Investigating Popular Water Models

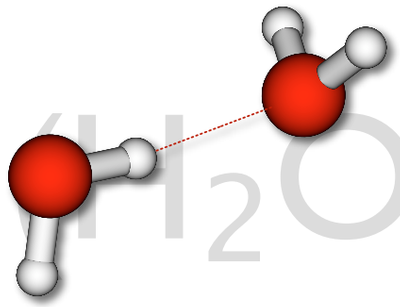
Albert DeFusco, Ken Jordan

Department of Chemistry Since 1875

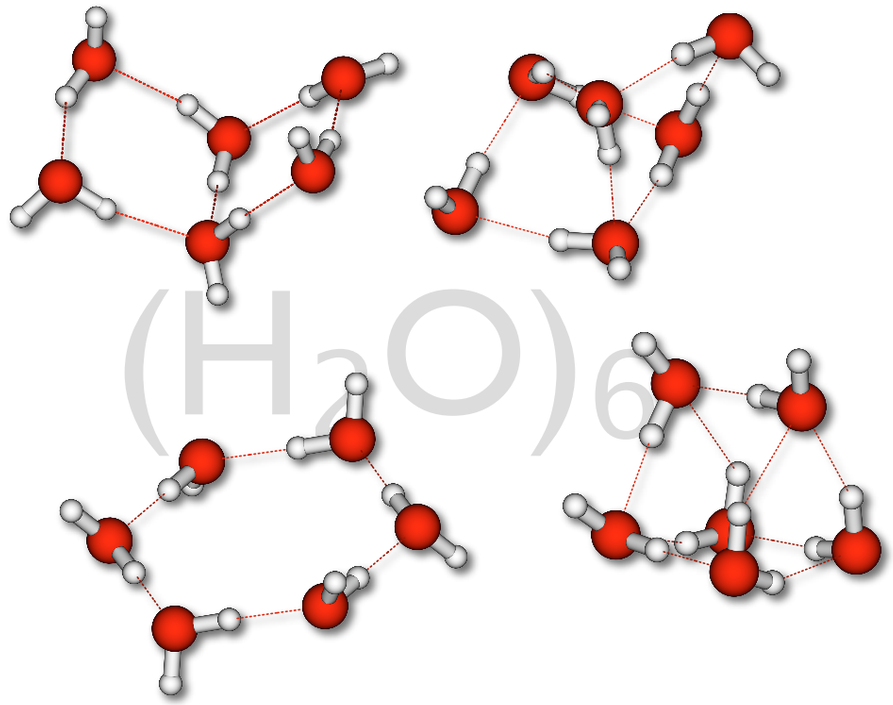
Center for Molecular and Materials Simulations

National Science Foundation
WHERE DISCOVERIES BEGIN

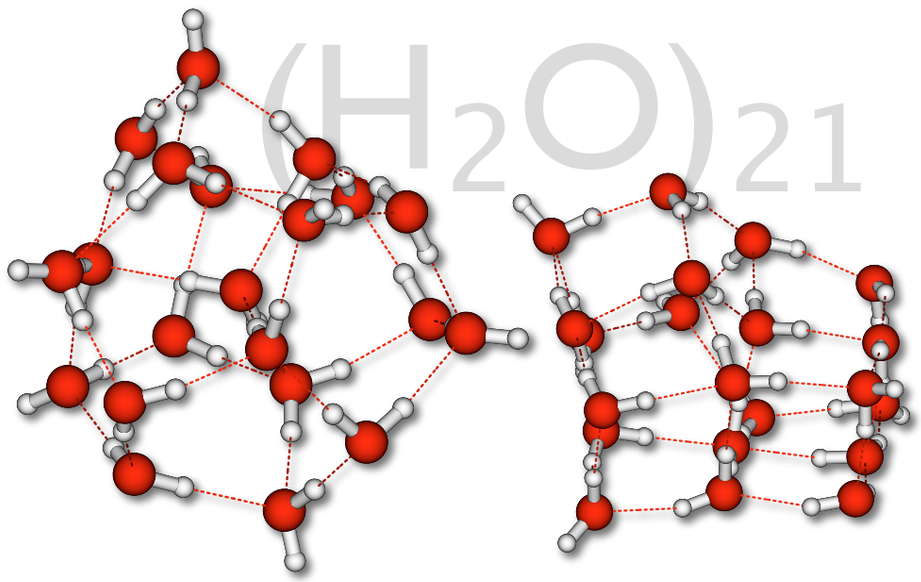
What are we modeling?



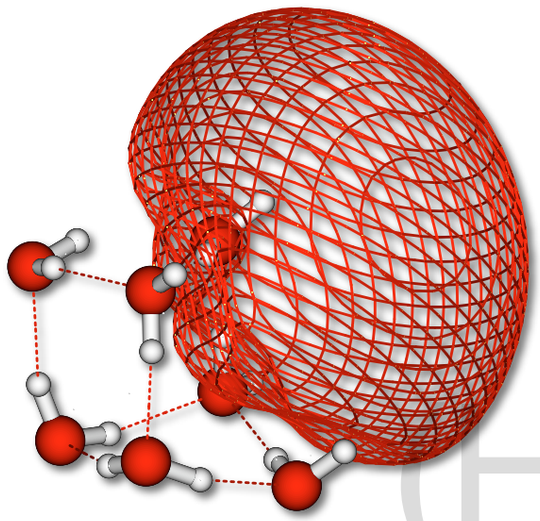
$(H_2O)_2$



$(H_2O)_6$



$(H_2O)_{21}$



$(H_2O)_7^-$

Making Simple Models

- Electrostatics

  Interaction of charge densities

- Polarization

  Distortions of charge density of one monomer due to the electric field from other monomers

- Exchange / Repulsion

  Short range interactions

- Dispersion

  Long range interactions

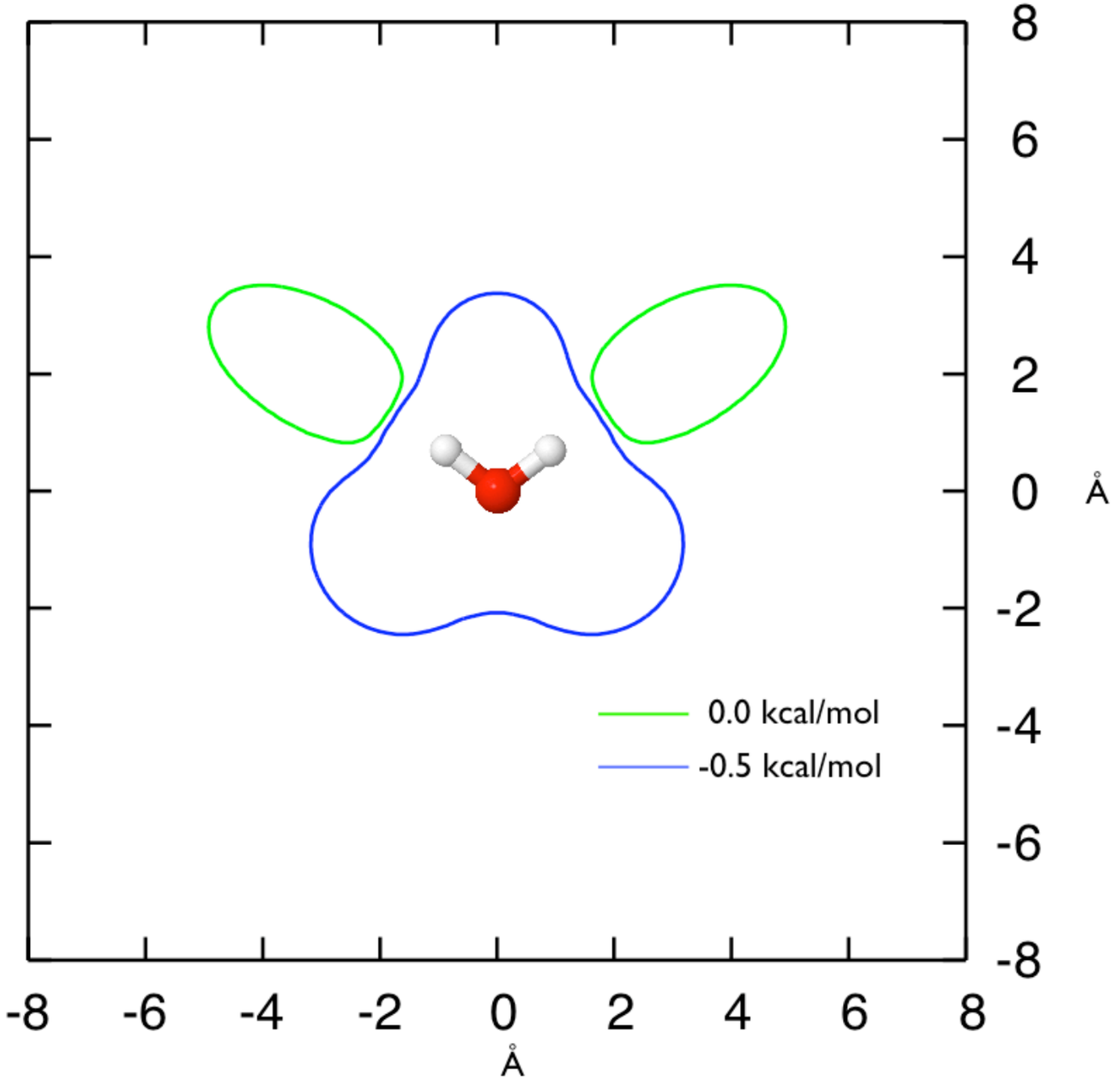
Overview

	Elec.	Pol.	Rep.	Disp.
DC	Charges	Single dipole	Oxygen: Lennard-Jones	
TTM2-R	Charges (damped)	Distributed dipoles	Oxygen: R^{12},R^{10},R^{6}	
AMOEBA	Multipoles	Distributed dipoles	All atom Buffered 14-7	
DPP	Charges	Distributed Dipoles	All atom exponential	Oxygen: damped R^{6}

Difference Plots

Point Charges

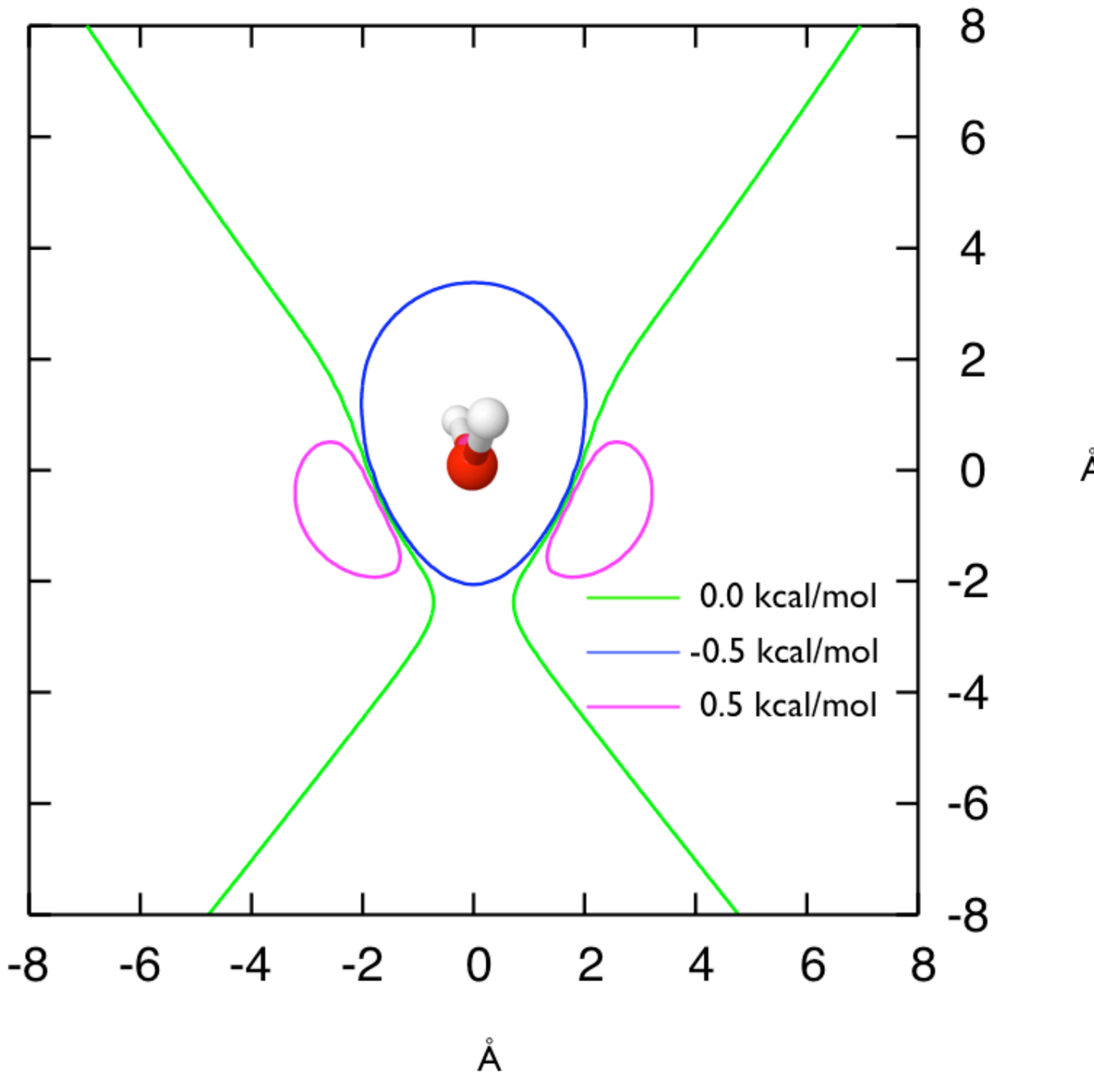
- compared to MP2/aug-cc-pVTZ
  - E(DPP)-E(MP2)



Difference Plots

Point Charges

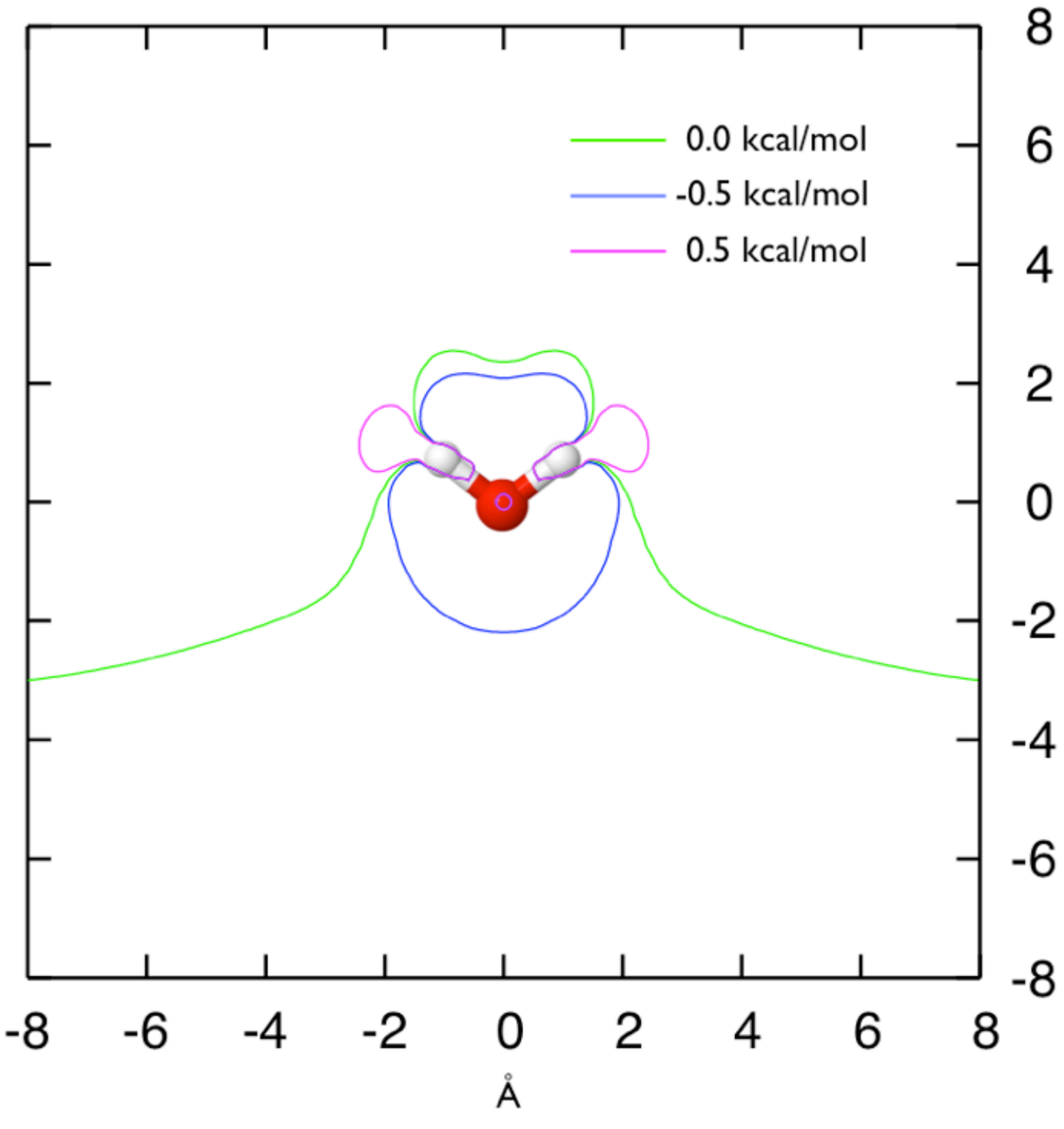
- compared to MP2/aug-cc-pVTZ
  - E(DPP)-E(MP2)
- large region of difference
  - Two out-of-plane regions where “lone pair electrons” may reside



Difference Plots

Multipoles

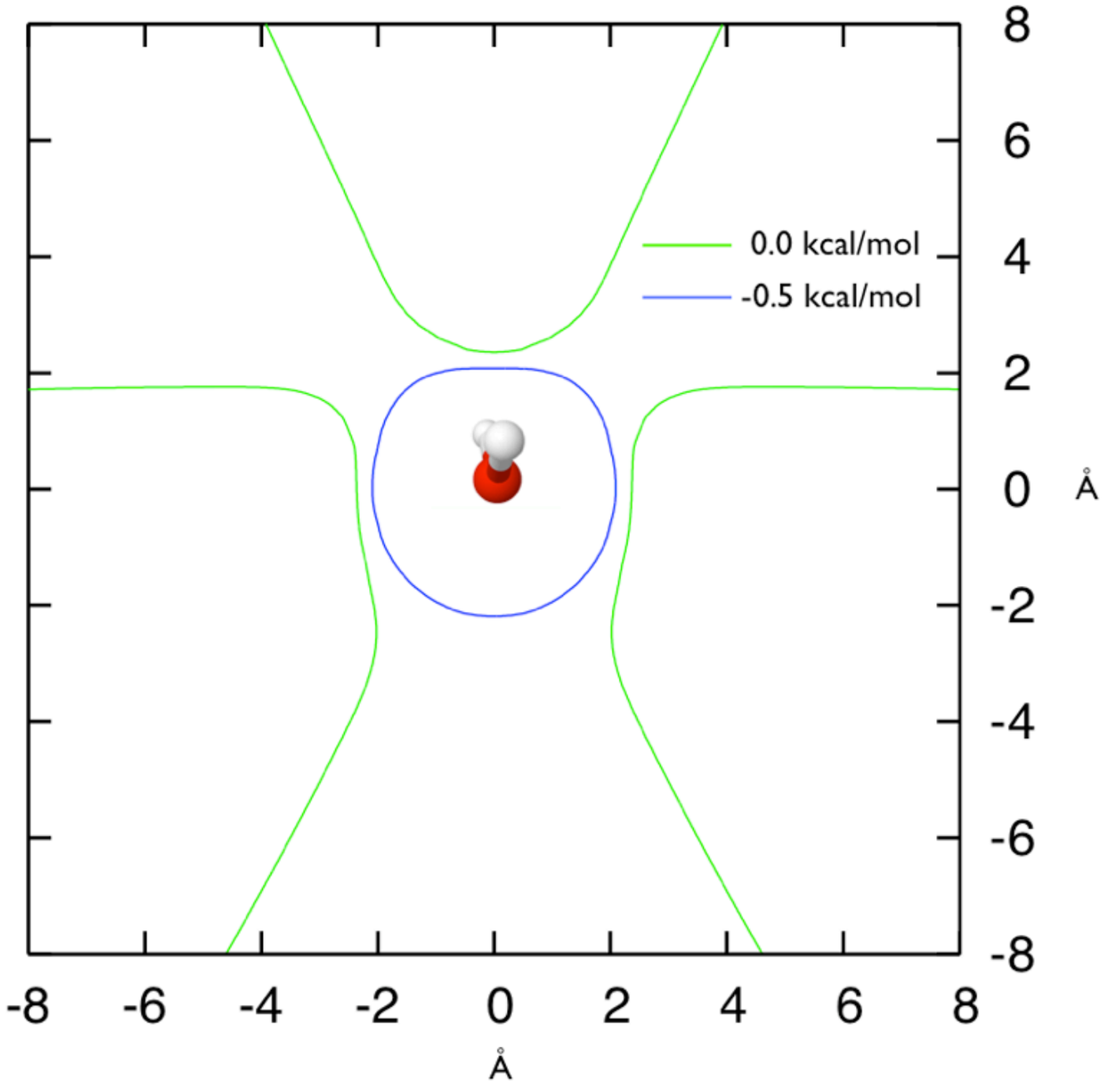
- charge, dipole, quadrupole from MP2/aug-cc-pVTZ calculation
- compared to MP2/aug-cc-pVTZ
  - E(GDMA)-E(MP2)



Difference Plots

Multipoles

- Very close to MP2
- Can be expensive to implement

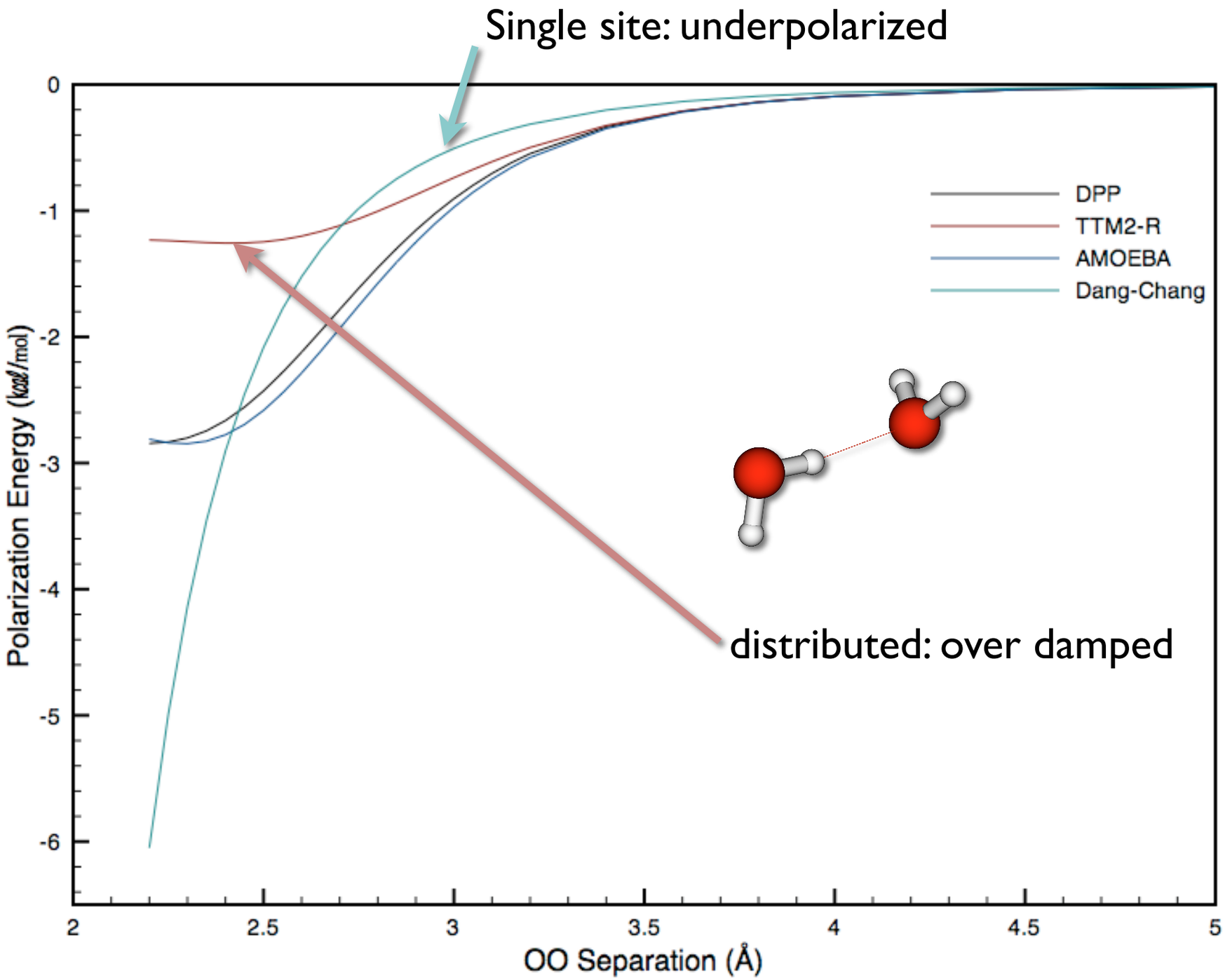


Polarization

by induced dipoles

- Induced dipole is the most popular method
- Single site
  - tends to underpolarize
- Distributed polarizability
  - must be damped at short range
- Can be compared to 3-body energies

Polarization Energy



3-body Decomposition
water hexamer isomers

	MP2[a]	DC	AMOEBA	TTM2-R	DPP
book	−−	−6.252	−9.959	−7.478	−9.215
cage	−7.41	−5.125	−9.067	−6.755	−8.187
	(−9.13)				
prism	−7.25	−5.547	−8.550	−6.203	−7.673
	(−8.90)				
ring	−9.67	−7.046	−10.946	−8.303	−10.386
	(−11.60)				

[a]MP2/aug-cc-pVTZ BSSE corrected energies. Numbers in parenthesis are flexible monomer calculations.

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DPP has only point-charges!

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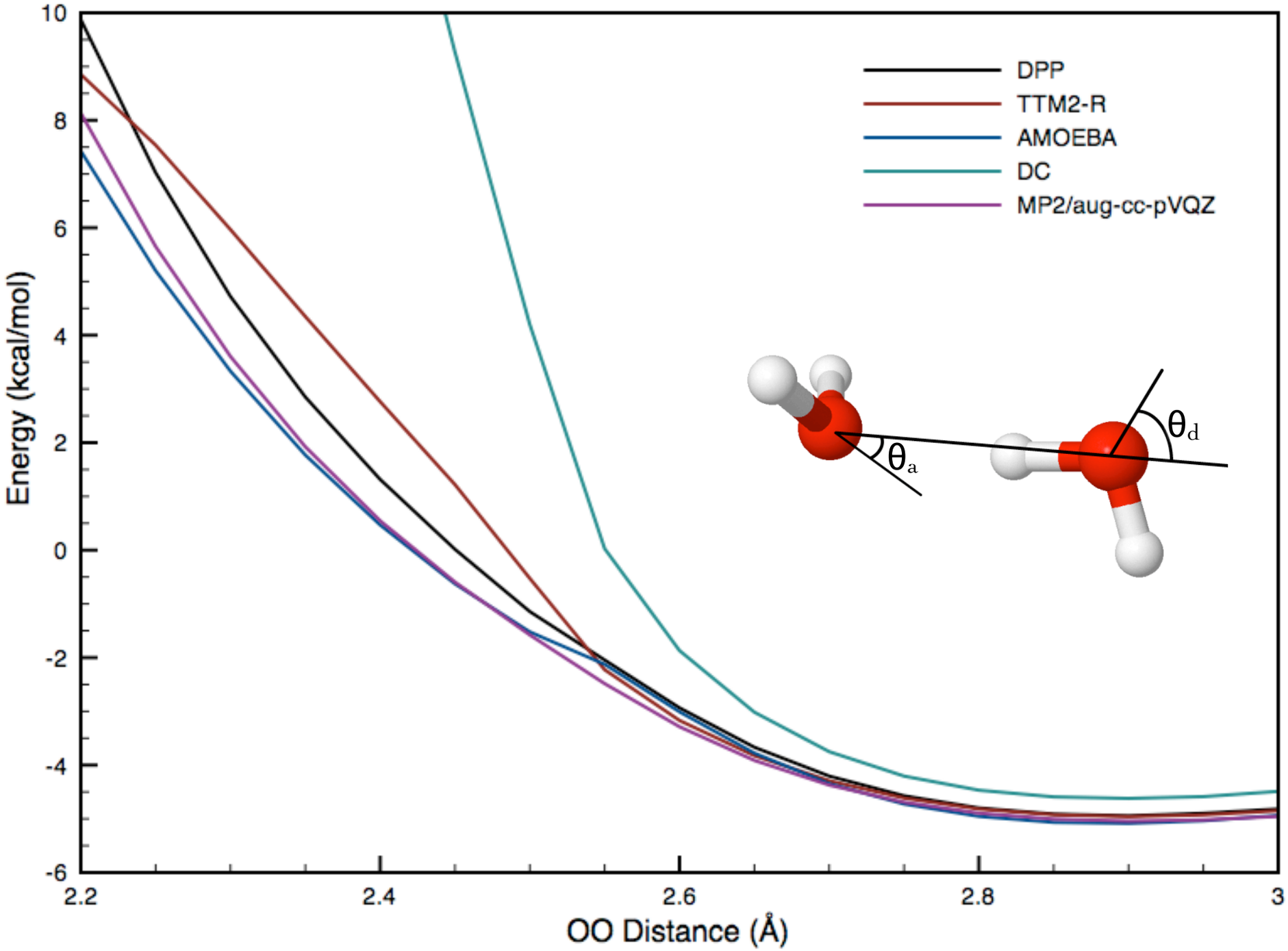
Repulsion/Dispersion

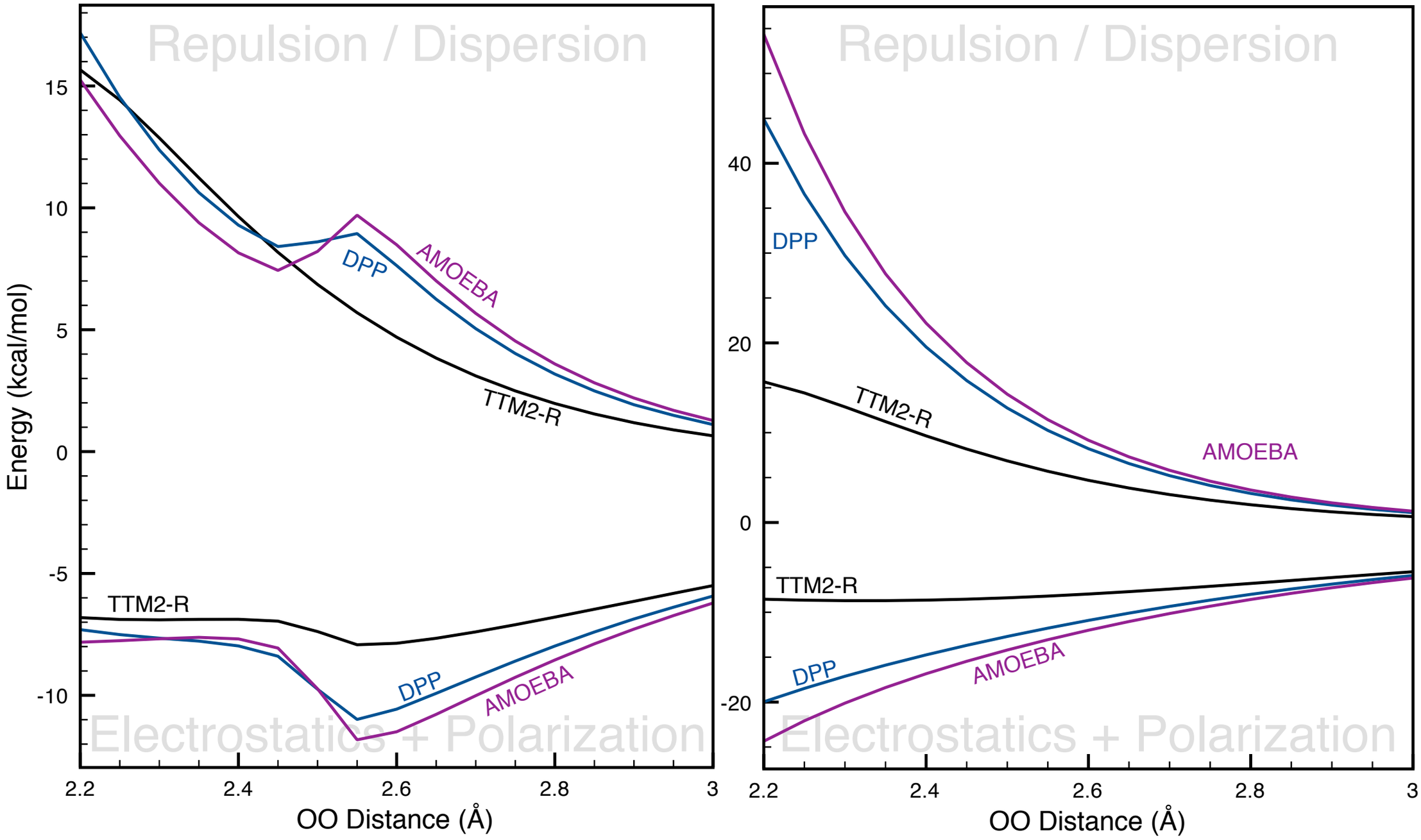
- Typically just oxygens are allowed to interact
  - Dang-Chang and TTM2-R
- Using all atoms allows for greater geometric flexibility
  - AMOEBA and DPP

Relaxed flap angles

Interaction energy



Relaxed versus fixed



relaxed flap angles

fixed flap angles

Distributed Point Polarizable Model

- Point charges
  - undamped interaction allows for charge-penetration-like effects
- Distributed induced dipoles
  - improves 3-body interactions
- Repulsion / Dispersion
  - all-atom repulsion
  - damped R^6 dispersion

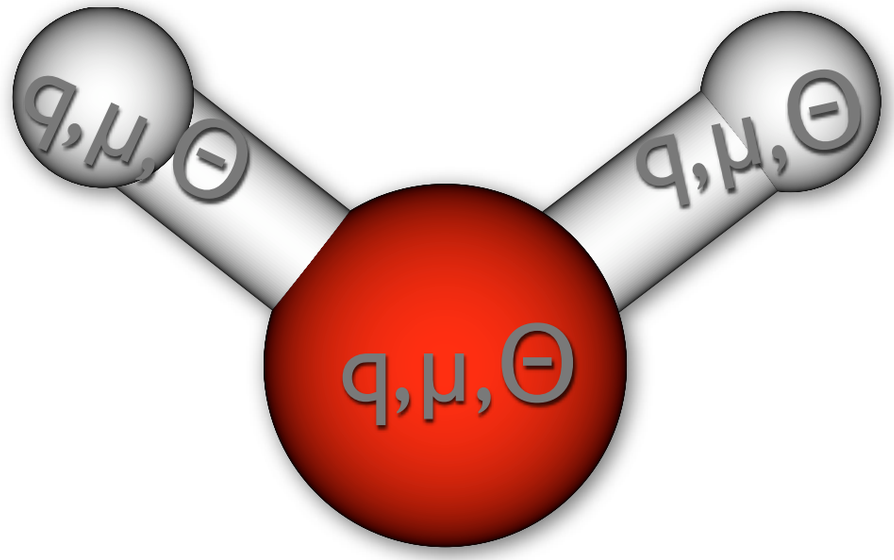
Acknowledgments

- The Jordan Group
  - Dr. Thomas Sommerfeld
  - Dr. Daniel Schofield
  - Jun Cui
  - Valerie McCarthy

National Science Foundation
WHERE DISCOVERIES BEGIN

Distributed Multipoles

- Based on Stone's Generalized Distributed Multipole Analysis (GDMA)
  - Point-moment expansion from *ab initio* density
- AMOEBA
  - Up to quadrupole on each atom
  - scaled to fix dimer geometry



Point Charges

- Reproduce experimental dipole
  - 1.85 Debye
- Negative charge on the M-site
  - 0.2 Å towards the hydrogens