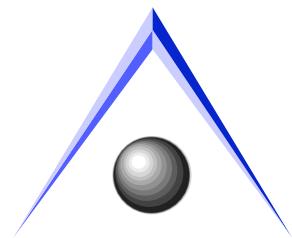


METHODS FOR TREATING SOLVENT EFFECTS AND INTERMOLECULAR FORCES

Mark S. Gordon
Iowa State University
Ames Laboratory



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)

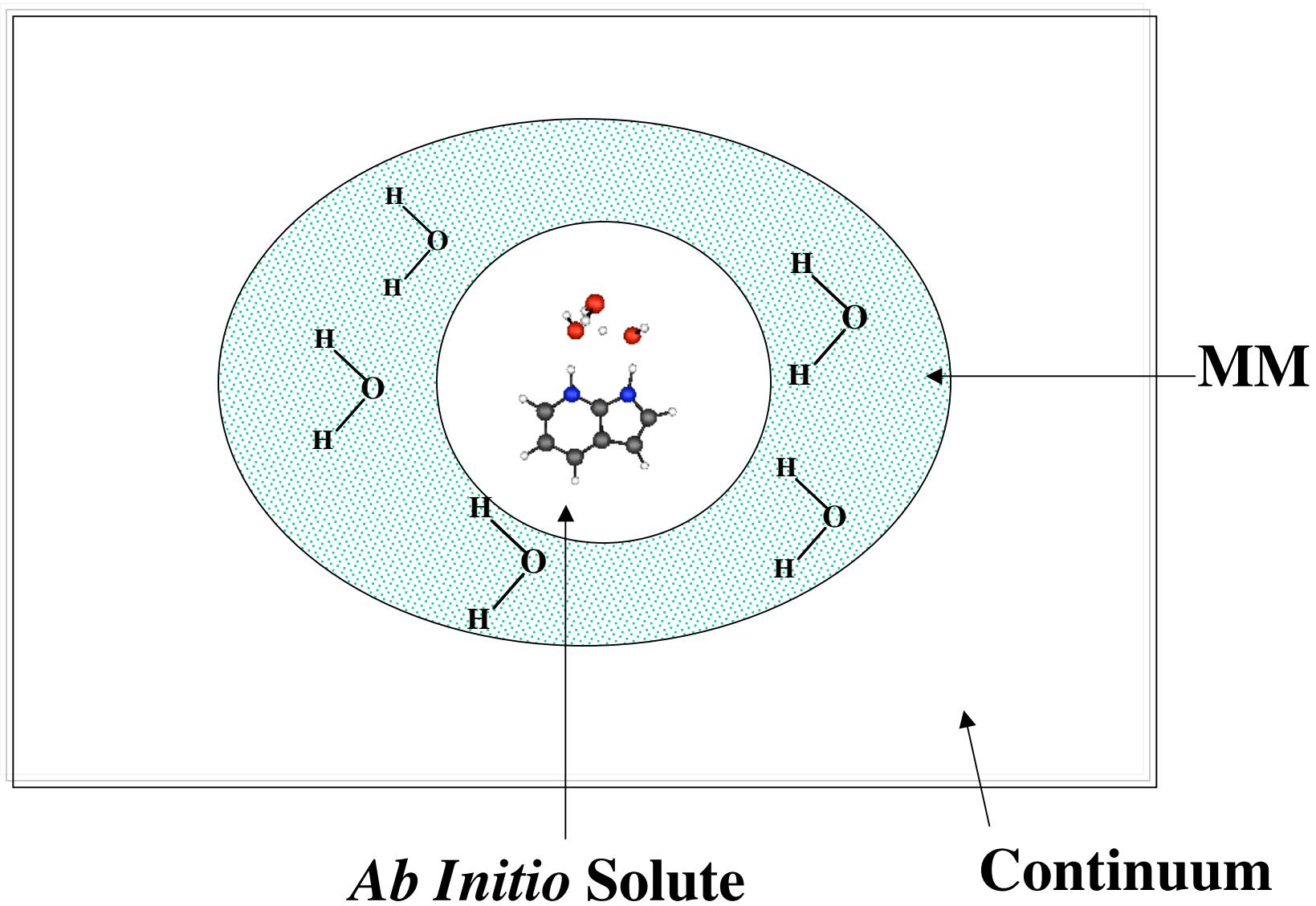
SOLVATION MODELS: CONTINUUM

- 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



DISCRETE/EXPLICIT MODELS

- TIP3P, TIP4P
 - Jorgensen *et al*, JCP, 79, 926 (1983)
 - Basically simple Lennard-Jones model

$$\varepsilon_{mn} = \sum_i^m \sum_j^n [q_i q_j / r_{ij}] + A / R^{12} - C / R^6$$

- ε_{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

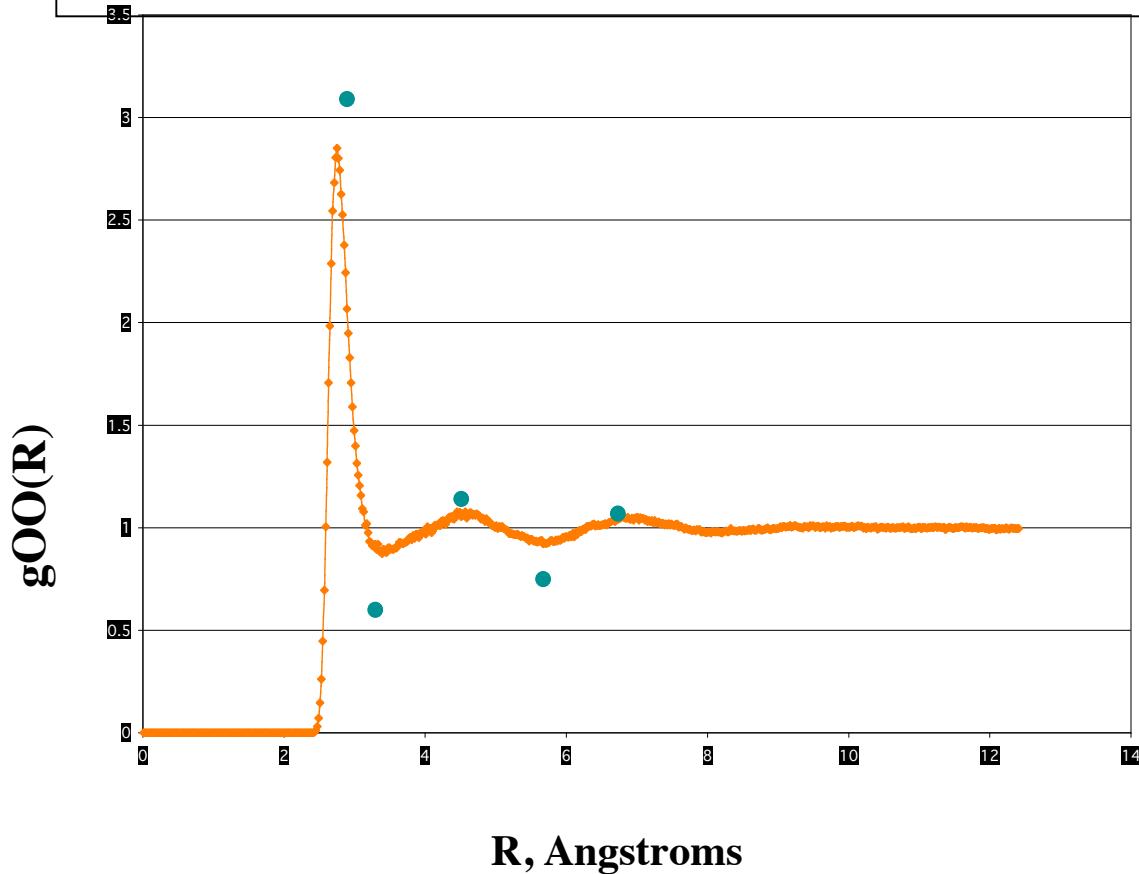
- SPC (Simple Point Charge), SPC/E

- Berendsen *et al*, 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

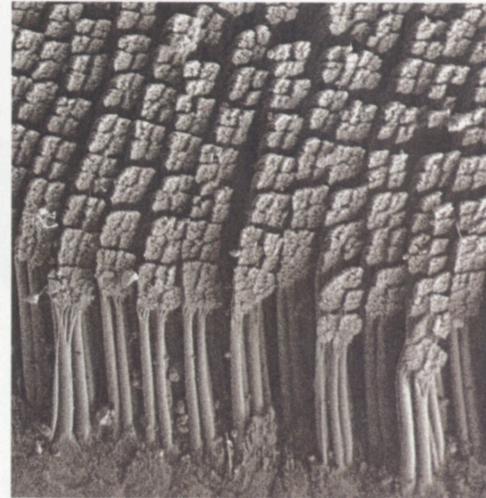
- Develop general approach to accurately describe intermolecular interactions
 - Solvent effects on
 - Ions and molecules
 - Chemical reaction mechanisms
 - Spectral shifts
 - Liquid behavior
 - Liquid-gas, liquid-surface interface
 - Van der Waals interactions
 - Polymer interactions
 - Enzyme interactions
- Incorporate all important physics
 - *No parameter fits*
- Efficient

KELLAR AUTUMN / BOTHY



STICKY FEET

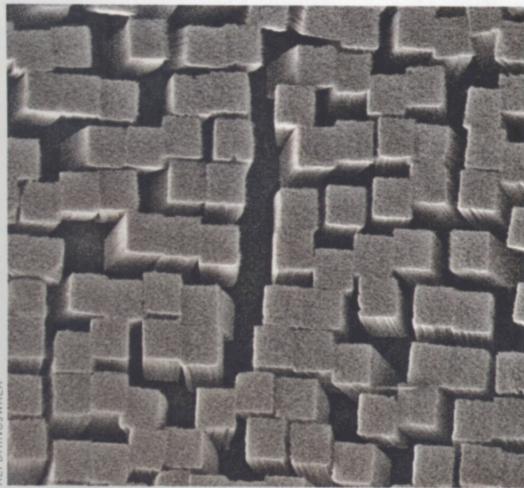
Densely packed bundles of hairlike setae (right, 50 μm long) cover the pads of a gecko's feet. The tips of the setae branch out into hundreds of smaller projections, known as spatulae (above, each tip is 200 nm across). These structures help geckos hang onto walls and ceilings via van der Waals interactions.



DREAMTIME



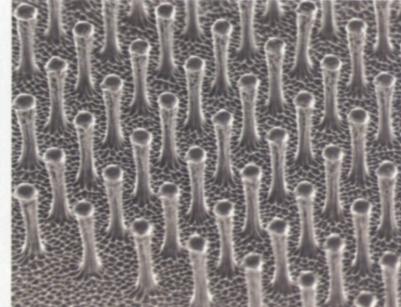
ALI DHINOWALA



GECKO TAPE

Scientists have used diverse materials to make "gecko tapes" that mimic the lizard's remarkable feet. Polyimide 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 Dhinowala 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).

ANDRE GEIM



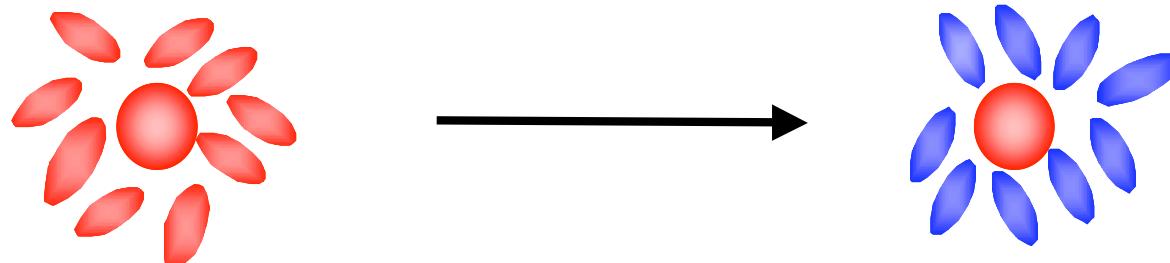
Effective Fragment Potential

System is divided into

an *ab initio* region for the “solute” and

a fragment region for the solvent molecules.

$$E = E_{\text{ab initio}} + E_{\text{interaction}}$$



General EFP Method

In the most general implementation EFP should include all relevant energy contributions:

$$E_{\text{interaction}} = E_{\text{coulomb}} + E_{\text{polarization}} + E_{\text{exch. rep.}} + E_{\text{dispersion}} + E_{\text{charge transfer}} + E_{\text{higher order terms}}$$

Hartree Fock based EFP

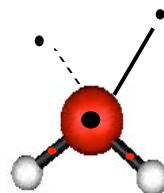
Interaction energy consists of : *electrostatic, polarization and exchange repulsion/charge transfer term*

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

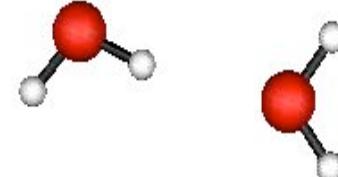
$$E_{\text{interaction}} = \sum_{k=1}^K V_k^{\text{Elec}}(\mu, s) + \sum_{l=1}^L V_l^{\text{Pol}}(\mu, s) + \sum_{m=1}^M V_m^{\text{Re } p}(\mu, s)$$



Distributed
Multipolar expansion



LMO polarizability
expansion



Fit to Functional
Form

Coulomb/Electrostatic Term

$$V_k^{Elec}(\mu, s) = \frac{q_k(\mu)q_s}{r_{sk}} - \sum_a^{\text{x,y,z}} \mu_a^k(\mu) F_a(\mathbf{r}_{sk}) - \frac{1}{3} \sum_{a,b}^{\text{x,y,z}} \Theta_{ab}^k(\mu) F_{ab}(\mathbf{r}_{sk}) - \frac{1}{15} \sum_{a,b,c}^{\text{x,y,z}} \Omega_{abc}^k(\mu) F_{abc}(\mathbf{r}_{sk})$$

where q , μ , Θ and Ω 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

$$V_l^{Pol}(\mu) = - \sum_{a,b}^{x,y,z} F_a(\mathbf{r}_l) \alpha_{ab}^l(\mu) \langle F_b(\mathbf{r}_l) \rangle$$

$$\alpha_{xy}^l = \lim_{F_y \rightarrow 0} \frac{\mu_x^l(F_y) - \mu_x^l(0)}{F_y}$$

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 *ab initio* part of the system

α_{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-*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:

$$\Delta = \sum_p^P w_p \left[\left\langle \Psi \left| \sum_m^M V_m^{\text{Re } p} \right| \Psi \right\rangle_p - E_{rem}^{(ab)}(p) \right]^2$$

ω_p is a weighting factor, usually = 1.0; Ψ = *ab initio* wavefunction

Exchange Repulsion/Charge Transfer Terms

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

MENSHUTKIN REACTION:

SIMON WEBB

- N. Menshutkin, *Z. Phys. Chem.*, **1890**, 5, 589; 6, 41
 - $\text{R}_3\text{N} + \text{RX} \rightarrow \text{R}_4\text{N}^+\text{X}^-$
- Reaction rate increases with polarity of solvent
- How does EFP method do?

PREVIOUS CALCS

- M. Sola et al
 - NH₃ + CH₃Br
 - Two *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 NH₃ + CH₃Cl
 - Free energy of activation = 26.3
- J. Rivail et al
 - Continuum study of NH₃ + CH₃Cl
 - Free Energy of activation ≈ 23 kcal/mol

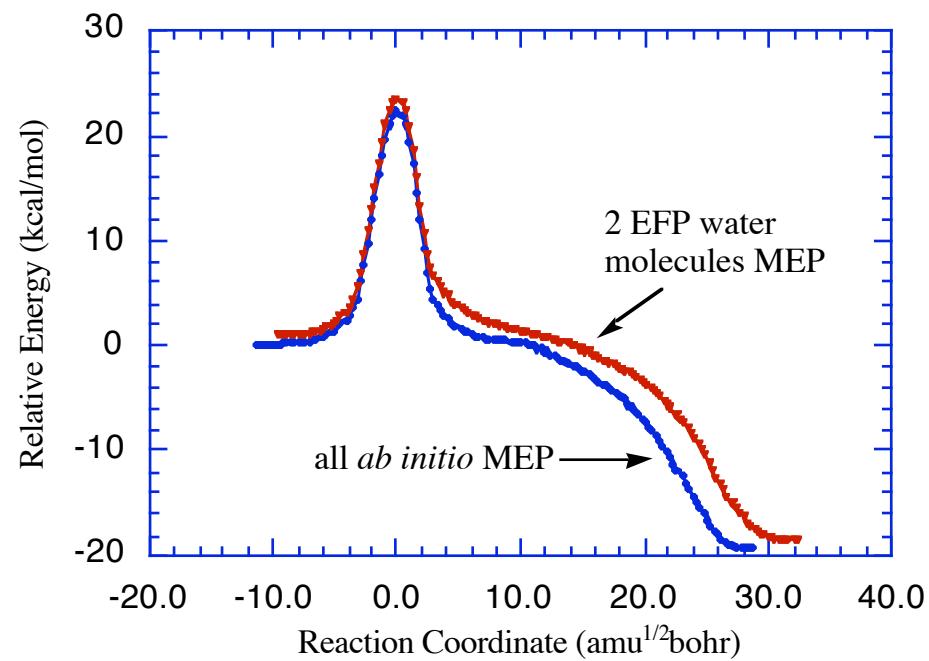
EXPERIMENTAL RESULTS

- 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 *ab initio* methods
- Solvent treated with both *ab initio* & EFP
- Geometries: RHF or MP2
- Basis set: VDZP + diffuse sp on Br

MEP FOR 2 WATERS



# waters			ΔE (kcal/mol)	
			EFP	AI
0		I-P REAC	0.0	
		TS		34.0
		I-P PROD		-4.7
2		I-P REAC	0.0	0.0
		TS	22.5	22.2
		I-P PROD	-19.4	-19.2
4	A	I-P REAC	3.9	3.5
		TS	17.6	16.9
		I-P PROD	-30.7	-31.2
4	B	I-P REAC	0.0	0.0
		TS	18.0	17.5
		I-P PROD	-26.2	-26.3
6	A	I-P REAC	0.9	0.0
		TS	23.0	20.3
		I-P PROD	-19.6	-23.5
6	B	I-P REAC	0.0	0.0
		TS	16.0	15.6
		I-P PROD	-29.1	-28.8
8		I-P REAC	0.0	0.0
		TS	20.3	19.4
		I-P PROD	-31.4	-31.3

# waters	ΔG_{298} (kcal/mol)	
	EFP	AI
0	I-P REAC	0.0
	TS	40.6
	I-P PROD	2.8
2	I-P REAC	0.0
	TS	28.3
	I-P PROD	-10.2
8	I-P REAC	0.0
	TS	22.7
	I-P PROD	-23.8

TIMINGS

# Waters	Wall Clock				Δ (Wall Clock)	
	0	8	8	9	AI	EFP
2		4006	1376		3117	487
		(5399)	(2118)		(3672)	(391)
4		11768	1658		7762	282
		(17905)	(2422)		(12506)	(304)
6		-	2054		-	396
		(26684)	(2981)		(8779)	(559)
8		-	1752		-	221
		(45029)	(3134)		(18345)	(153)

() = 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

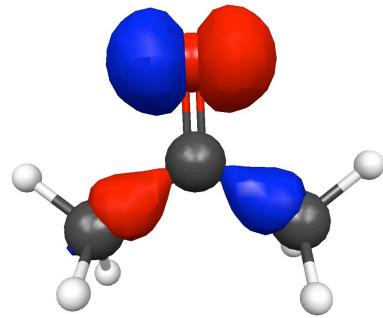


SOLVENT-INDUCED UV SHIFTS: SOOHAENG YOO

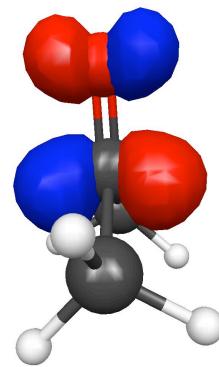
- How well can EFP represent the effect of solvent on UV shifts?
 - Test case is acetone ($\text{CH}_3\text{C=O}$), $n \rightarrow \pi^*$
 - Experimental data is available
 - Solute described by
 - DFT for ground state
 - Time-dependent DFT (TDDFT) for excited states
 - B3LYP functional
 - Solvent represented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



Acetone (in the gas phase)



HOMO (n)

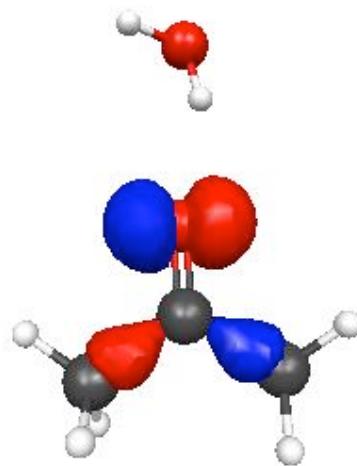


LUMO (π^*)

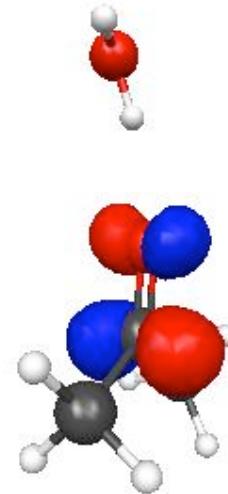
	QM	Experiment
$\omega(n \rightarrow \pi^*)$	4.42 eV	4.48 eV

Basis Set: DH(d,p)
B3LYP DFT

Acetone + EFP1



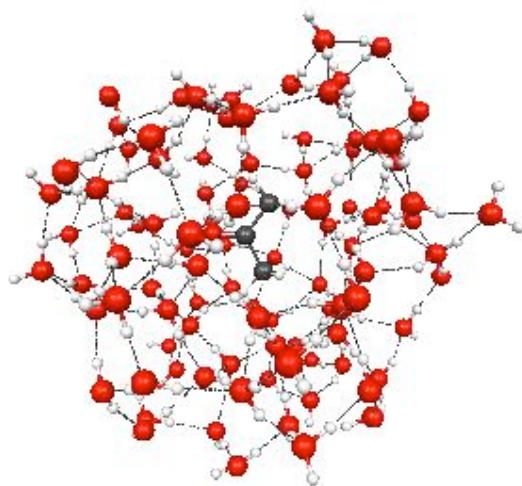
HOMO



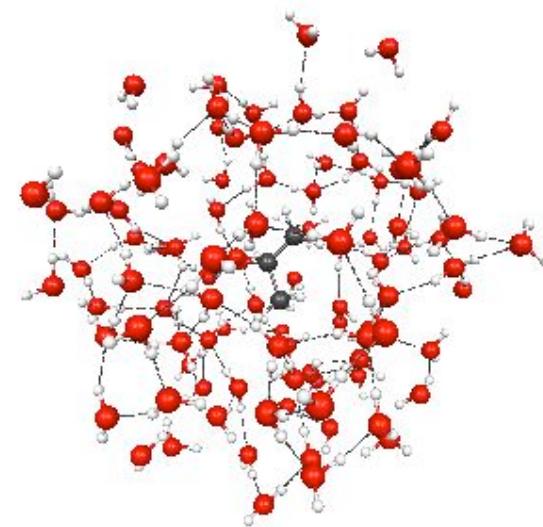
LUMO

All DFT: 4.481 eV; DFT/EFP: 4.461 eV

Acetone + 100 EFP1



Optimized Snapshot

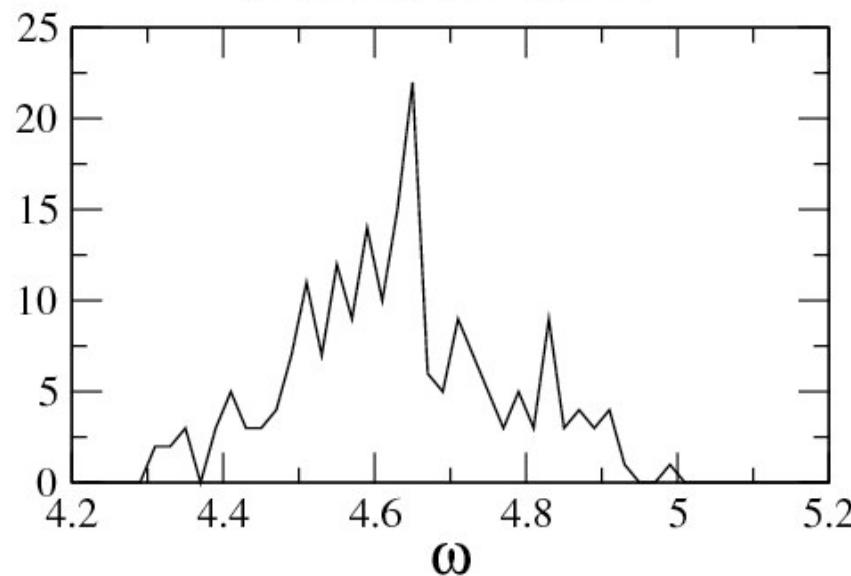


Snapshot During MD (T=300K)

Simulated Spectrum for n-> π^*

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

Binding Energy	DFT B3LYP	MP2	CCSD (T)	HF
prism	62.37	58.25	55.10	42.86
cage	61.84	57.52	54.30	42.49
book	61.34	56.49	53.10	42.44
cyclic	60.57	55.75	52.20	43.10
boat	59.13	54.29	50.80	42.12

- basis set: DH(d,p)

-units: kcal/mol

Water hexamer isomers

Binding Energy	DFT B3LYP	EFP1/ DFT	MP2	CCSD (T)	HF	EFP1/ HF
prism	62.37	61.08	58.25	55.10	42.86	42.42
cage	61.84	61.53	57.52	54.30	42.49	41.90
book	61.34	61.79	56.49	53.10	42.44	41.45
cyclic	60.57	60.65	55.75	52.20	43.10	41.14
boat	59.13	59.37	54.29	50.80	42.12	40.09

- basis set: DH(d,p)

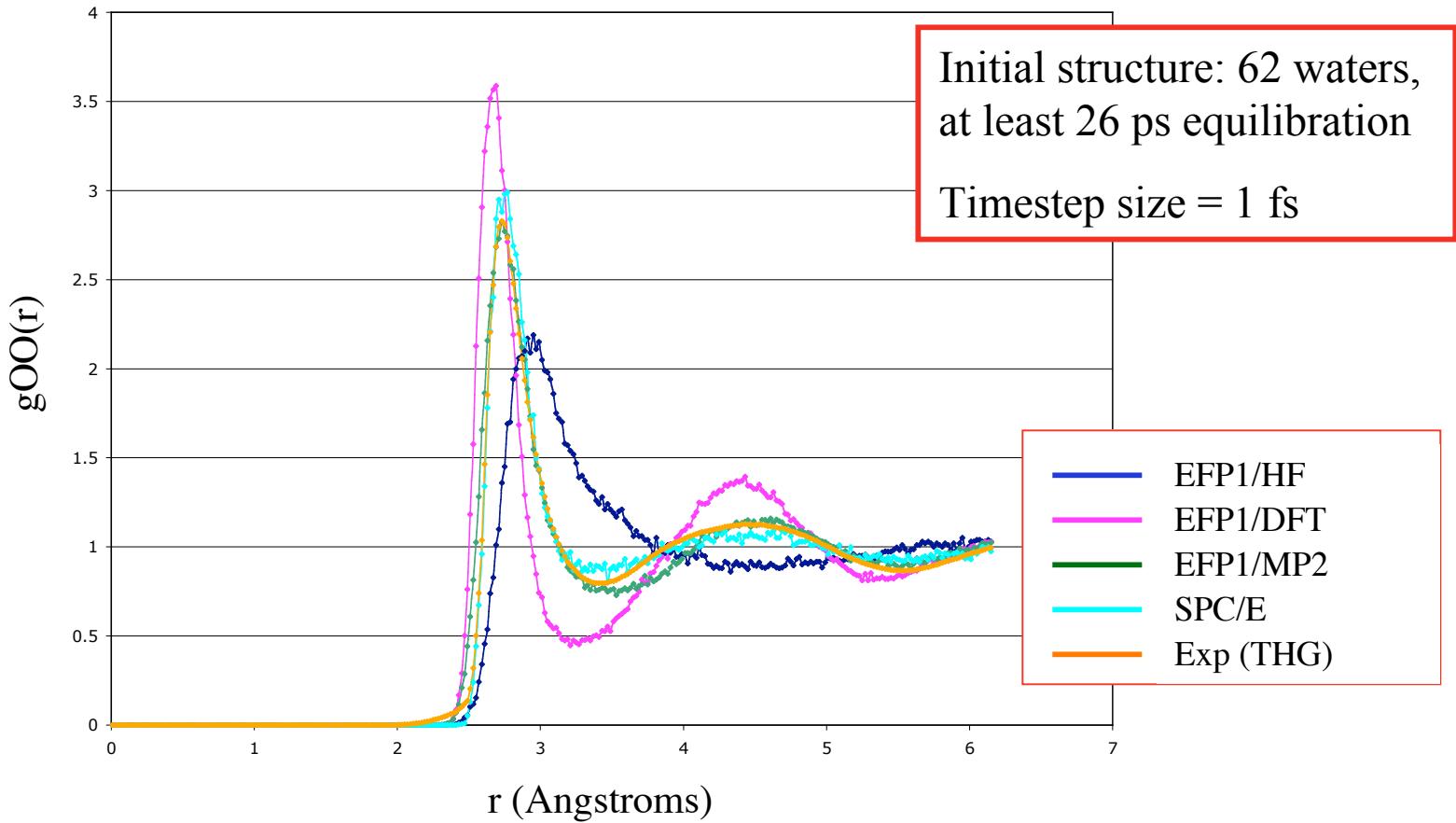
-units: kcal/mol

Water hexamer isomers

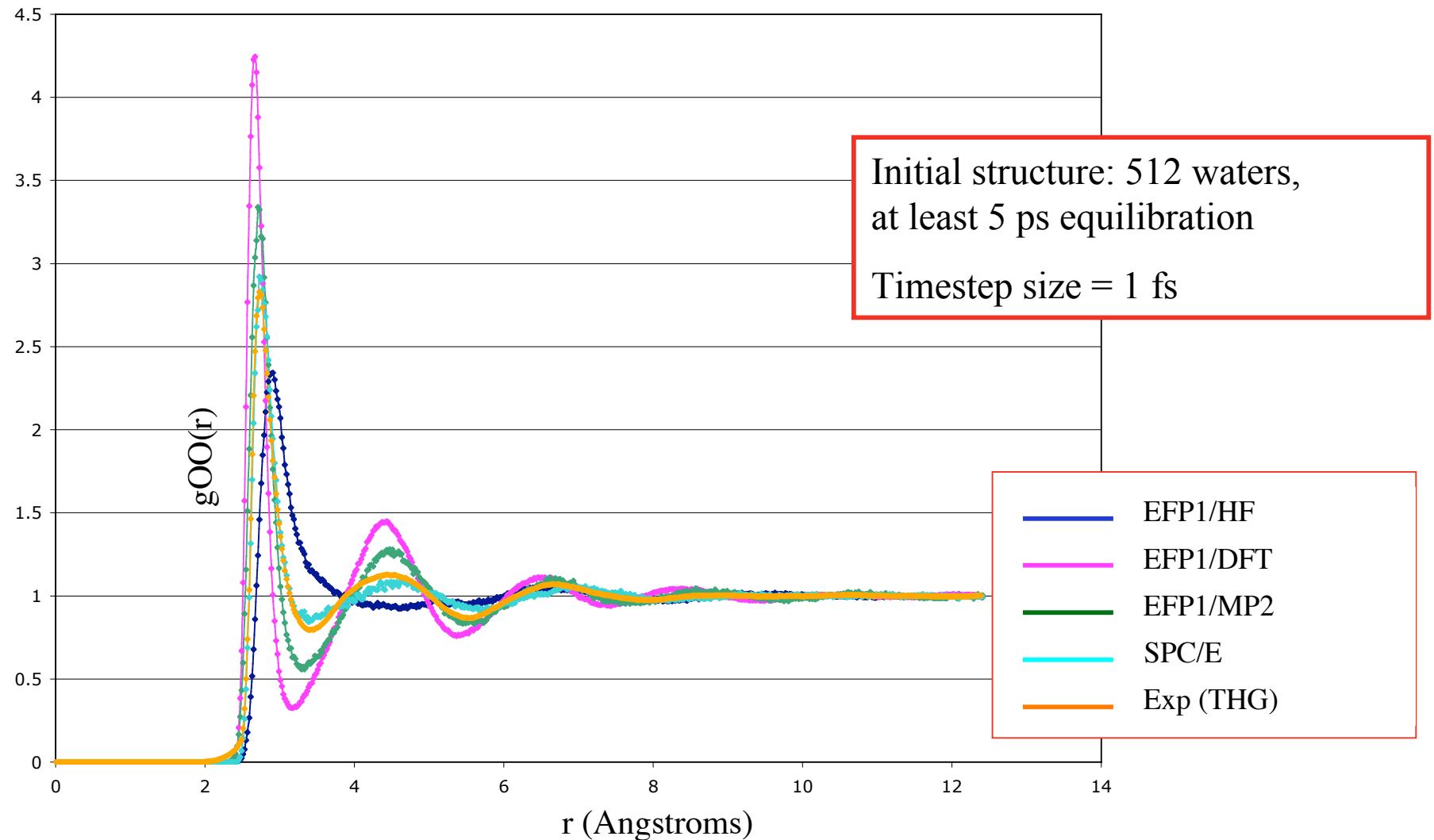
Binding Energy	DFT B3LYP	EFP1/ DFT	MP2	EFP1/ MP2	CCSD (T)	HF	EFP1/ HF
prism	62.37	61.08	58.25	58.26	55.10	42.86	42.42
cage	61.84	61.53	57.52	57.64	54.30	42.49	41.90
book	61.34	61.79	56.49	56.67	53.10	42.44	41.45
cyclic	60.57	60.65	55.75	55.24	52.20	43.10	41.14
boat	59.13	59.37	54.29	53.92	50.80	42.12	40.09

- basis set: DH(d,p)

-units: kcal/mol



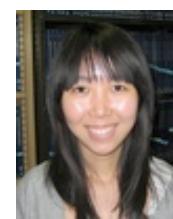
Exp (THG): X-ray; Sorenson et. al. J. Chem. Phys. **113**, 9149 (2000).



Exp (THG): X-ray; Sorenson et. al. J. Chem. Phys. **113**, 9149 (2000).

GENERAL EFP METHOD: EFP2

- Jan Jensen
- Mark Freitag
- Ivana Adamovic
- Hui Li
- Lyuda Slipchenko
- Dan Kemp
- Tony Smith
- Peng Xu
- Mol. Phys., 89, 1313 (1996)
- JCP, 108, 4772 (1999)
- JCP, 112, 7300 (2000)
- Mol. Phys., 103, 379 (2005)
- Mol. Phys., 107, 999 (2009)

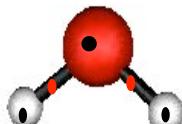


Generalized EFP2 Method

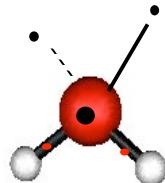
Interaction energy consists of : *electrostatic, polarization, exchange repulsion, dispersion, and charge transfer terms*

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

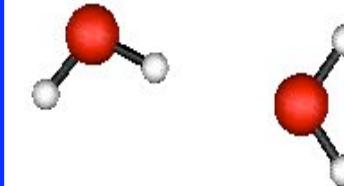
No Parameter Fits



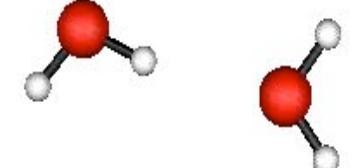
Distributed
Multipolar expansion



LMO polarizability
expansion



From first principles
using LMO overlaps



Distributed LMO dispersion
from first principles

Screening: near field

Iterate to self-consistency

Summary

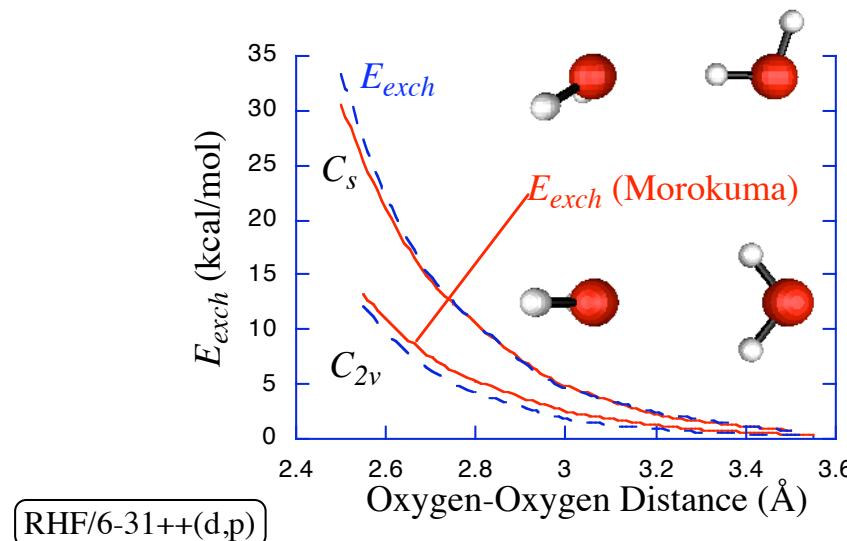
If all approximations presented above are combined, E_{exch} can be approximated as (provided LMOs are used)

$$E_{exch} \approx -2 \sum_{i \in A} \sum_{j \in B} 2 \sqrt{\frac{-2 \ln S_{ij}}{\pi}} \frac{S_{ij}^2}{R_{ij}} - 2 \sum_{i \in A} \sum_{j \in B} S_{ij} \left[\sum_{k \in A} F_{ik}^A S_{kj} + \sum_{l \in B} F_{jl}^B S_{li} - 2T_{ij} \right] \\ + 2 \sum_{i \in A} \sum_{j \in B} S_{ij}^2 \left[\sum_{J \in B} -Z_J R_{iJ}^{-1} + 2 \sum_{l \in B} R_{il}^{-1} + \sum_{I \in B} -Z_I R_{Ij}^{-1} + 2 \sum_{k \in A} R_{kj}^{-1} - R_{ij}^{-1} \right]$$

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

$$E_{disp} = \frac{C_6}{R^6} + \frac{C_7}{R^7} + \frac{C_8}{R^8} + \dots$$



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

$$E_{disp} = \sum_{k \in A} \sum_{j \in B} \sum_{\alpha\beta\gamma\delta}^{x,y,z} T_{\alpha\beta}^{kj} T_{\gamma\delta}^{kj} \int_0^\infty dv \alpha_{\alpha\gamma}^k(iv) \alpha_{\beta\delta}^j(iv) = \sum_{k \in A} \sum_{j \in B} C_6^{kj} / R_6^{kj}$$

- 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

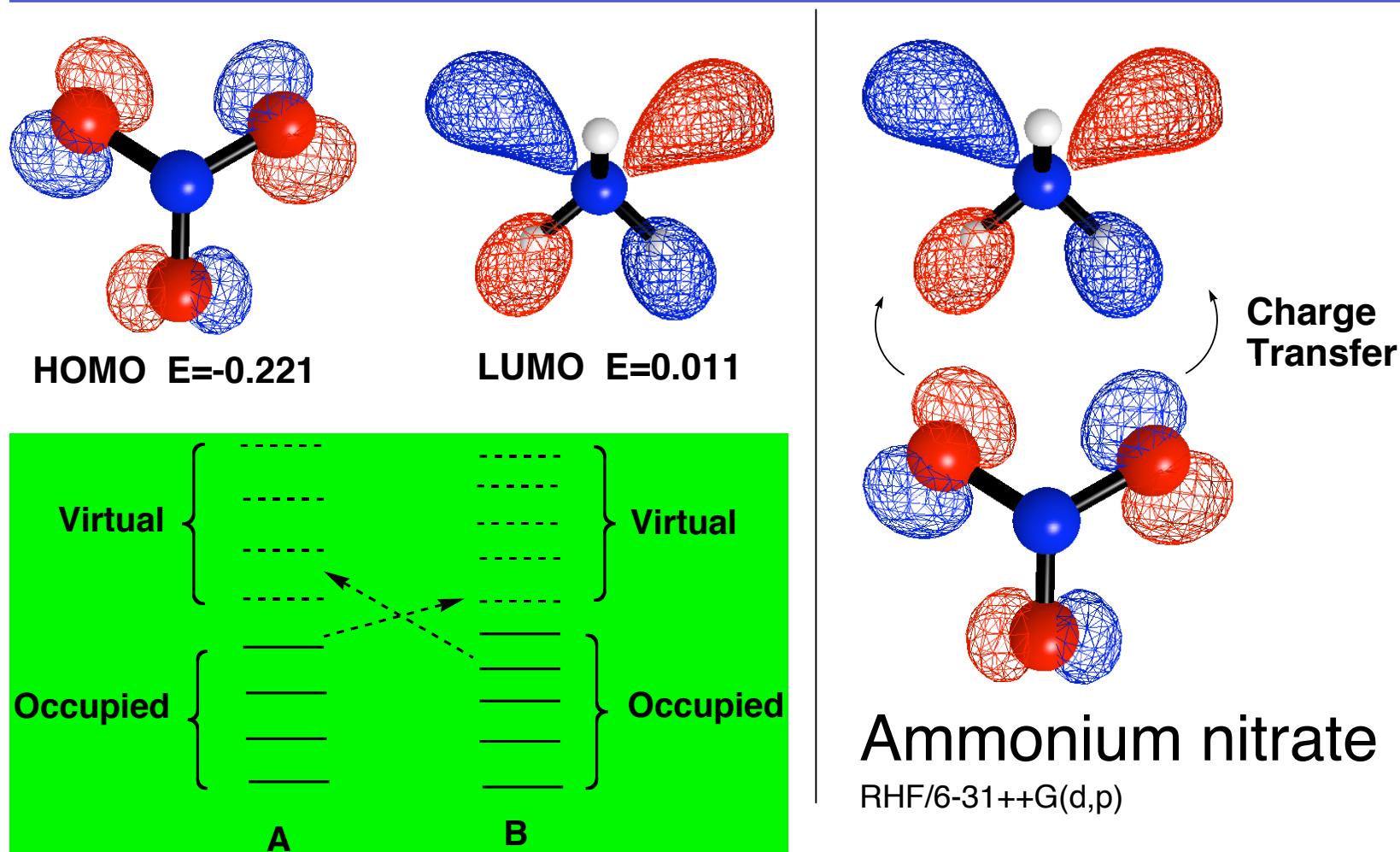
- Based on intermolecular overlap
 - Already available for exchange repulsion
 - No fitting required, no additional cost

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

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

$$f_S^6 = 1 - S^2 (1 - 2 \ln |S| + 2 \ln^2 |S|),$$

Charge transfer (CT)



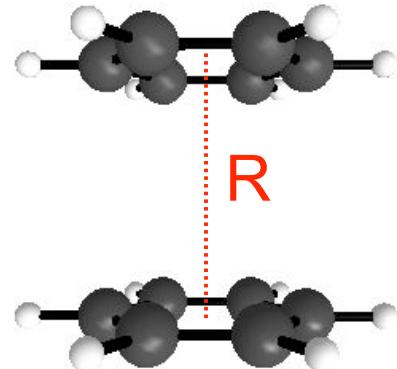
- Excitation of electrons in A to the unoccupied orbitals of B
- Significant in **ionic systems**

Benzene Dimer: Lyuda Slipchenko

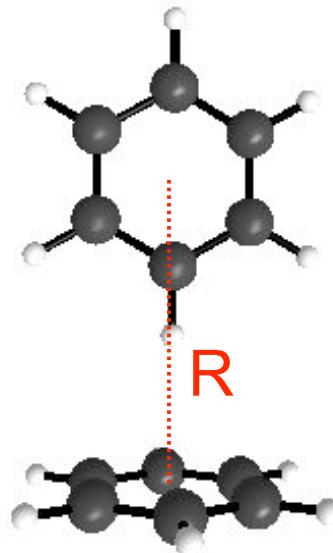
- **Some structures dominated by dispersion**
 - Especially $\pi-\pi$ interactions
 - HF cannot get this right
 - DFT only with special effort
 - Requires correlated methods: MP2, CCSD(T)
- **Good test of EFP**



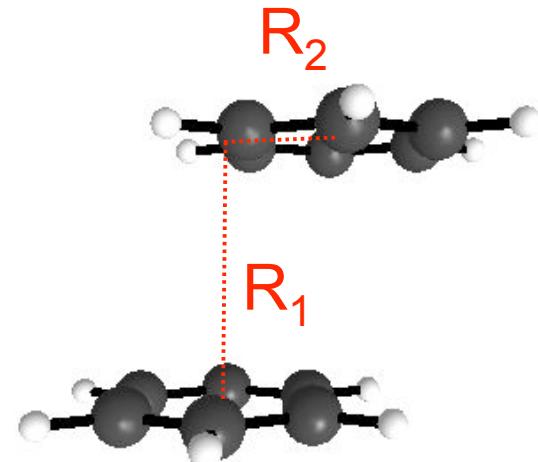
Low-energy configurations of benzene dimer



sandwich



T-shaped



parallel-displaced

High-level *ab initio* calculations:

M.O. Sinnokrot, E.F. Valeev, and C.D. Sherrill,

JACS, 124, 10887 (2002);

M.O. Sinnokrot and C.D. Sherrill, JPC, 108, 10200 (2004)

Compare EFP2 with Symmetry Adapted Perturbation Theory

Sandwich & T-shape:

SAPT: aug-cc-pVDZ

M.O. Sinnokrot and C.D. Sherrill, JPC, **108**, 10200 (2004)

EFP2: 6-311++G(3df,2p)

electrostatic with charge-charge damping term

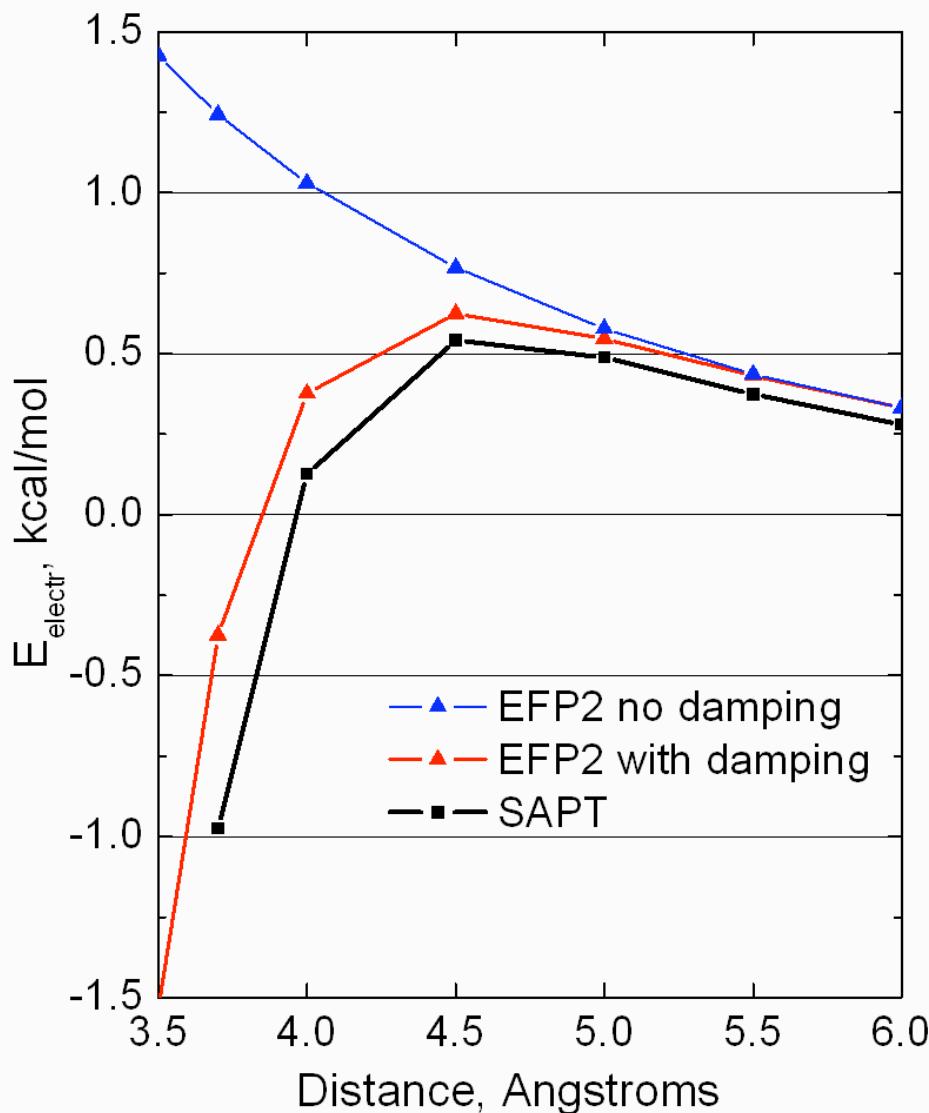
exchange repulsion

polarization

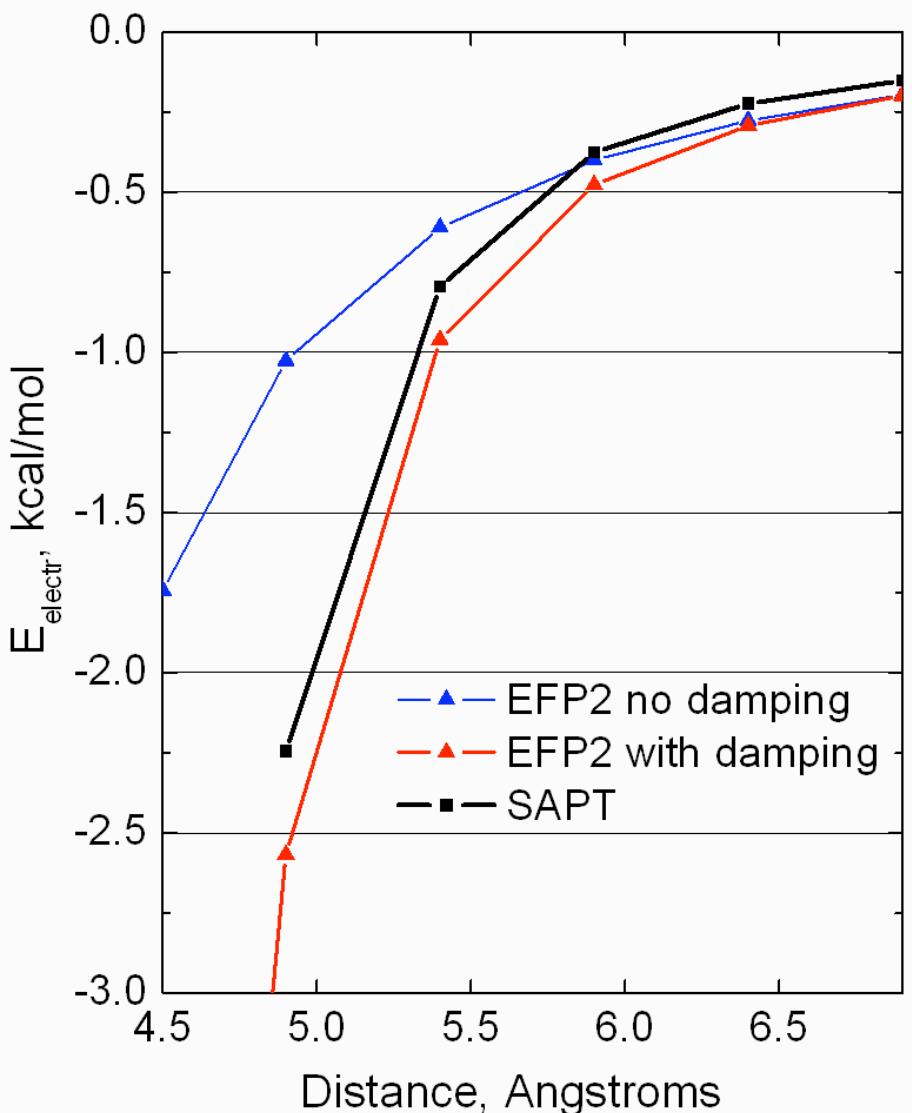
dispersion

Electrostatic Term

sandwich

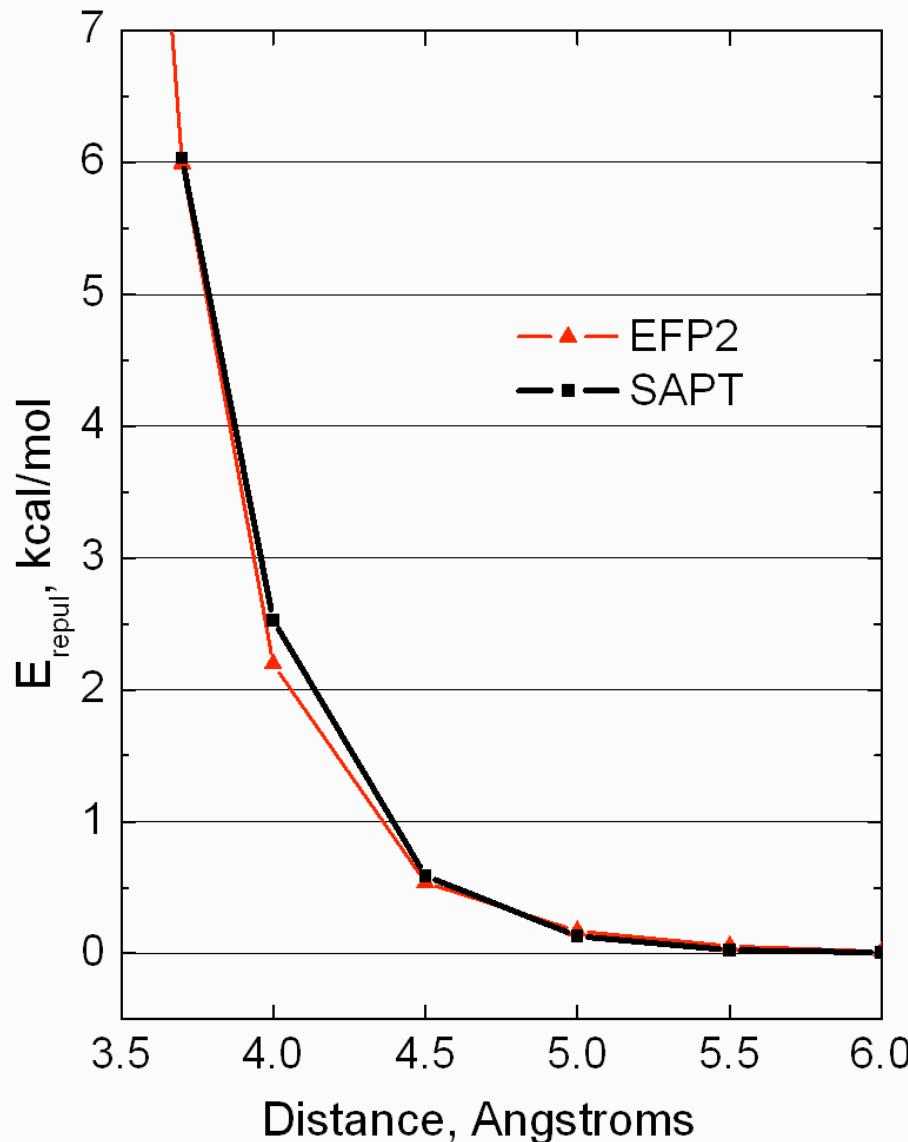


T-shaped

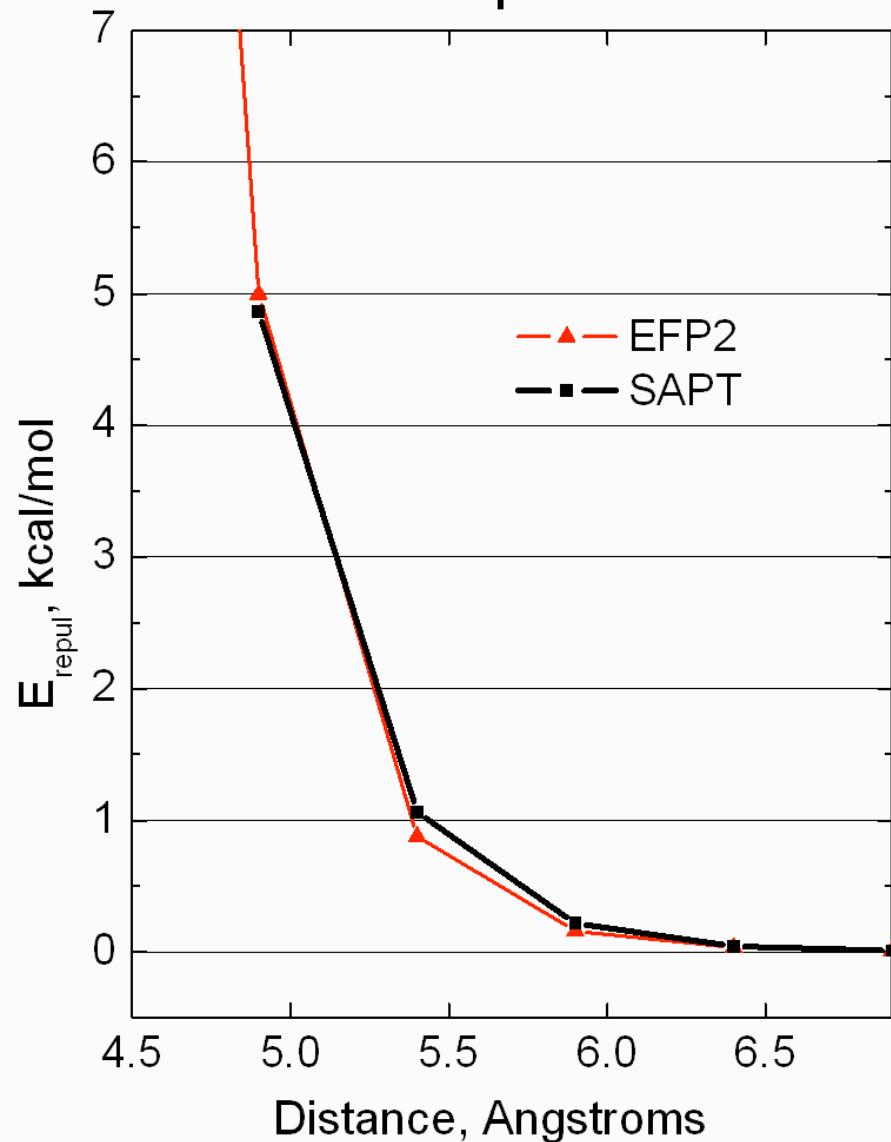


Exchange Repulsion

sandwich

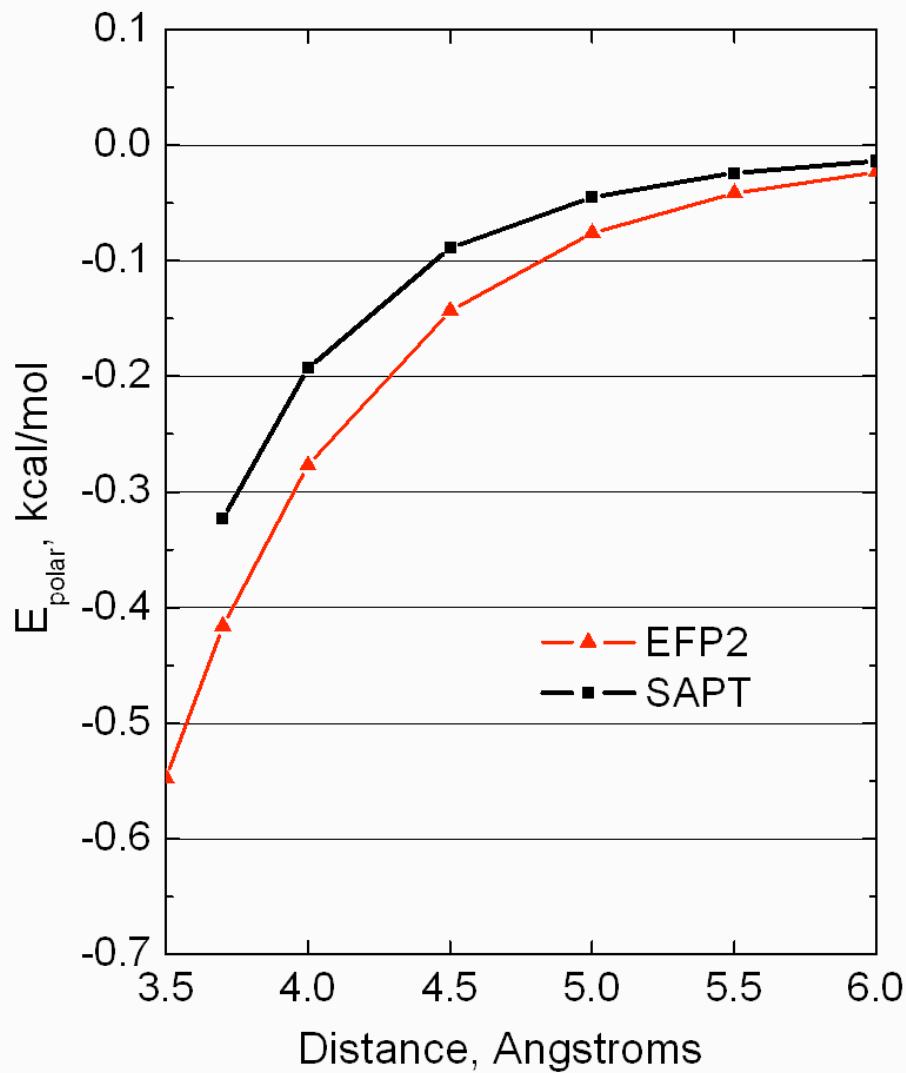


T-shaped

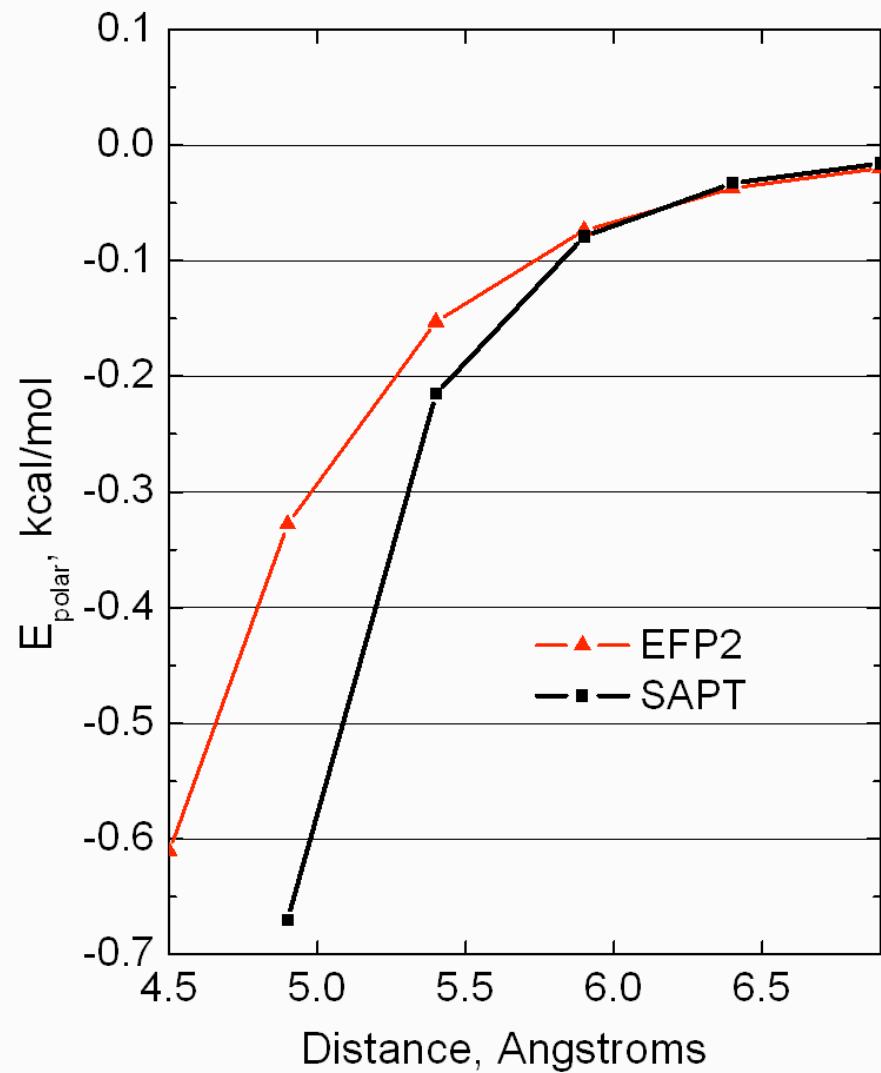


Polarization

sandwich

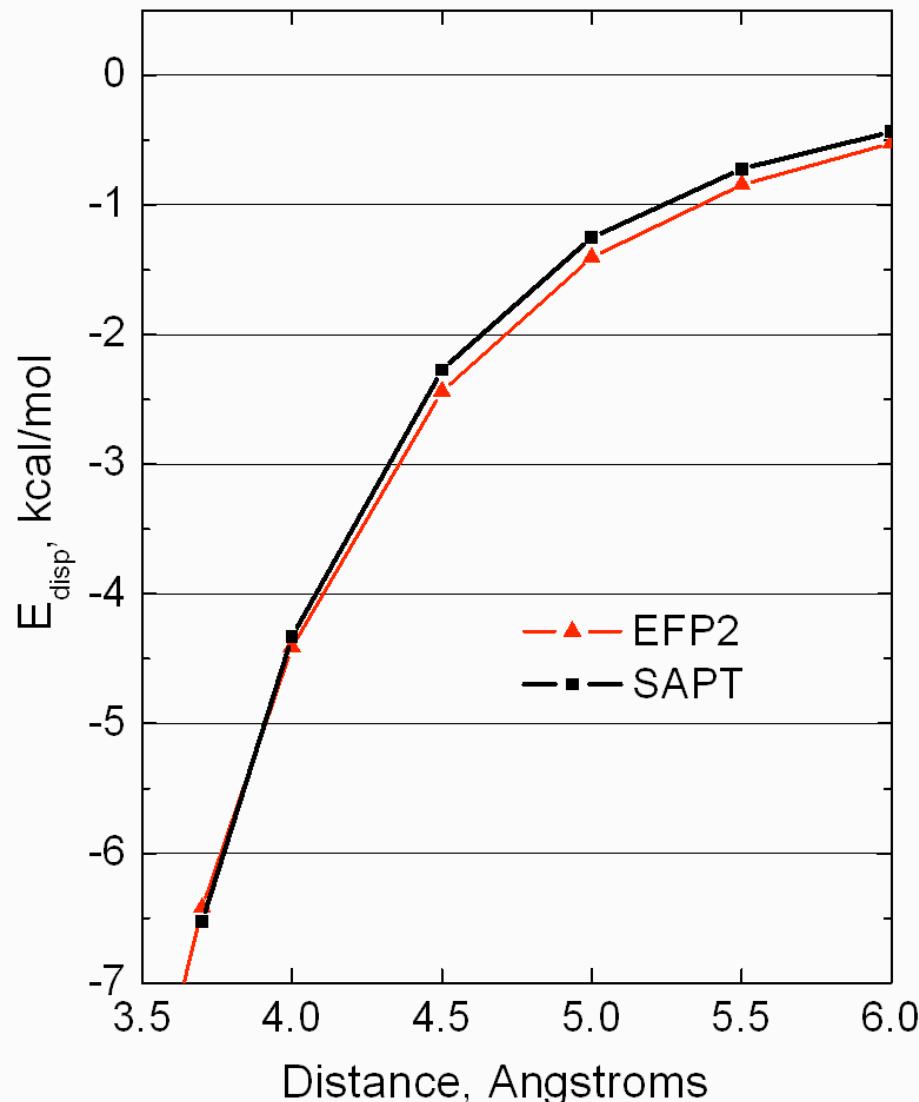


T-shaped

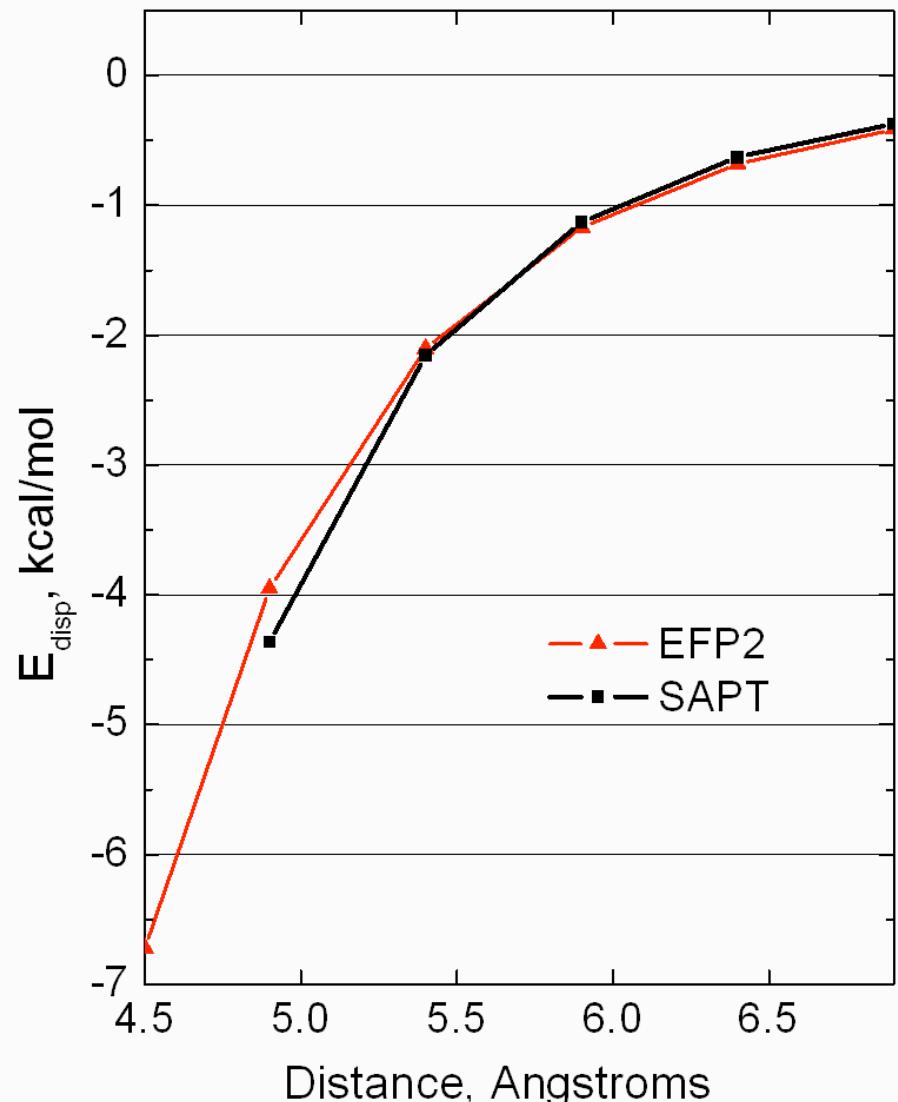


Dispersion

sandwich

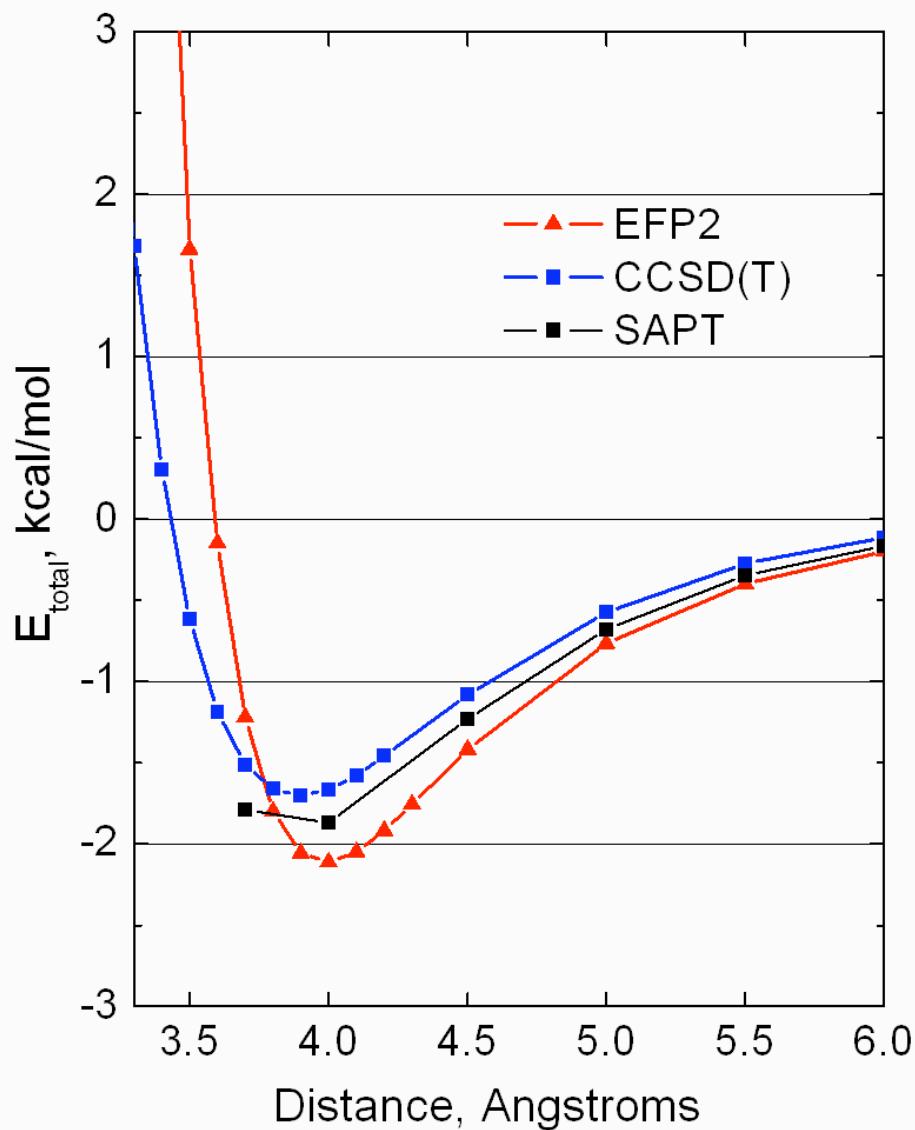


T-shaped

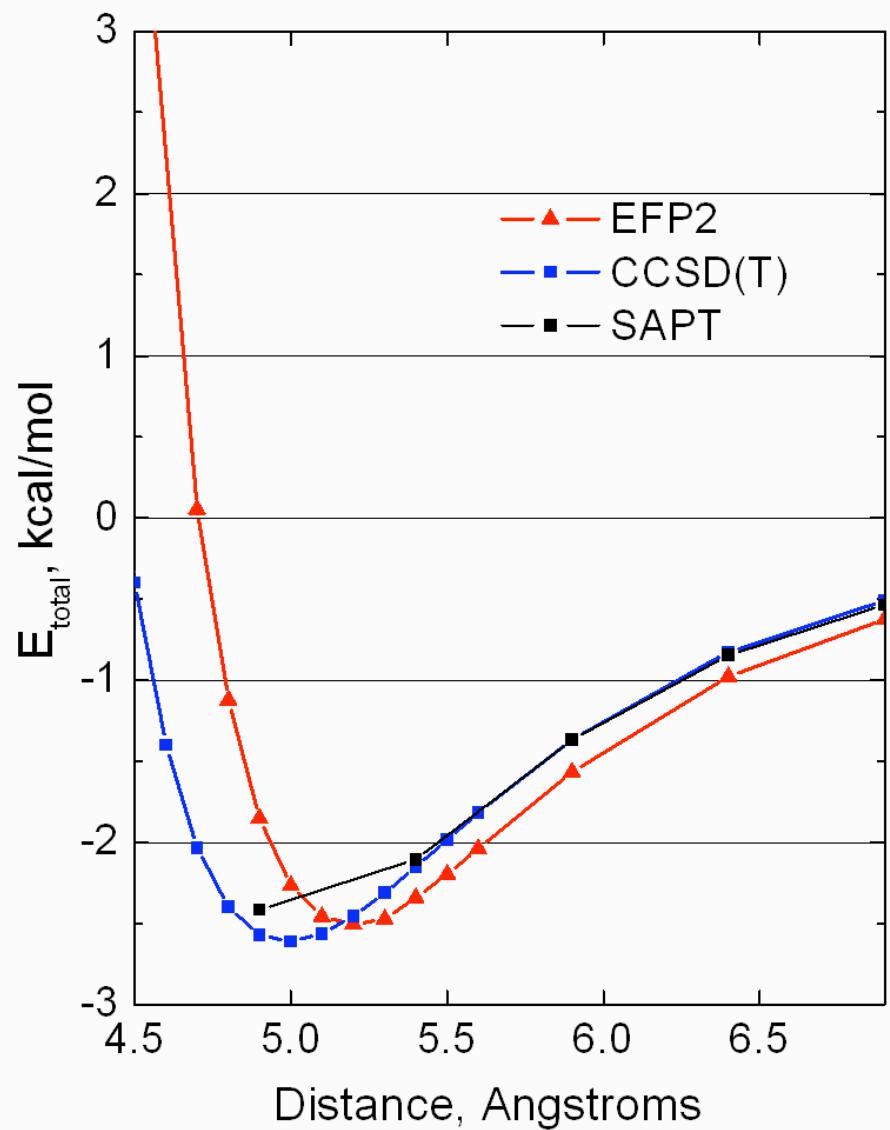


Total Binding Energy

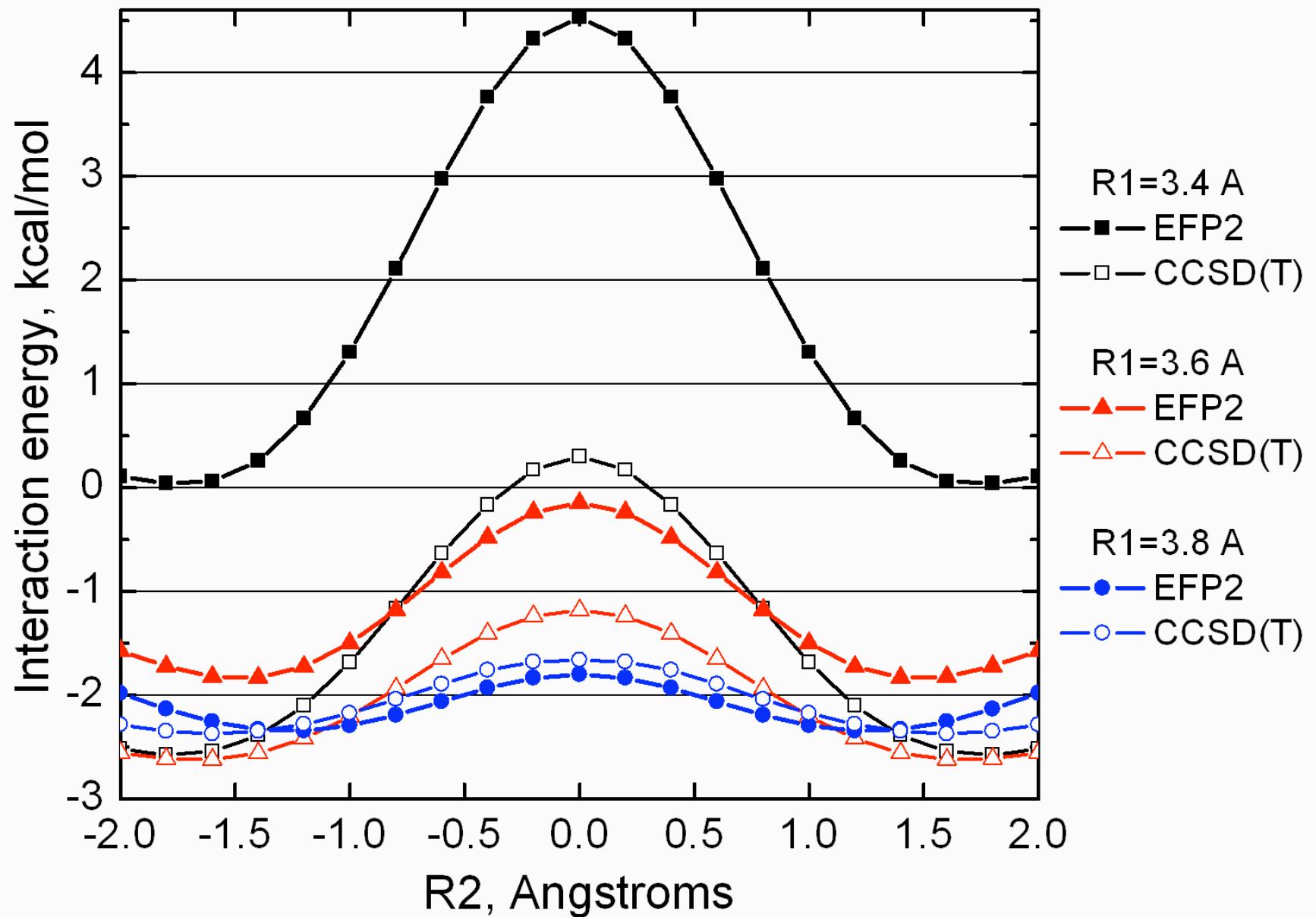
sandwich



T-shaped



Parallel-Displaced Configuration



Benzene Dimer: Summary

method	basis	sandwich		T-shape		parallel-displaced		
		R	energy	R	energy	R1	R2	energy
CCSD(T)	aug-cc-pVDZ	4.0	-1.33	5.1	-2.24	3.6	1.8	-2.22
CCSD(T)	aug-cc-pVQZ	3.9	-1.70	5.0	-2.61	3.6	1.6	-2.63
EFP2	6-311++G (3df,2p)	4.0	-2.11	5.2	-2.50	3.8	1.2	-2.34

distances: angstroms, energies: kcal/mol

EFP: ~.4 sec
CCSD(T): ~10 days

Benzene Dimer: Summary

method	basis	sandwich		T-shape		parallel-displaced		
		R	energy	R	energy	R1	R2	energy
MP2	aug-cc-pVDZ	3.8	-2.83	5.0	-3.00	3.4	1.6	-4.12
MP2	aug-cc-pVTZ	3.7	-3.25	4.9	-3.44	3.4	1.6	-4.65
MP2	aug-cc-pVQZ	3.7	-3.35	4.9	-3.48	3.4	1.6	-4.73
CCSD(T)	aug-cc-pVDZ	4.0	-1.33	5.1	-2.24	3.6	1.8	-2.22
CCSD(T)	aug-cc-pVQZ	3.9	-1.70	5.0	-2.61	3.6	1.6	-2.63
EFP2	6-311++G (3df,2p)	4.0	-2.11	5.2	-2.50	3.8	1.2	-2.34

distances: angstroms, energies: kcal/mol

EFP: ~.4 sec
MP2/QZ: ~10 hours

Contributions to the Interaction Energy

dimer	Electro-static	Exchange	Induction	Dispersion	Total
sandwich	0.38	2.20	-0.28	-4.41	-2.11
T-shaped	-1.38	1.78	-0.21	-2.69	-2.50
parallel-displaced	0.02	2.95	-0.31	-5.01	-2.34

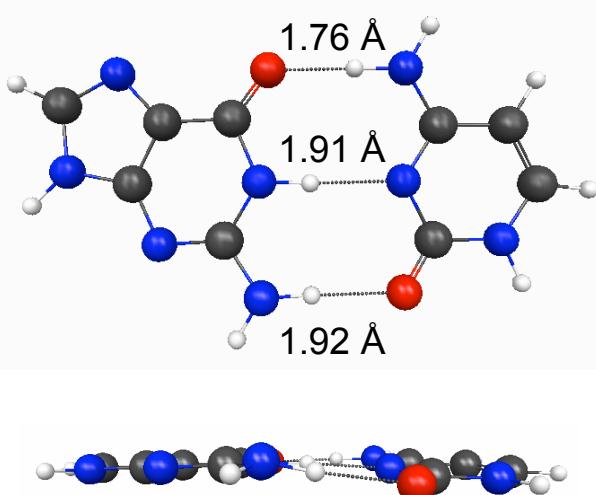
DNA BASES: Q.T. SMITH



- 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**
 - Δ CCSD(T) correction added
 - Counterpoise corrected for BSSE
- EFP generated with 6-311++G(3df,2p) basis set

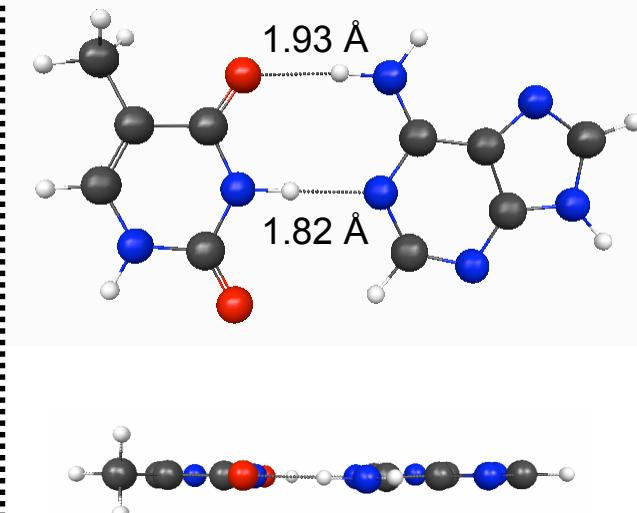
Guanine-Cytosine H-Bonded

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

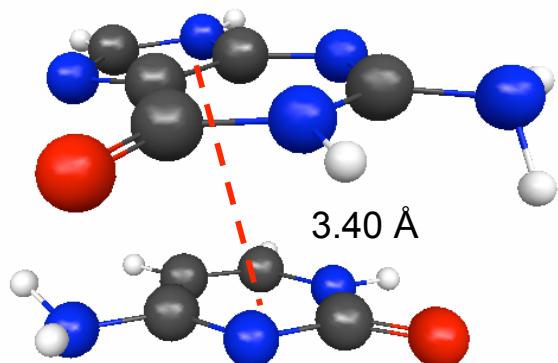
COUL	-43.3
REP	36.4
POL	-14.7
DISP	-10.7
TOTAL	-32.3

EFP

COUL	-27.1
REP	26.7
POL	-7.2
DISP	-8.2
TOTAL	-15.8

Guanine-Cytosine stacked

RI-MP2/TVZPP optimized



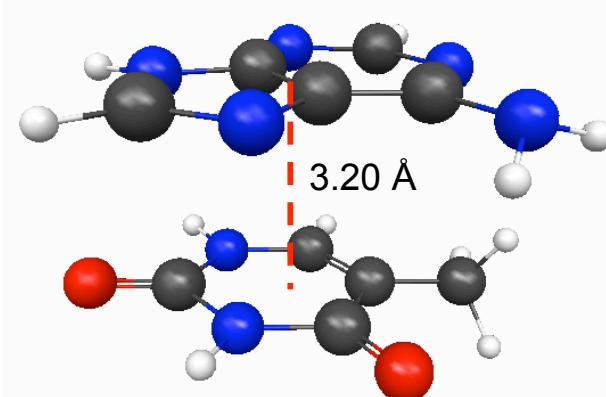
CCSD(T)/CBS energy: -19.0 kcal/mol

EFP

COUL	-19.2
REP	20.6
POL	-3.1
DISP	-17.5
TOTAL	-19.2

Adenine-Thymine Stacked

RI-MP2/TVZPP optimized

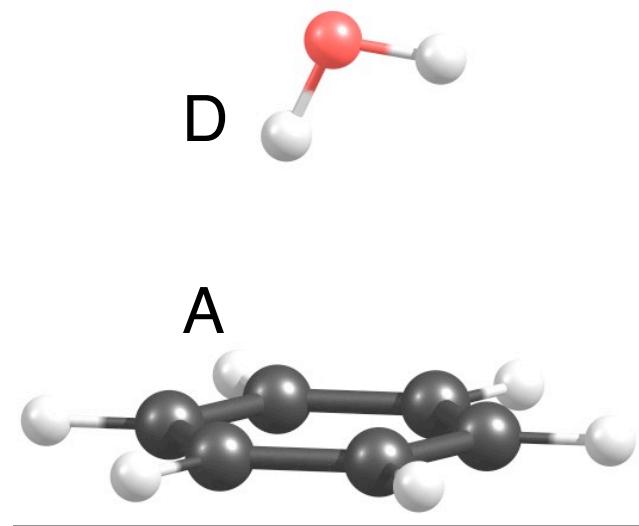


CCSD(T)/CBS energy: -12.3 kcal/mol

EFP

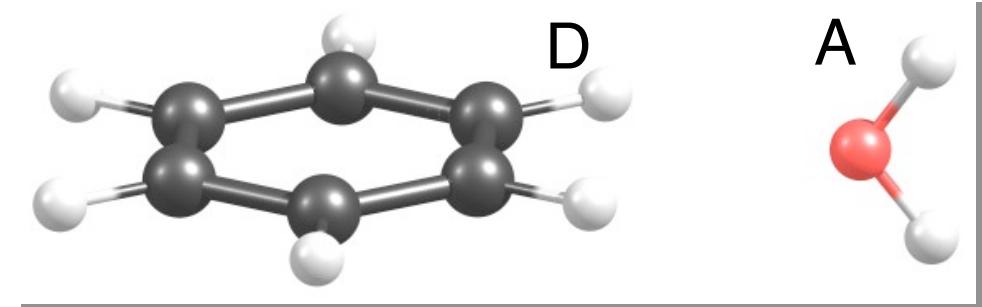
COUL	-7.8
REP	16.1
POL	-0.7
DISP	-17.6
TOTAL	-10.0

Benzene-water dimer

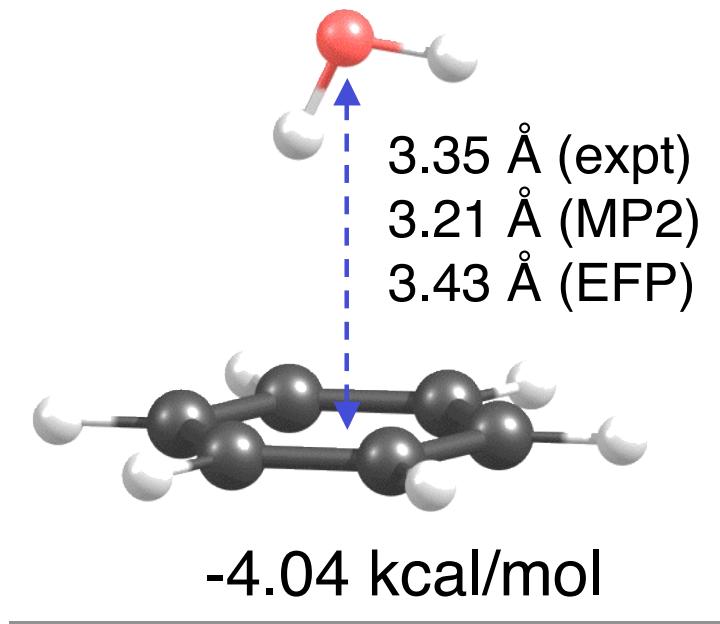


EFP:

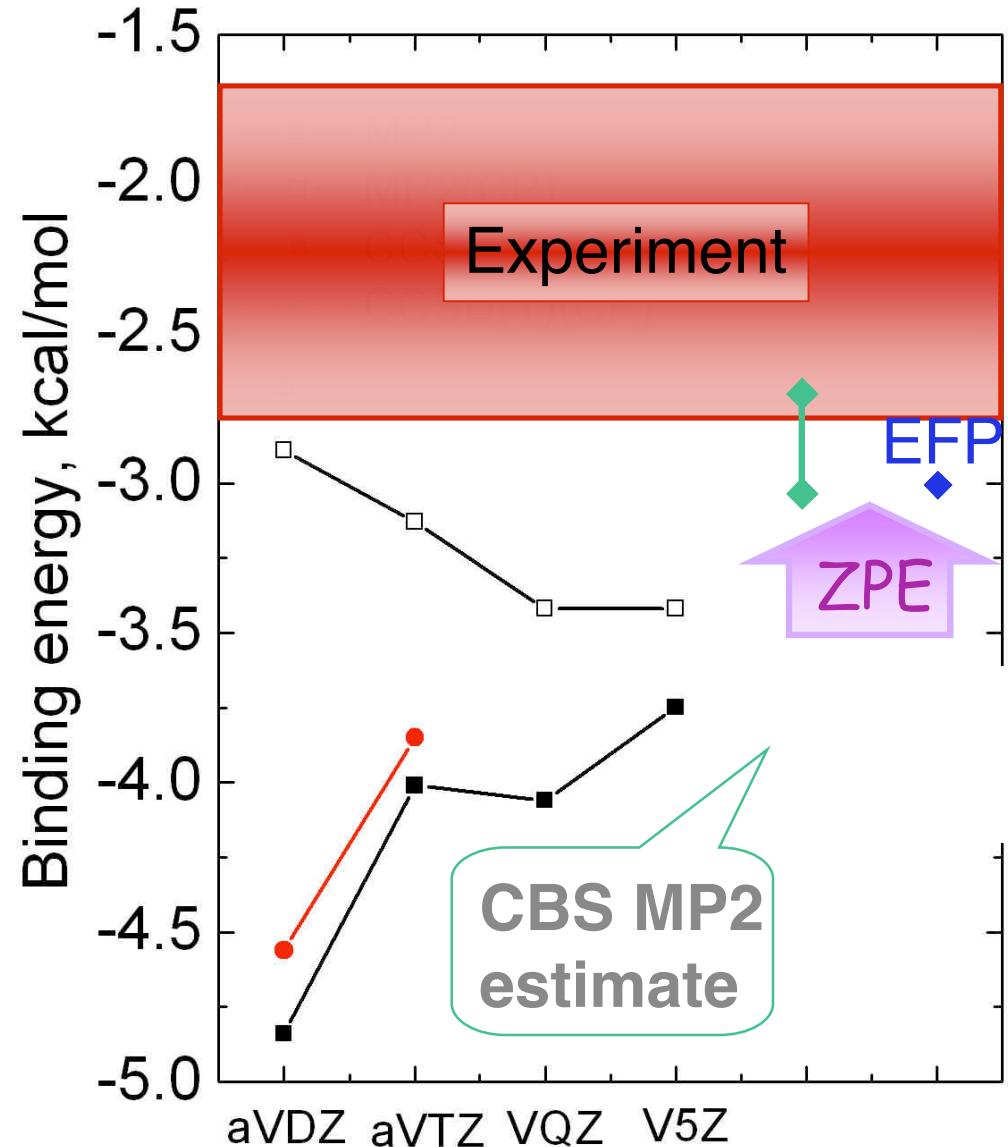
benzene: 6-311++G(3df,2p)
water: 6-311++G(3df,3pd)



Benzene-water dimer



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

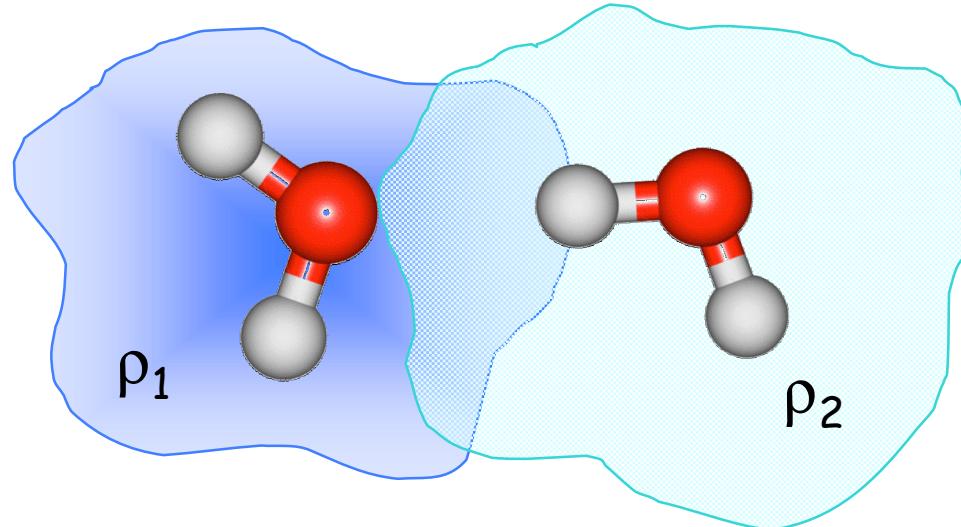


π - and H-bonding

	electrost.	ex.-rep.	polariz.	disper.	total binding	total+ ΔZPE
	-8.30	4.92	-0.99	-0.86	-5.20	-3.00
	-3.87	2.32	-0.59	-1.92	-4.04	-3.05
	-4.51	3.65	-0.56	-1.66	-3.08	-1.95
	0.02	2.95	-0.31	-5.01	-2.34	-1.98
	-1.38	1.78	-0.21	-2.69	-2.50	-2.09

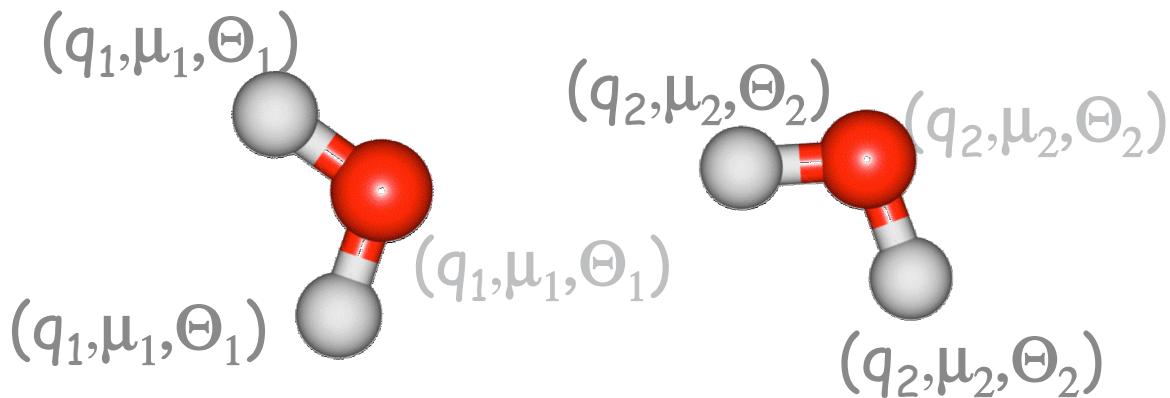
Electrostatic energy in EFP

Quantum-chemical model



$$\begin{aligned} E^{ES} &= \int \frac{\rho_1 \rho_2}{R_{12}} dv_1 dv_2 \\ &= \int \rho_1 V_2(1) dv_1 \end{aligned}$$

Classical model

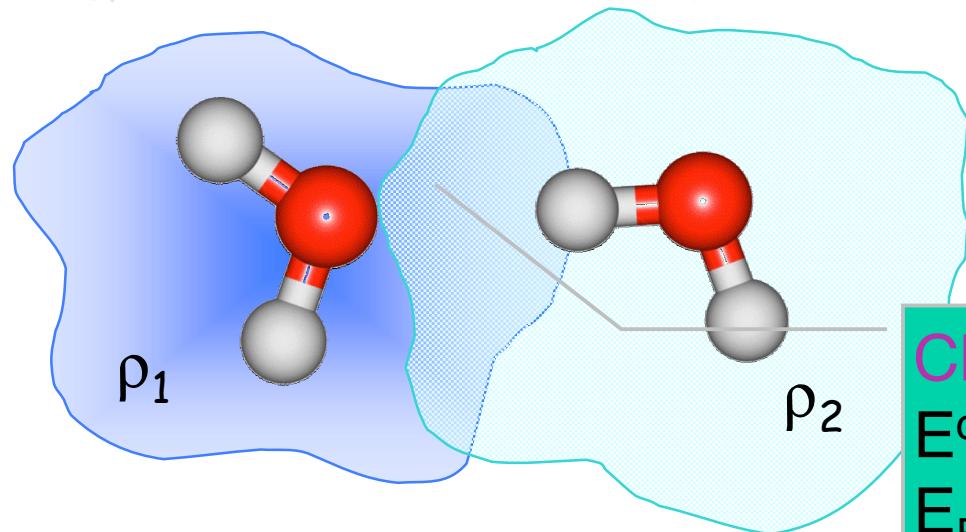


$$\begin{aligned} E^{ES} = & \sum (q_1 q_2 T^{ch} \\ & + (q_1 \mu_2 - q_2 \mu_1) T^{dip} \\ & - \mu_1 \mu_2 T^{quad} + \dots) \end{aligned}$$

multipole expansion @ each atom and bond mid-point

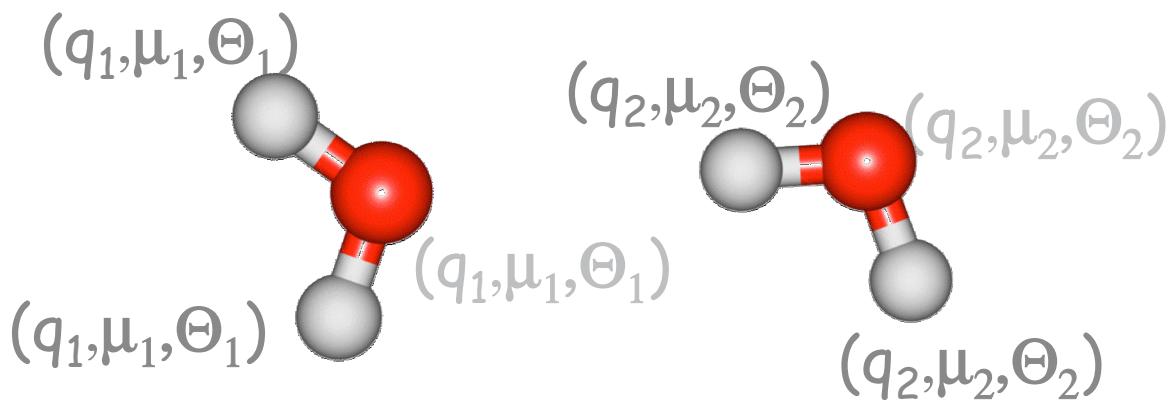
Electrostatic energy in EFP

Quantum-chemical model



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

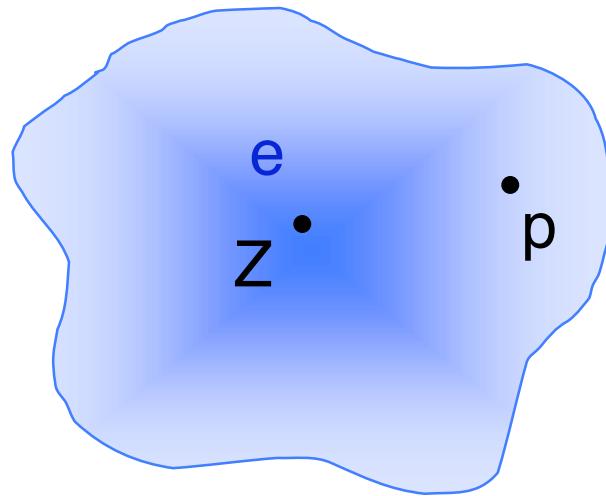
Classical model



multipole expansion @ each atom and bond mid-point

Damping of potential

Hydrogen-like atom & proton



Exact quantum-chemical solution:

$$V = -e/R (1 - \exp(-2ZR)(1 + ZR))$$

A red circle highlights the term $-e/R$. A blue bracket below the equation is labeled "damping function".

Classical charge potential

General case

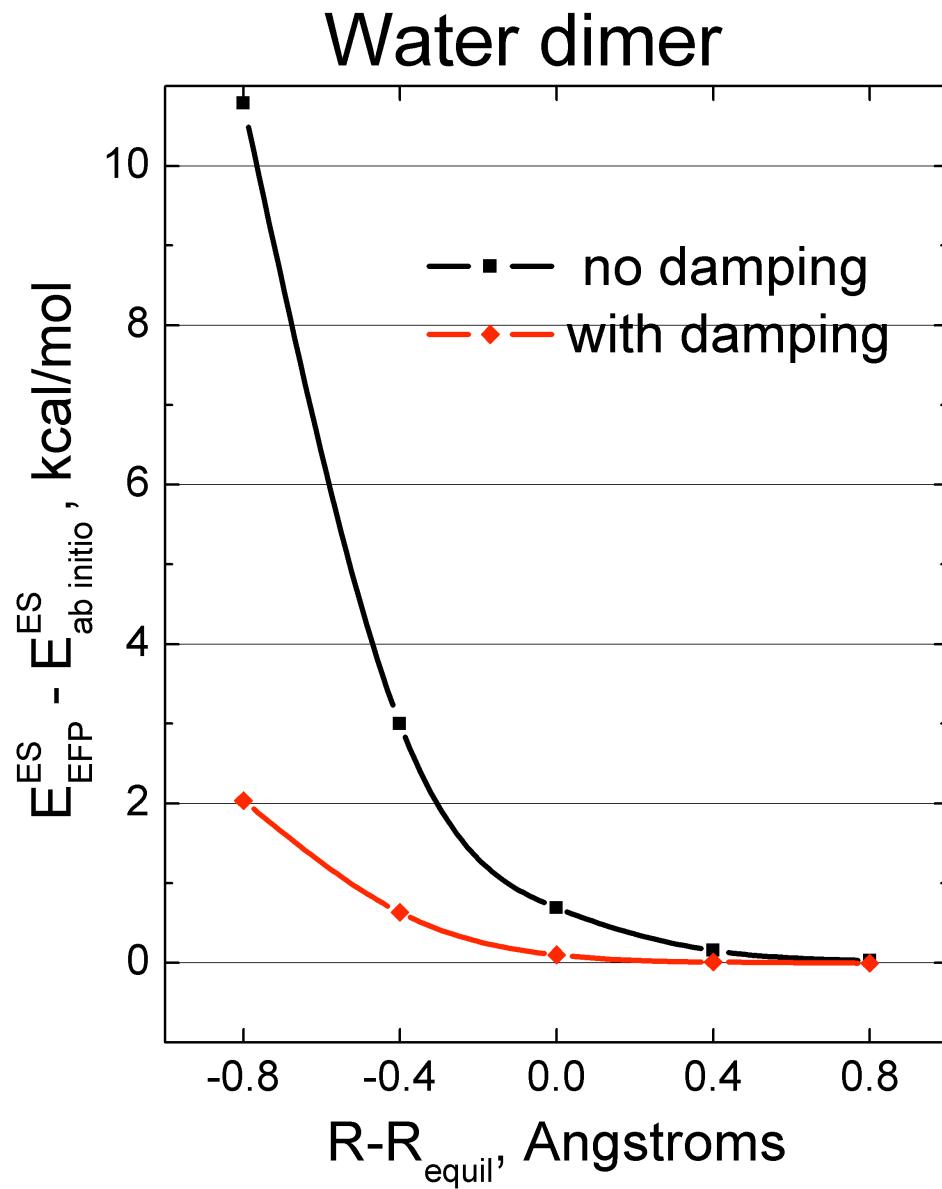
$$V^{\text{ch}} = q/R f_{\text{damp}}$$
$$f_{\text{damp}} = (1 - \exp(-\alpha R))$$

Damping coefficients α are determined by minimizing the difference between *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

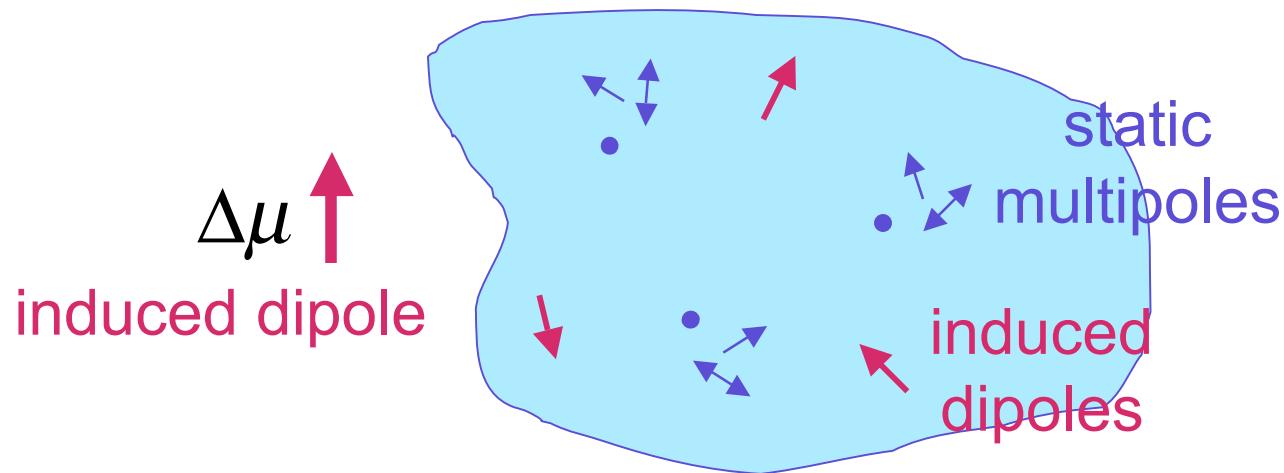
Electrostatic damping: summary



- 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



$$\Delta\mu_\gamma^a = \alpha_{\gamma\alpha}^a (F_\alpha^a + \sum_{b \neq a} T_{\alpha\beta}^{ab} \Delta\mu_\beta^b)$$

Induced dipole

polarizability
tensors

$b \neq a$

field due to
static multipoles

field due to
other
induced dipoles

Polarization collapse

$$(\alpha^a)_{\alpha\beta}^{-1} \Delta\mu_\beta^a - \sum T_{\alpha\beta}^{ab} \Delta\mu_\beta^b = F_\alpha^a$$

$$\xrightarrow{b \neq a}$$
$$B_{\alpha\beta}$$

$$\sum_{b\beta} B_{\alpha\beta}^{ab} \Delta\mu_\beta^b = F_\alpha^a$$

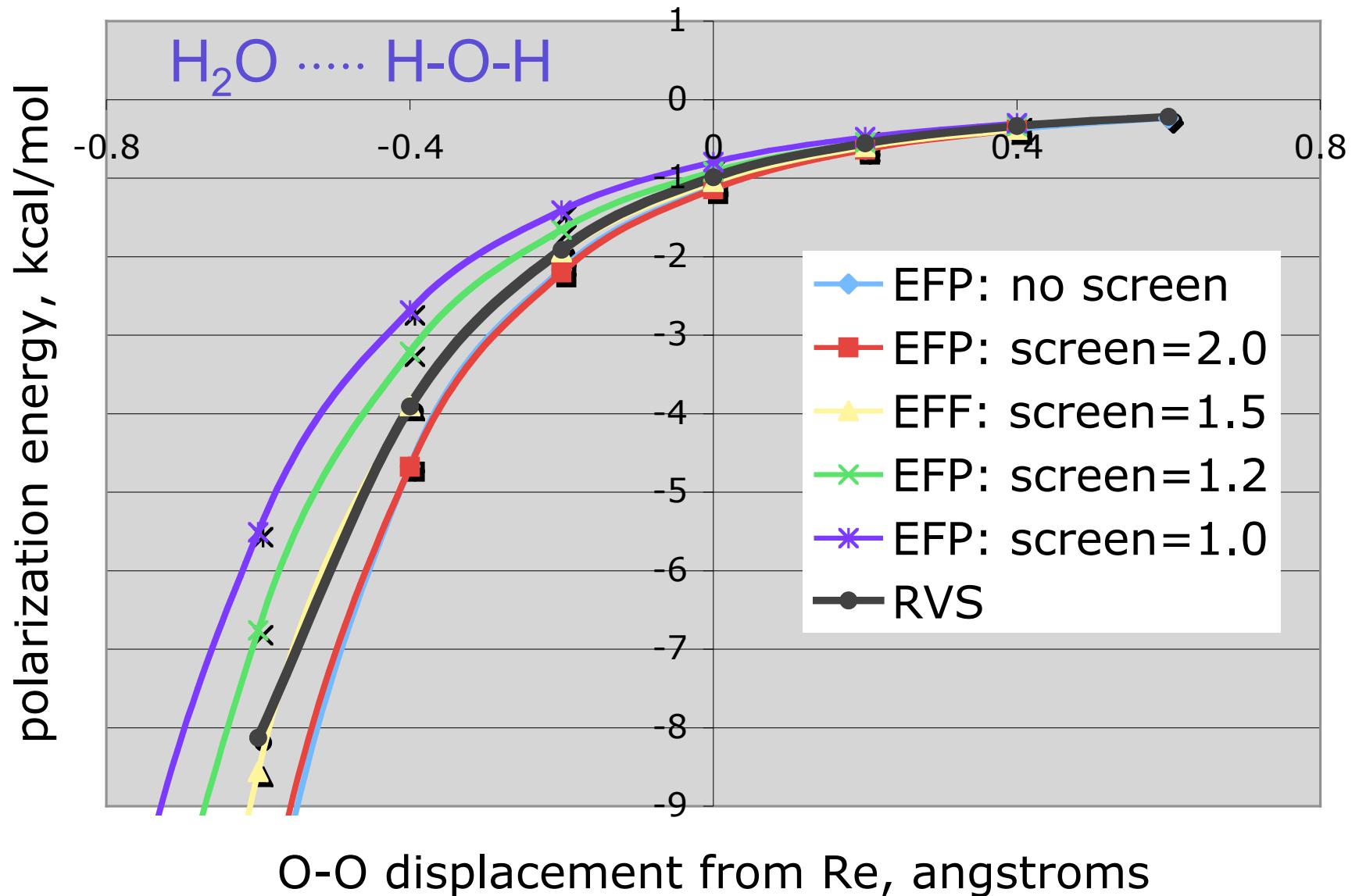
$$\Delta\mu_\alpha^a = \sum_{b\beta} (B^{-1})_{\alpha\beta}^{ab} F_\beta^b$$

at small R →

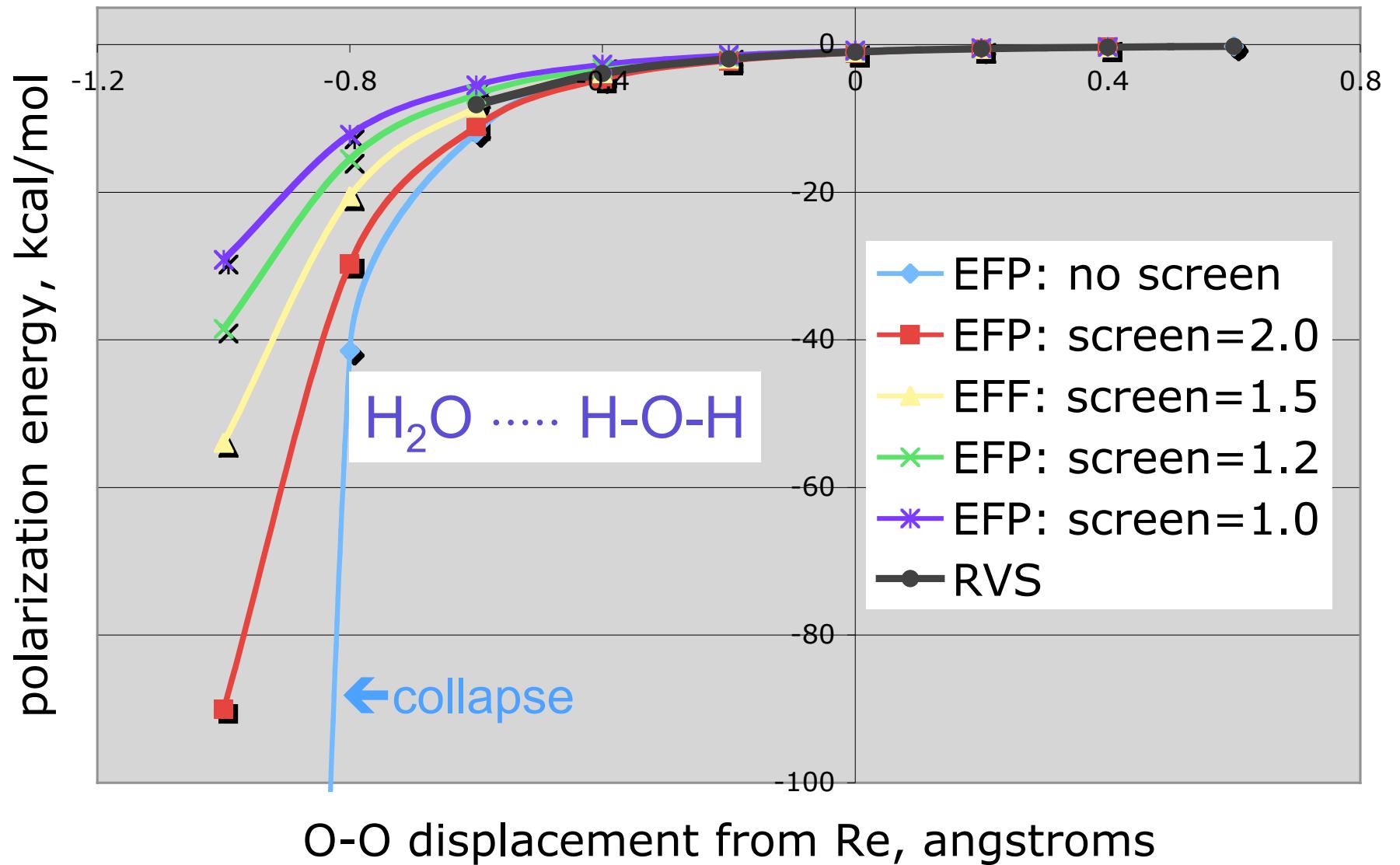
matrix B ceases to be positive definite,
elements of (B)⁻¹ diverge →

polarization collapse

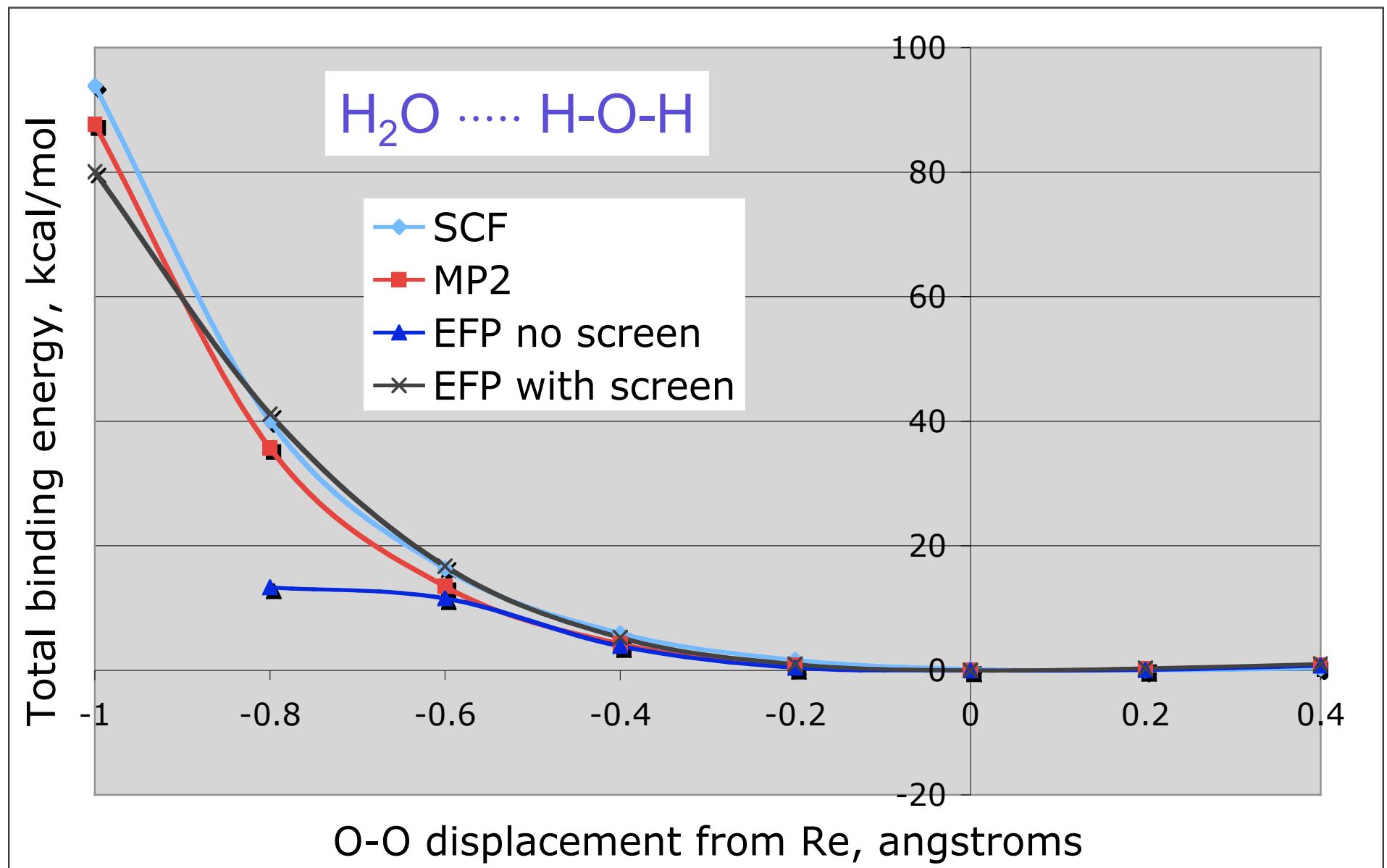
Damping of polarization



Damping of polarization



Water dimer



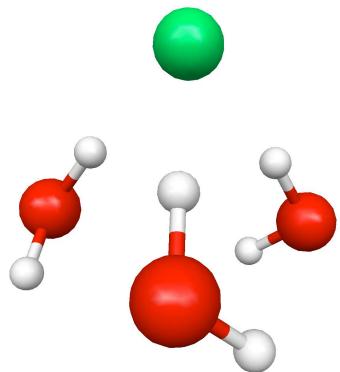
$F^- (H_2O)_n$



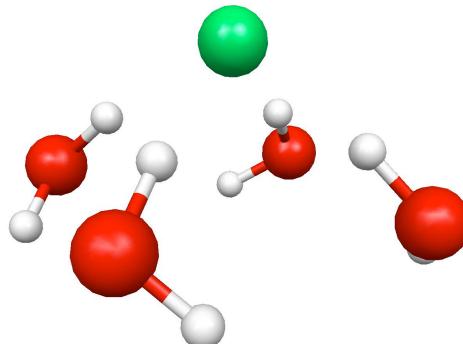
EFP: -22.3
MP2: -20.8
Expt: -23.3



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



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



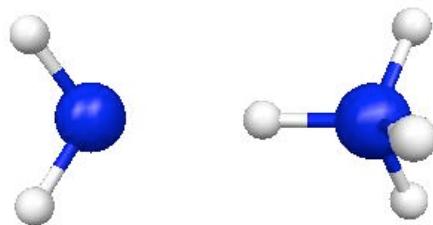
EFP: -67.7
MP2: -66.7
Expt: -71.7

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

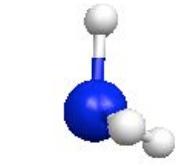
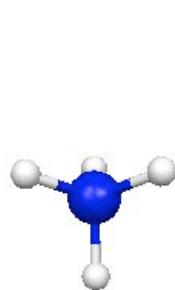
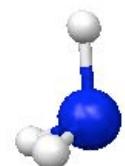
QCISD: -22.5

Expt: -21.5^a

-24.8^b

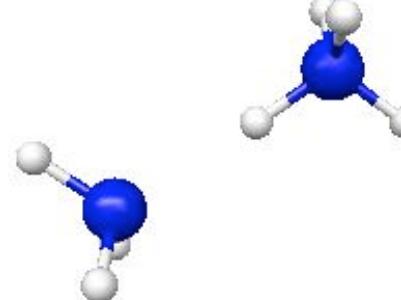
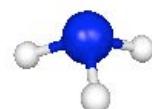
-25.4^c

-27.0^d



EFP: -53.6

MP2: -53.1

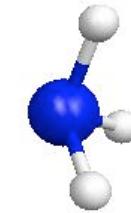
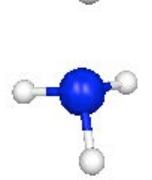
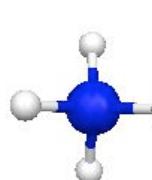
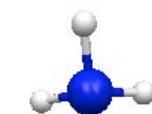


EFP: -39.1

MP2: -39.7

EFP: -65.8

MP2: -64.3



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

MP2/6-31+G*, QCISD/6-311++G**: Wang, Chang, Jiang, Lin, CP, 276, 93 (2001) ;

Experiments: ^aArshadi, Futrell, JPC, 78, 1482 (1974); ^bKebarle, RPC, 28, 455 (1977);

^cTang, Castleman, JCP, 62, 4576 (1972); ^dSearles, 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.

CONTINUUM SOLVATION MODELS

- Simplest is Onsager self-consistent reaction field (SCRF) model (\$SCRF)
 - Solute (QM) dipole moment μ polarizes “medium” (solvent) through dielectric ϵ
 - 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
 - $R = g\mu$
 - μ = dipole vector
 - $g = 2(\epsilon - 1)/[(2\epsilon + 1)(a^3)]$
 - a = radius of cavity
 - Usually assume spherical cavity
 - Radius can be pretty arbitrary
 - Adds simple $\langle \chi_i | x | \chi_j \rangle$ integrals - very cheap

PCM MODEL

- Polarizable Continuum Model (PCM)
 - Tomasi et al., Chem. Phys. Lett., 255, 327 (1996)
 - 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