Supporting Information for:

Electrostatically Embedded Many-Body Expansion for Large Systems, with Applications to Water Clusters

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Results for Truncation after V1

In the traditional many-body expansion, since results with only one-body terms are expected to be poor, equation 1 is rarely truncated after the first term. One might wonder, however, if the inclusion of the point charges for the other $N - 1$ water molecules could introduce enough polarization to make the results quantitatively correct. Table S1 provides the mean errors relative to the true energies for the traditional one-body result (1B), as well as the five EE-1B results. We can see that two of the electrostatically embedded one-body methods, namely EE-1B-AM1 and EE-1B-AM1M, do provide an improvement over the traditional one-body approximation, but the other three methods do not, indicating a much larger sensitivity to the charges than we see with the EE-PA methods. This is likely due to the fact that the inclusion of the dimer term explicitly introduces the two-body terms that are known to be very important in the many-body expansion (see reference 50 for more information). The higher-order many-body terms are much smaller in magnitude, and appear to be much less sensitive to the choice in charge model, as evidenced by the results in Table 1. We further note that comparing the results in Table 1 and Table S1 shows that none of the EE-1B methods improves upon the results of the conventional pairwise additive approximation.

Table S1: Comparison of Mean Errors[a] (kcal/mol) for One-Body Approximation and EE-1B Approximations

	1B			EE-1B-AM1			EE-1B-AM1M			EE-1B-B3LYPM			EE-1B-CM4M			EE-1B-TIP3P		
	MSE	MUE	RMSE	MSE	MUE	RMSE	MSE	MUE	RMSE	MSE	MUE	RMSE	MSE	MUE	RMSE	MSE	MUE	RMSE
PBE1W/MG3S	16.00	16.00	16.41	-7.29	7.29	8.59	-3.86	3.86	5.01	-26.32	26.32	27.77	-16.82	16.83	18.66	-29.68	29.68	31.25
PBE/MG3S	15.50	15.50	16.45	-5.68	5.68	7.18	-2.58	2.58	3.85	-23.04	23.04	25.30	-14.33	14.34	16.64	-26.10	26.10	28.60
BLYP/MG3S	12.23	12.23	13.11	-8.84	8.84	10.45	-5.76	5.76	7.02	-26.15	26.15	28.60	-17.27	17.31	19.91	-29.20	29.20	31.89
B3LYP/MG3S	13.82	13.82	14.73	-7.74	7.74	9.38	-4.59	4.59	5.90	-25.34	25.34	27.81	-16.42	16.46	19.02	-28.44	28.44	31.14
PBE/ATZ	14.46	14.46	15.40	-6.11	6.11	7.53	-3.05	3.05	4.18	-23.41	23.41	25.67	-14.67	14.67	16.95	-26.50	26.50	29.00
BLYP/DIDZdp	14.58	14.58	15.57	-7.63	7.63	9.30	-4.41	4.41	5.83	-25.49	25.49	27.90	-16.47	16.51	19.05	-28.61	28.61	31.25
B3LYP/DIDZd2p	14.72	14.72	15.68	-7.20	7.20	8.81	-4.02	4.02	5.36	-24.90	24.90	27.29	-15.99	16.02	18.51	-28.00	28.00	30.62
PBE1W/DITZ2d2p	14.45	14.45	15.34	-6.70	6.70	8.28	-3.60	3.60	4.88	-24.03	24.03	26.40	-15.27	15.28	17.73	-27.08	27.08	29.69
MP2/aug'-cc-pVTZ	14.79	14.79	15.67	-6.53	6.53	8.17	-3.39	3.39	4.75	-24.19	24.19	26.66	-15.35	15.37	17.88	-27.32	27.32	30.04

[a] MSE, MUE, and RMSE denote mean signed, mean unsigned, and root mean squared errors respectively

[b] aug′-cc-PVTZ denotes cc-pVTZ on hydrogen and aug-cc-pVTZ on oxygen