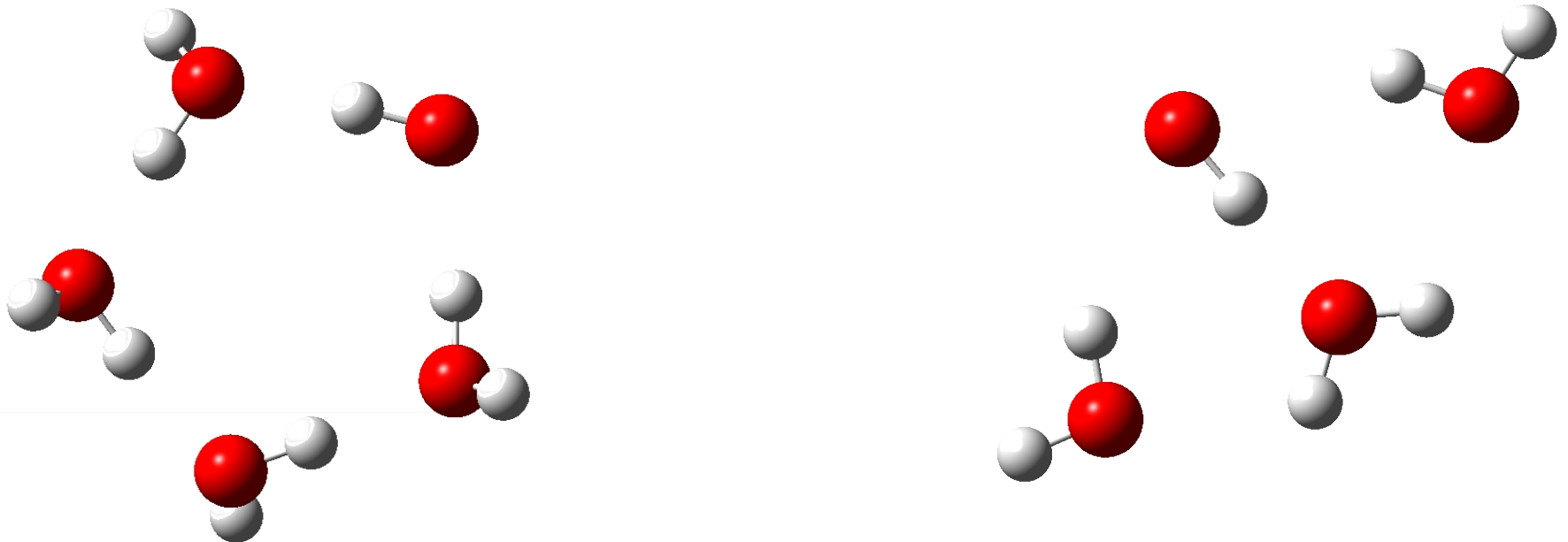


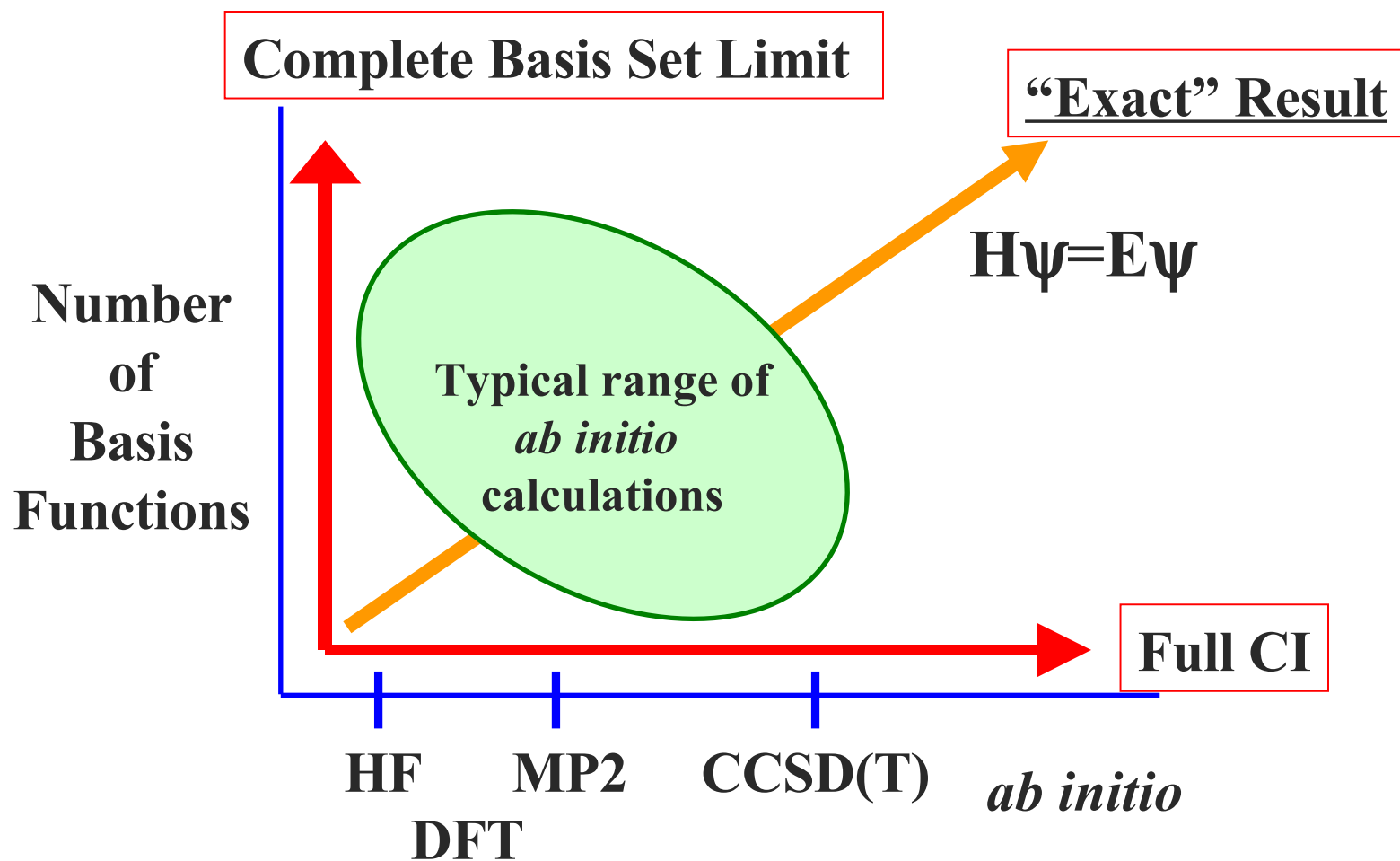
# Method Studies of Water Systems Containing Hydroxyl

Ian Haken, Erin Dahlke, Donald G. Truhlar



# Introduction to Computational Chemistry

Approach to the “exact” solution to the Schrödinger Equation



# [ Objectives of Study ]

- Create a data set of accurate binding energies from high level calculations for water systems containing a hydroxyl radical
- Compare results of DFT and multilevel methods to the data set
- Determine relative accuracy of the DFT and multilevel methods, optimizing parameters if necessary

# [ Procedure ]

- Find QCISD/6-311g(d,p) optimized geometries for 17 conformations, ranging in size from 2 to 6 molecules
- Calculate bonding energies for these geometries with a set of DFT (with MG3S basis set) and multilevel methods
- Calculate bonding energies for smaller clusters with W1, a high accuracy (though very high cost) method
- Determine optimum multilevel method to be used with the larger systems for comparison to DFT

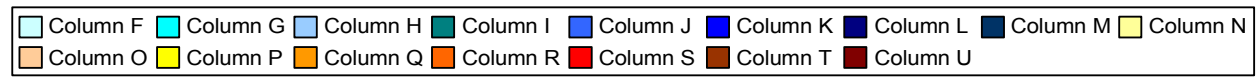
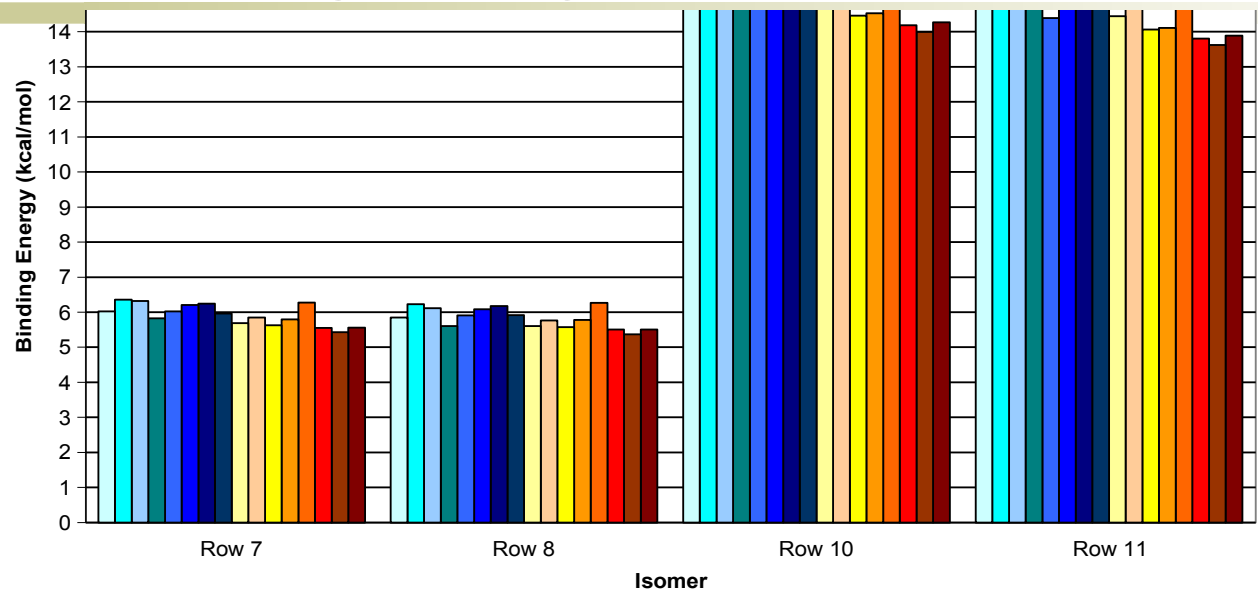
# [ Preliminary Results ]

- All but three of the largest systems completed geometry optimizations
- For all optimized systems, all DFT and multilevel energies calculated

However...

- W1 calculations met with unexpected results, and energies were not considered reliable

# W1 Dilemma



OH-H<sub>2</sub>O A

OH-H<sub>2</sub>O B

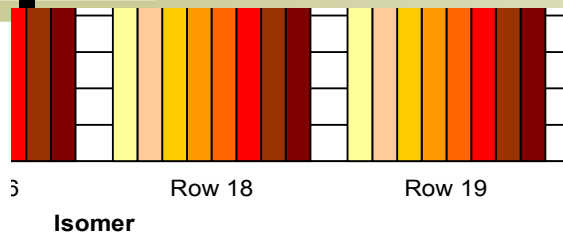
OH-(H<sub>2</sub>O)<sub>2</sub> A

OH-(H<sub>2</sub>O)<sub>2</sub> B

## Attempts to Identify Source of Problem

- Find binding energies for both FH and NH<sub>2</sub> systems
- Determine if problem exists with the MP2 energies
- Perform original W1 calculations with different software

# [ FH Results ]



\*W1 for trimers is CCSD(T)/aug'-cc-pVTZ energy

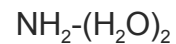
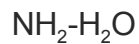
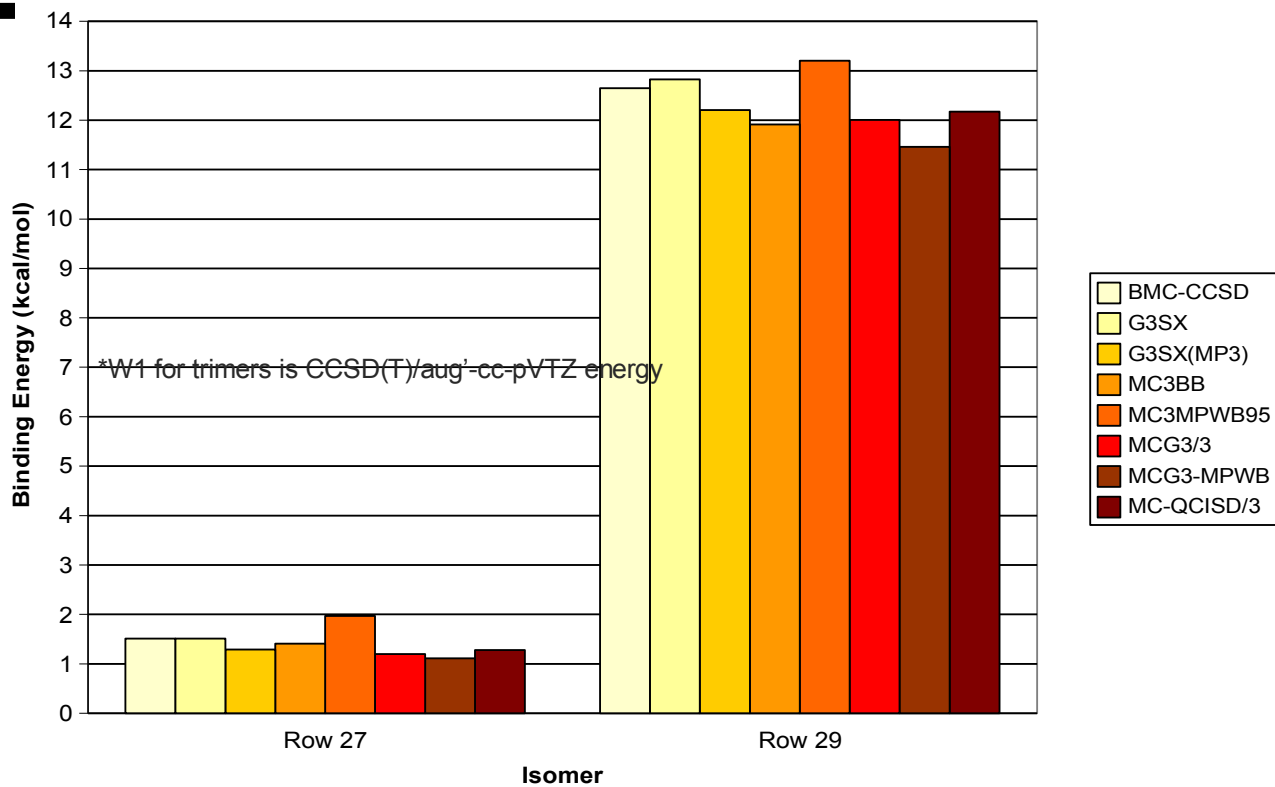
FH-H<sub>2</sub>O A

FH-H<sub>2</sub>O B

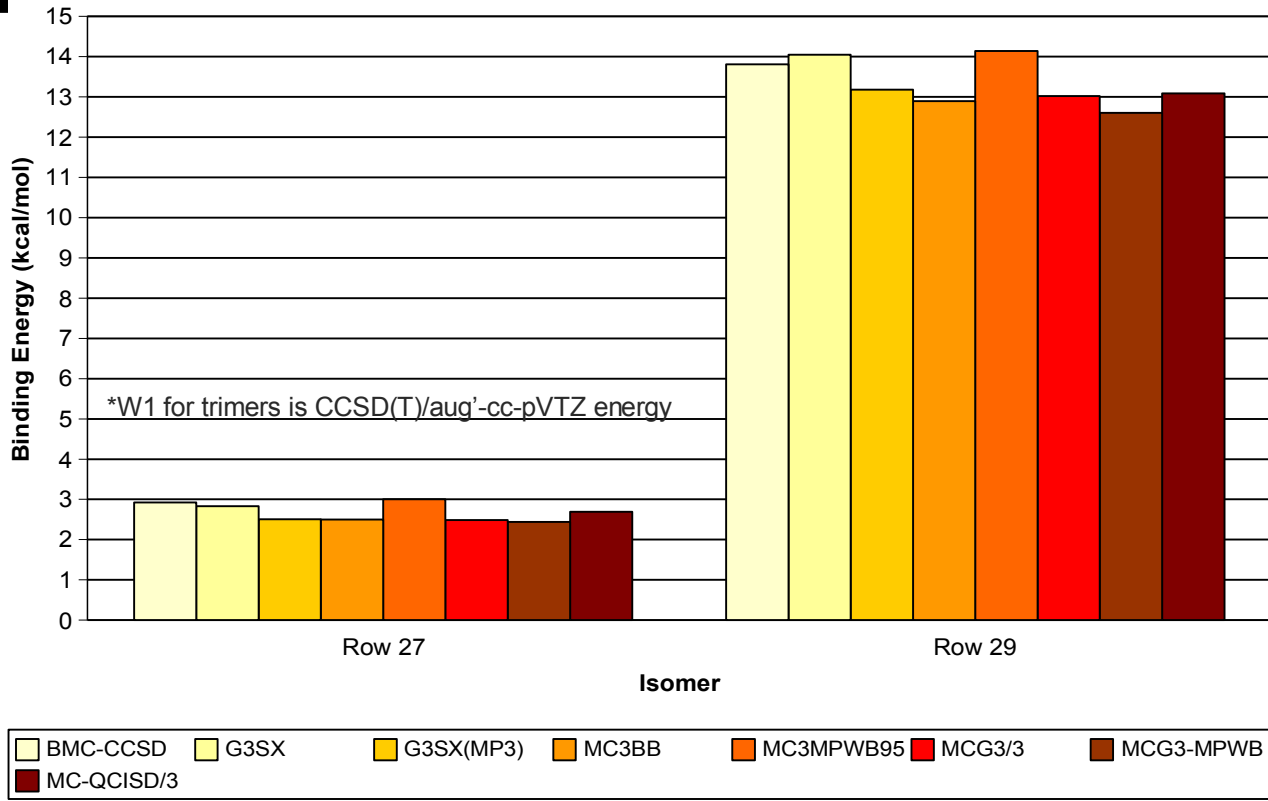
FH-(H<sub>2</sub>O)<sub>2</sub> A

FH-(H<sub>2</sub>O)<sub>2</sub> B

# NH<sub>2</sub> Results



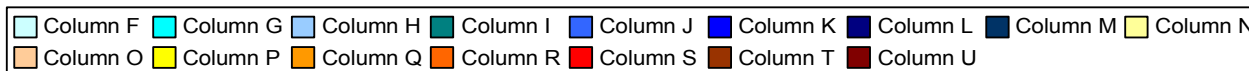
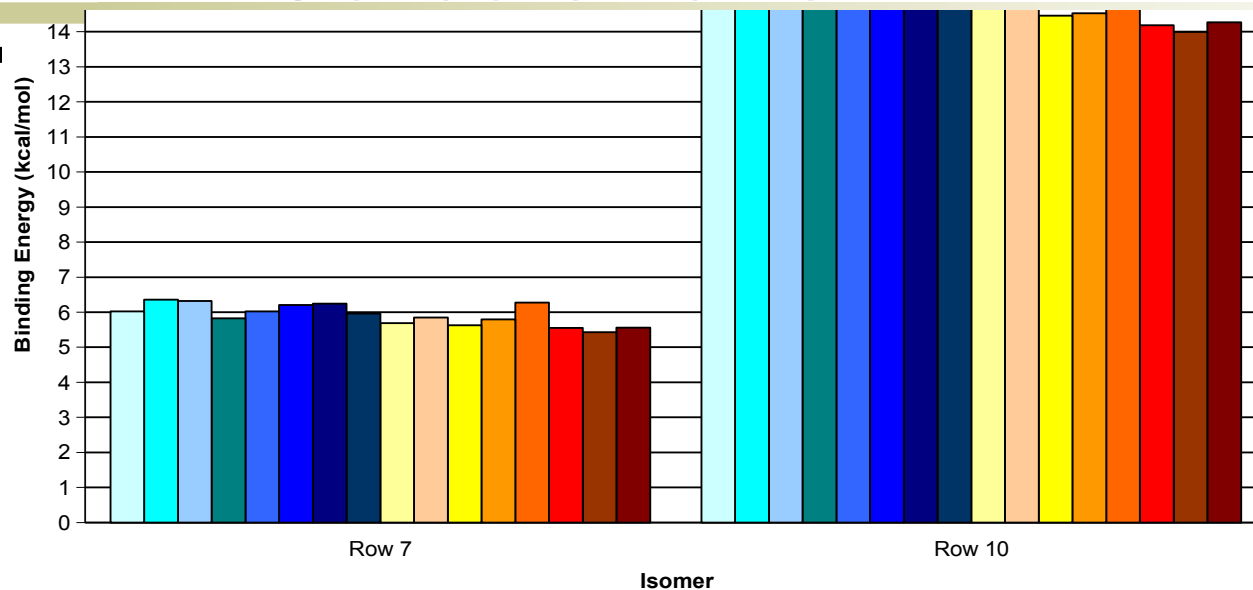
# [ NH<sub>2</sub> (Linear) Results ]



NH<sub>2</sub>-H<sub>2</sub>O

NH<sub>2</sub>-(H<sub>2</sub>O)<sub>2</sub>

# MP2 Calculations



OH-H<sub>2</sub>O

OH-(H<sub>2</sub>O)<sub>2</sub>

# [ Wavefunction Guess ]

After results of MP2 calculations, it is believed that the difference between RHF and UHF wavefunction guesses is a likely source of the problem

## Molpro

Method	Guess
RCCSD(T)	RHF
UCCSD(T)	RHF
RMP2	RHF
UMP2	UHF

## Gaussian (open shell)

Method	Guess
RCCSD(T)	N/A
UCCSD(T)	UHF
RMP2	N/A
UMP2	UHF

# W1 with Gaussian

Basis Sets		6-311G(d,p)		MG3S						
System	Isomer	MP2 (opt)	QCISD (opt)	PBE1W (opt)	PBE1W	mPWLYP	PBEPBE	TPSSTPSS	B98	B97-1
H2O	A	-76.26	-76.27	-76.46	-76.46	-76.44	-76.38	-76.46	-76.43	-76.44
OH	A	-75.57	-75.59	-75.76	-75.76	-75.75	-75.68	-75.77	-75.73	-75.74
OH-W1	A	-151.85	-151.87	-152.23	-152.23	-152.2	-152.06	-152.24	-152.18	-152.18
	B	-151.85	-151.87	-152.23	-152.23	-152.2	-152.06	-152.24	-152.18	-152.18
OH-W2	A	-228.13	-228.16	-228.71	-228.71	-228.66	-228.46	-228.72	-228.62	-228.63
	B	-228.13	-228.16	-228.72	-228.71	-228.66	-228.46	-228.72	-228.62	-228.63
OH-W3	A	-304.42	-304.45	-305.2	-305.2	-305.13	-304.85	-305.2	-305.07	-305.09
	B	-304.41	-304.44	-305.2	-305.19	-305.12	-304.84	-305.19	-305.06	-305.08
	C	-304.4	-304.44	-305.18	-305.18	-305.11	-304.84	-305.18	-305.06	-305.07
	D	-304.4	-304.44	-305.19	-305.18	-305.11	-304.84	-305.18	-305.06	-305.07
	E	-304.4	-304.43	-305.19	-305.18	-305.11	-304.84	-305.18	-305.05	-305.07
OH-W4	A	-380.7	-380.74	-381.68	-381.67	-381.59	-381.25	-381.68	-381.52	-381.54
	B	-380.7	-380.74	-381.68	-381.67	-381.58	-381.24	-381.67	-381.52	-381.53
	C	-380.7	-380.74	-381.68	-381.67	-381.58	-381.24	-381.67	-381.52	-381.53
	D	-380.7	-380.74	-381.68	-381.67	-381.58	-381.24	-381.67	-381.51	-381.53
*W1 is CCSD(T)/aug-cc-pVDZ energy										
OH-W5	A	-456.99	ALTIX							
	B	-456.99	ALTIX							
	C	-456.98	-457.03	-458.16	-458.15	-458.04	-457.64	-458.15	-457.97	-457.98
	D	-456.99	ALTIX							
OH-W6	A									
	B									
	C									
	D									

OH-H<sub>2</sub>O A

OH-H<sub>2</sub>O B

OH-(H<sub>2</sub>O)<sub>2</sub> A

OH-(H<sub>2</sub>O)<sub>2</sub> B

# [ Conclusions ]

---

- DFT and multilevel methods have produced a range of binding energies, but without accurate data for comparison, no conclusions about relative accuracy can yet be made
- W1 problem still being worked on

# [ Acknowledgments ]

UNIVERSITY OF MINNESOTA



*The Truhlar Group*