

Supplementary Material for “Understanding the many-body expansion for large systems. II. Accuracy considerations”

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CCSD(T)/CBS and MP2/CBS benchmarks for ten low-energy isomers of $(\text{H}_2\text{O})_{20}$,^{1,2} are taken from Ref. 3. Those benchmarks and the corresponding $\omega\text{B97X-V}/\text{def2-TZVPPD}$ interaction energies with counterpoise correction are shown in Table S1. All of these benchmarks are counterpoise-corrected.

Tables S2 and S3 present what we believe is a nearly exhaustive list of MBE(2) and MBE(3) results from the literature, subject to the following caveats:

- We consider only clusters with $N > 10$ monomers.
- We only consider cases where the MBE calculation was compared against a supersystem benchmark computed at the same level of theory.
- Multi-layer methods, and those based on overlapping fragments, have been excluded from this comparison for simplicity, although many such benchmarks for water clusters can be found in the literature.⁴⁻¹¹

That said, direct comparison of the various literature calculations presented in these tables must proceed with caution. In particular, the results in the tables correspond to different structures (*e.g.*, the 16-mer examined in Ref. 12 is different from the one considered here). Differences in electrostatic embeddings and, in a few cases, the use of two H_2O molecules per fragment are noted in footnotes to Tables S2 and S3. Unless care is taken to ensure that all of these points are addressed similarly between implementations, finite-precision issues can easily cause a user to obtain results that are different from those in the literature.¹³

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Isomer	Interaction Energy / kcal mol ⁻¹		
	CCSD(T)/CBS	MP2/CBS	ω B97X-V/def2-TZVPPD
1	-200.54	-197.97	-198.91
2	-199.20	-196.68	-197.58
3	-198.93	-196.51	-197.35
4	-197.89	-195.02	-195.98
5	-198.15	-195.58	-196.51
6	-198.17	-195.24	-196.38
7	-197.67	-194.62	-195.94
8	-197.44	-194.90	-195.80
9	-197.03	-194.29	-195.37
10	-196.59	-193.92	-194.97

Table S1: CCSD(T)/CBS, MP2/CBS, and ω B97X-V/def2-TZVPPD interaction energies for isomers (H₂O)₂₀. All values (including those used in the CBS extrapolations) have been counterpoise corrected.

Table S2: Mean absolute errors (in kcal/mol) in EE-2B interaction energies for $(\text{H}_2\text{O})_N$ clusters, as predicted by various fragment-based methods. Only published calculations with $N > 10$ are considered.

N	Ref.	Method	Basis Set					
			STO-3G	3-21G	6-31G*	6-31++G**	6-311++G(3df,2p)	other
16	12	HF ^a	0.15	5.70	4.97	1.00		
	12	HF ^{a,b}	0.10	4.12	3.54	0.42		
	14	B3LYP ^a			9.83	6.78		
	14	B3LYP ^{a,b}			7.06	4.42		
	9	MP2 ^a			4.64	2.88	10.88	
	15	CCSD(T)						3.59 ^c
20	9	MP2 ^a			6.20	4.00	14.00	
	16	MP2 ^c						2.01 ^c
21	17	MP2						2.97 ^d
32	12	HF ^a	0.48	15.66	13.2	4.51		
	12	HF ^{a,b}	0.43	13.1	10.69	3.22		
	14	B3LYP ^a			26.27	23.58		
	14	B3LYP ^{a,b}			21.5	18.28		
	9	MP2 ^a			10.56	12.16	26.88	
57	10	B3LYP						20.52 ^e
64	12	HF ^a	1.29	38.6	32.73	12.06		
	12	HF ^{a,b}	0.94	27.37	23.15	8.81		
	14	B3LYP ^a			65.63	64.24		
	14	B3LYP ^{a,b}			46.85	48.2		
	9	MP2 ^a			22.4	27.52		

^aEE is defined to be density embedding at close range, density embedding with the Mulliken approximation at mid-range, and Mulliken point-charge embedding at long range.¹⁸

^bTwo water molecules per fragment.

^cBasis set is aug-cc-pVTZ.

^dBasis set is aug-cc-pVTZ for oxygen and cc-pVTZ for hydrogen.

^eBasis set is 6-31+G(d,2p).

Table S3: Mean absolute errors (kcal/mol) in EE-3B interaction energies for water clusters, as predicted by various fragment-based methods. Only published calculations with $N > 10$ are considered.

N	Ref.	Method	Basis Set					other
			STO-3G	3-21G	6-31G*	6-31++G**	6-311++G(3df,2p)	
16	12	HF ^a	0.01	0.28	0.39	1.17		
	12	HF ^{a,b}	0.01	0.23	0.26	0.40		
	14	B3LYP ^a			0.51	3.12		
	14	B3LYP ^{a,b}			0.36	0.78		
	9	MP2 ^a			1.44	0.80	0.64	
	15	CCSD(T)						1.52 ^c
20	9	MP2 ^a			1.8	0.40	0.40	
	16	MP2 ^d						1.56 ^c
21	17	MP2						0.38 ^e
32	12	HF ^a	0.04	0.80	1.33	3.71		
	12	HF ^{a,b}	0.02	0.57	0.93	1.67		
	14	B3LYP ^a			1.85	14.71		
	14	B3LYP ^{a,b}			1.36	0.39		
	9	MP2 ^a			3.52	2.24	1.28	
64	9	MP2 ^a		6.4	3.2			

^aEE is defined to be density embedding at close range, density embedding with the Mulliken approximation at mid-range, and Mulliken point-charge embedding at long range.¹⁸

^bTwo water molecules per fragment.

^cBasis set is aug-cc-pVTZ.

^dEE uses point dipoles instead of point charges.

^eBasis set is aug-cc-pVTZ for oxygen and cc-pVTZ for hydrogen.

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