters, at least 26 ps equilibration
Timestep size = 1 fs

Initial structure: 512 waters, at least 5 ps equilibration
Timestep size = 1 fs

GENERAL EFP METHOD: EFP2

- Jan Jensen
- Mark Freitag
- Ivana Adamovic
- Hui Li
- Lyuda Slipchenko
- Dan Kemp
- Tony Smith
- Peng Xu
- JCP, 112, 7300 (2000)
Interaction energy consists of: electrostatic, polarization, exchange repulsion, dispersion, and charge transfer terms.

\[
E_{\text{interaction}} = E_{\text{Coulomb}} + E_{\text{Polarization}} + E_{\text{exrep}} + E_{\text{dispersion}} + E_{\text{Charge Transfer}}
\]

Generalized EFP2 Method

- Distributed Multipolar expansion
- LMO polarizability expansion
- From first principles using LMO overlaps
- Distributed LMO dispersion from first principles

Screening: near field

Iterate to self-consistency

No Parameter Fits
Summary

If all approximations presented above are combined, $E_{exch}$ can be approximated as (provided LMOs are used)

$$E_{exch} = -2 \sum_{i \in A} \sum_{j \in B} 2 \sqrt{-\frac{2 \ln S_{ij}}{\pi}} \frac{S_{ij}^2}{R_{ij}} - 2 \sum_{i \in A} \sum_{j \in B} S_{ij} \left[ \sum_{k \in A} F_{ik}^A S_{kj} + \sum_{l \in B} F_{jl}^B S_{li} - 2T_{ij} \right]$$

$$+ 2 \sum_{i \in A} \sum_{j \in B} S_{ij}^2 \left[ -Z_j R_{ij}^{-1} + 2 \sum_{l \in B} R_{il}^{-1} + \sum_{l \in B} -Z_j R_{lj}^{-1} + 2 \sum_{k \in A} R_{kj}^{-1} - R_{ij}^{-1} \right]$$

This equation requires only the computation of intermolecular overlap and electronic kinetic energy integrals, i.e. no two-electron integrals other than those calculated once for the isolated molecules. It contains no adjustable parameters, only fixed parameters computed for the isolated molecules, such as the LMOs in some AO basis, Fock matrices in the LMO bases, and the LMO centroids of charge.

Numerical Tests
EFP2 Dispersion: Ivana Adamovic

\[ E_{\text{disp}} = \frac{C_6}{R^6} + \frac{C_7}{R^7} + \frac{C_8}{R^8} + \ldots \]

- Simplest approximation: terminate at \( C_6 \) term
  - Calculate \( E_{\text{disp}} \) using distributed LMO expansion,

\[
E_{\text{disp}} = \sum_{k \in A} \sum_{j \in B} \sum_{x,y,z} T^{kj} T^{kj}_{\alpha\beta} T^{kj}_{\gamma\delta} \int_{0}^{\infty} dv \alpha^{k}_{\alpha\gamma}(iv) \alpha^{j}_{\beta\delta}(iv) = \sum_{k \in A} \sum_{j \in B} C^{kj}_{6} / R^{kj}_{6}
\]

- In terms of dynamic polarizability over imaginary frequency range and field gradient components, \( T \)
- Accomplished using dynamic TDHF equations
  - Amos et al., JPC, 89, 2186 (1985); CPL, 278, 278 (1997)
Overlap Damping

• Based on intermolecular overlap
  – Already available for exchange repulsion
  – No fitting required, no additional cost

\[ S = \exp \left( -\frac{\alpha R^2}{2} \right) \]

\[ f_S^n = 1 - \exp(-\alpha R^2) \sum_{n=1}^{N/2} \frac{(\alpha R^2)^n}{n!} = 1 - S^2 \sum_{n=1}^{N/2} \frac{(-2 \ln |S|)^n}{n!} \]

\[ f_S^6 = 1 - S^2 \left( 1 - 2 \ln |S| + 2 \ln^2 |S| \right), \]
Charge transfer (CT)

- Excitation of electrons in A to the unoccupied orbitals of B
- Significant in ionic systems
• Some structures dominated by dispersion
  – Especially $\pi-\pi$ interactions
  – HF cannot get this right
  – DFT only with special effort
  – Requires correlated methods: MP2, CCSD(T)

• Good test of EFP
Low-energy configurations of benzene dimer

sandwich

T-shaped

parallel-displaced

High-level ab initio calculations:
M.O. Sinnokrot, E.F. Valeev, and C.D. Sherrill, JACS, 124, 10887 (2002);
Compare EFP2 with Symmetry Adapted Perturbation Theory

Sandwich & T-shape:

**SAPT**: aug-cc-pVDZ

**EFP2**: 6-311++G(3df,2p)
electrostatic with charge-charge damping term
exchange repulsion
polarization
dispersion
Polarization

sandwich

T-shaped

\[ E_{\text{polar}} \text{ kcal/mol} \]

\begin{align*}
E_{\text{polar}} & = -0.1 \text{ kcal/mol} \\
E_{\text{polar}} & = -0.2 \text{ kcal/mol} \\
E_{\text{polar}} & = -0.3 \text{ kcal/mol} \\
E_{\text{polar}} & = -0.4 \text{ kcal/mol} \\
E_{\text{polar}} & = -0.5 \text{ kcal/mol} \\
E_{\text{polar}} & = -0.6 \text{ kcal/mol} \\
E_{\text{polar}} & = -0.7 \text{ kcal/mol}
\end{align*}

Distance, Angstroms

\begin{align*}
\text{Distance, Angstroms} & = 3.5 \\
\text{Distance, Angstroms} & = 4.0 \\
\text{Distance, Angstroms} & = 4.5 \\
\text{Distance, Angstroms} & = 5.0 \\
\text{Distance, Angstroms} & = 5.5 \\
\text{Distance, Angstroms} & = 6.0 \\
\text{Distance, Angstroms} & = 4.5 \\
\text{Distance, Angstroms} & = 5.0 \\
\text{Distance, Angstroms} & = 5.5 \\
\text{Distance, Angstroms} & = 6.0 \\
\text{Distance, Angstroms} & = 6.5
\end{align*}

- Red triangle: EFP2
- Black square: SAPT
Dispersion

sandwich

T-shaped

\[ E_{\text{disp}} \text{ kcal/mol} \]

Distance, Angstroms

\[ E_{\text{disp}} \text{ kcal/mol} \]

Distance, Angstroms

- EFP2
- SAPT
Parallel-Displaced Configuration
# Benzene Dimer: Summary

<table>
<thead>
<tr>
<th>method</th>
<th>basis</th>
<th>sandwich</th>
<th>T-shape</th>
<th>parallel-displaced</th>
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<tbody>
<tr>
<td></td>
<td>R energy</td>
<td>R energy</td>
<td>R1</td>
<td>R2 energy</td>
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<tr>
<td>CCSD(T)</td>
<td>aug-cc-pVDZ</td>
<td>4.0</td>
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<td>CCSD(T)</td>
<td>aug-cc-pVQZ</td>
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<td>EFP2</td>
<td>6-311++G (3df,2p)</td>
<td>4.0</td>
<td>-2.11</td>
<td>5.2</td>
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</tbody>
</table>

distances: angstroms, energies: kcal/mol

EFP: ~.4 sec
CCSD(T): ~10 days
## Benzene Dimer: Summary

<table>
<thead>
<tr>
<th>method</th>
<th>basis</th>
<th>sandwich</th>
<th>T-shape</th>
<th>parallel-displaced</th>
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<tr>
<td></td>
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<td>R</td>
<td>energy</td>
<td>R</td>
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<tr>
<td>MP2</td>
<td>aug-cc-pVDZ</td>
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<td>aug-cc-pVTZ</td>
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<td>4.0</td>
<td>-2.11</td>
<td>5.2</td>
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</tbody>
</table>

Distances: angstroms, energies: kcal/mol

- EFP: ~0.4 sec
- MP2/QZ: ~10 hours
# Contributions to the Interaction Energy

<table>
<thead>
<tr>
<th>dimer</th>
<th>Electro-static</th>
<th>Exchange</th>
<th>Induction</th>
<th>Dispersion</th>
<th>Total</th>
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<td>-2.50</td>
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<td>parallel-displaced</td>
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<td>2.95</td>
<td>-0.31</td>
<td>-5.01</td>
<td>-2.34</td>
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</tbody>
</table>
DNA BASES: Q.T. SMITH

- Compare with Jurecka, P.; Hobza, P. J. Am. Chem. Soc. 2003, 125, 15608)
  - RI-MP2 / ext. cc-pVTZ or TZVPP geometries
  - RI-MP2/aug-cc-pVXZ (X = D, T, Q) to CBS limit energies
  - $\Delta$CCSD(T) correction added
  - Counterpoise corrected for BSSE

- EFP generated with 6-311++G(3df,2p) basis set
Guanine-Cytosine H-Bonded
RI-MP2/TVZPP optimized

CCSD(T)/CBS energy: -32.1 kcal/mol

Adenine-Thymine H-Bonded

CCSD(T)/CBS energy: -16.9 kcal/mol

EFP

<table>
<thead>
<tr>
<th>Type</th>
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<tbody>
<tr>
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<tr>
<td>TOTAL</td>
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EFP

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<td>POL</td>
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<td>DISP</td>
<td>-8.2</td>
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<tr>
<td>TOTAL</td>
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</table>
Guanine-Cytosine stacked
RI-MP2/TVZPP optimized

CCSD(T)/CBS energy: -19.0 kcal/mol

3.40 Å

Adenine-Thymine Stacked
RI-MP2/TVZPP optimized

CCSD(T)/CBS energy: -12.3 kcal/mol

3.20 Å

EFP

<table>
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<tr>
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<th>COUL</th>
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<th>DISP</th>
<th>TOTAL</th>
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<td>20.6</td>
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<td>-17.5</td>
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EFP

<table>
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<tr>
<th></th>
<th>COUL</th>
<th>REP</th>
<th>POL</th>
<th>DISP</th>
<th>TOTAL</th>
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<td>16.1</td>
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<td>-17.6</td>
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</tbody>
</table>
Benzene-water dimer

EFP:
benzene: 6-311++G(3df,2p)
water: 6-311++G(3df,3pd)
Benzene-water dimer

Experiment:
- Gotch and Zwier, JCP, 96, 3388 (1992);
- Suzuki et al., Science, 275, 942 (1992);
- MP2 & CCSD(T) data: Feller, JPCA A, 103, 7558 (1999)

-4.04 kcal/mol

3.35 Å (expt)
3.21 Å (MP2)
3.43 Å (EFP)

Experiment: CBS MP2 estimate

ZPE

EFP
## π- and H-bonding

<table>
<thead>
<tr>
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<th>electrost.</th>
<th>ex.-rep.</th>
<th>polariz.</th>
<th>disper.</th>
<th>total binding</th>
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</tr>
<tr>
<td><img src="image5.png" alt="Molecule 5" /></td>
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<td>1.78</td>
<td>-0.21</td>
<td>-2.69</td>
<td>-2.50</td>
<td>-2.09</td>
</tr>
</tbody>
</table>
Electrostatic energy in EFP

Quantum-chemical model

Classical model

\[ E^{ES} = \int \frac{\rho_1 \rho_2}{R_{12}} dv_1 dv_2 \]
\[ = \int \rho_1 V_2(1) dv_1 \]

\[ E^{ES} = \sum (q_1 q_2 T^{ch} + (q_1 \mu_2 - q_2 \mu_1) T^{dip} - \mu_1 \mu_2 T^{quad} + \ldots ) \]

multipole expansion @ each atom and bond mid-point
Electrostatic energy in EFP

Quantum-chemical model

Classical model

Charge-penetration energy:
\[ E_{\text{ch-pen}} = E_{\text{ES quant-chem}} - E_{\text{ES classical}} \]

multipole expansion @ each atom and bond mid-point
Damping of potential

Hydrogen-like atom & proton

Exact quantum-chemical solution:

\[ V = -\frac{e}{R} (1 - \exp(-2ZR)(1+ZR)) \]

Classical charge potential

Damping function

V\text{\,\,ch} = q/R \, f_{\text{damp}}

\[ f_{\text{damp}} = (1 - \exp(-\alpha R)) \]

Damping coefficients \( \alpha \) are determined by minimizing the difference between \textit{ab initio} and classical damped potential:

\[ \Delta = \sum_{\text{grid}} (V_{\text{\,ab initio}} - V_{\text{\,damped classical}})^2 \]

Higher multipole moments are damped in a similar way.
Electrostatic damping: summary

- Computationally not expensive
- Stable minimization procedure for determining damping parameters
- Recovers more than 70% of the penetration energy
Polarization/Induction

- Distributed polarizability tensors $\alpha_{\alpha\beta}$ at LMO centroids from coupled Hartree-Fock equations

\[ \Delta \mu_a^\gamma = \alpha_{\gamma\alpha}^a (F_{\alpha}^a + \sum_{b \neq a} T_{\alpha\beta}^{ab} \Delta \mu_b^b) \]

Induced dipole

- Induced dipole polarizability tensors
- Field due to static multipoles
- Field due to other induced dipoles
Polarization collapse

\[
(\alpha^a)_{\alpha\beta}^{-1} \Delta \mu^a_{\beta} - \sum_{b \neq a} T^{ab}_{\alpha\beta} \Delta \mu^b_{\beta} = F^a_{\alpha}
\]

\[
B_{\alpha\beta} = \sum_{b\beta} B^{ab}_{\alpha\beta} \Delta \mu^b_{\beta} = F^a_{\alpha}
\]

\[
\Delta \mu^a_{\alpha} = \sum_{b\beta} (B^{-1})^{ab}_{\alpha\beta} F^b_{\beta}
\]

at small \( R \) ➞
matrix \( B \) ceases to be positive definite,
elements of \( (B)^{-1} \) diverge ➞
polarization collapse
Damping of polarization

H₂O ⋅⋅⋅⋅⋅ H-O-H

O-O displacement from Re, angstroms

O-O displacement from Re, angstroms

polarization energy, kcal/mol

EFP: no screen
EFP: screen=2.0
EFF: screen=1.5
EFP: screen=1.2
EFP: screen=1.0
RVS
Damping of polarization

---

Damping of polarization is illustrated in the graph below, depicting the relationship between O-O displacement from Re (in angstroms) and polarization energy (in kcal/mol). The graph shows different energy levels for various electron correlation methods and screen settings:

- **EFP: no screen**
- **EFP: screen=2.0**
- **EFF: screen=1.5**
- **EFP: screen=1.2**
- **EFP: screen=1.0**
- **RVS**

The graph highlights the impact of different electron correlation methods and screen settings on the damping of polarization energy, with distinct markers indicating the energy levels at various O-O displacement points. The graph indicates a collapse of energy levels at certain displacement points, reflecting the effectiveness of different methods in reducing polarization energy.
Water dimer

H₂O .... H-O-H

- Total binding energy, kcal/mol
- O-O displacement from Re, angstroms
- SCF
- MP2
- EFP no screen
- EFP with screen
F⁻ (H₂O)ₙ

EFP: -22.3
MP2: -20.8
Expt: -23.3

EFP: -39.9
MP2: -38.2
Expt: -42.5

EFP: -54.5
MP2: -54.0
Expt: -57.8

EFP: -67.7
MP2: -66.7
Expt: -71.7

EFP: 6-311++G(3df,2p)

MP2/6-311++G(2df,p): Kemp and Gordon, JPC A, 109, 7689 (2005);

Experiment: Arshadi, Yamdagni, Kebarle, JPC, 74, 1475 (1970);
Hiraoka, Mizuse, Yamabe, JPC 92, 3943 (1988)
\[ \text{NH}_4^+ - (\text{NH}_3)_n \]

EFP: -21.6
MP2: -22.8
QCISD: -22.5
Expt: -21.5$^a$
-24.8$^b$
-25.4$^c$
-27.0$^d$

EFP: -39.1
MP2: -39.7

EFP: -53.6
MP2: -53.1

EFP: 6-311++G(3df,2p)
MP2/6-31+G*, QCISD/6-311++G**: Wang, Chang, Jiang, Lin, CP, 276, 93 (2001);
Experiments: $^a$Arshadi, Futrell, JPC, 78, 1482 (1974); $^b$Kebarle, RPC, 28, 455 (1977);
$^c$Tang, Castleman, JCP, 62, 4576 (1972); $^d$Searles, Kebarle, JPC, 72, 742 (1986);
CURRENT LIMITATIONS

- **EFP1 is for water only**
  - QM part can be any level of theory
  - Solvent must be water

- **EFP2 can be generated for any species**
  - Interface with QM is limited.
Simplest is Onsager self-consistent reaction field (SCRF) model ($SCRF$)
- Solute (QM) dipole moment $\mu$ polarizes “medium” (solvent) through dielectric $\varepsilon$
- Newly polarized solvent alters solute dipole moment
- Iterated to self-consistency
- Accomplished by adding new term to QM Hamiltonian
ONSAGER SCRF MODEL

- $V_{\sigma} = -r \cdot R$
  - $r =$ position vector
  - $R$ is proportional to molecular dipole moment
  - $R = g \mu$
  - $\mu =$ dipole vector
  - $g = 2 (\varepsilon - 1)/[(2 \varepsilon + 1)(a^3)]$
  - $a =$ radius of cavity
  - Usually assume spherical cavity
  - Radius can be pretty arbitrary
  - Adds simple $<\chi_i|\chi_j>$ integrals - very cheap
PCM MODEL

- Polarizable Continuum Model (PCM)
  - Van der Waals type surface cavity
  - Uses detailed knowledge of electrostatic potential
  - Cavity dispersion potential determined from surface area
  - Can include dispersion effects
  - Interfaced with EFP in GAMESS: $PCM$
  - See both input and reference sections in manual
OTHER METHODS

• COSMO
  – Initially developed by Klamt
  – Further developed by Baldridge (U. Zurich)
  – No gradients, not interfaced with EFP

• SVP
  – Chipman (Notre Dame Radiation Laboratory)
  – Accounts for charge leakage outside cavity

• SM5
  – Truhlar, Cramer (Minnesota)
  – Highly parametrized, interfaced with GAMESS