Supplementary Information for

Automatic generation of reaction energy databases from highly accurate atomization energy benchmark sets

Johannes T. Margraf, Duminda Ranasinghe, Rodney J. Bartlett
Quantum Theory Project, University of Florida, Gainesville, Florida 32611, USA

Contents

The supplementary information to this article consists of several parts:

SI.pdf:

This document, which contains Fig. S1-S2 and Tab. S1-S3

autoRE.zip:

Contains the autoRE Perl script, a README file with instructions and two exemplary input files (reference.txt and bondlist.txt).

geo.zip:

Contains the W4-11 geometries and *autoRE* input files, which can be used to generate different reaction energy benchmark sets.

reference_data.xlsx:

Contains the reaction energies and net bond differences for all reaction energy sets mentioned in the paper.

benchmarks.xlsx:

Contains the data for the performance of different electronic structure methods.

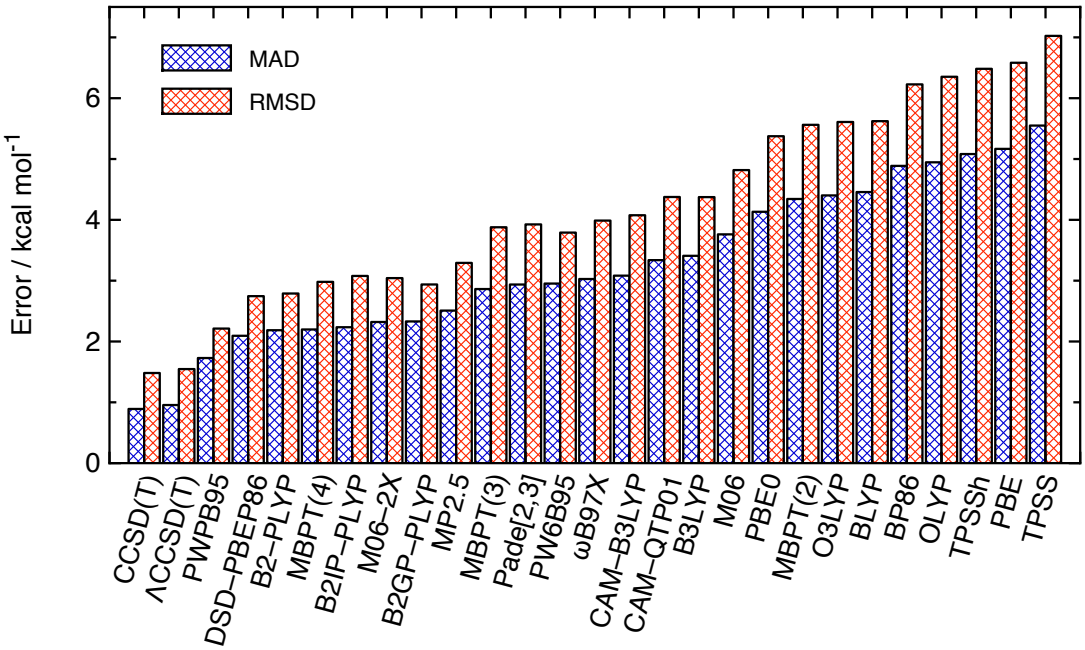

Fig. S1: Error statistics of different electronic structure methods for the W4-11-RE-noMR set. RMSD = Root mean square deviation, MAD = mean absolute deviation

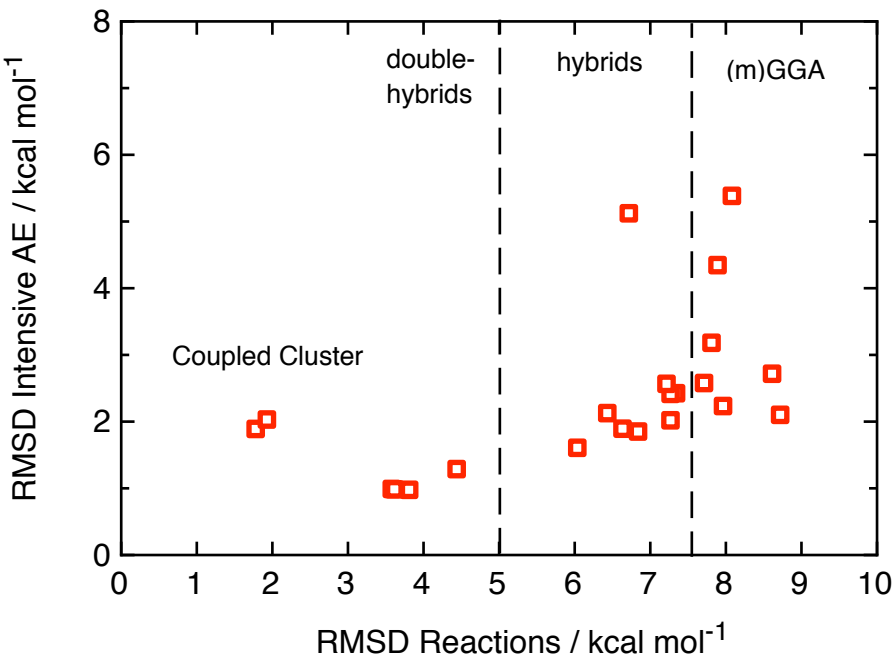

Fig. S2: RMSD values for intensive atomization energies versus reactions energies for different DFAs and CCSD(T). The dashed lines roughly delimit the approximate accuracy for the different types of DFAs.

Tab. S1: Mean absolute deviations (MAD) and root mean square deviations (RMSD) of CCSD(T) and DFAs for the reaction energies (RE) and atomization energies (AE) of the W4-11 set. All values given in kcal mol^{-1}. A negative value in the last column indicates that the error for AEs is larger than for REs.

Method	**MAD(RE)**	**RMSD(RE)**	**MAD(AE)**	**RMSD(AE)**	**MAD(RE)-MAD(AE)**
CCSD(T)	1.08	1.78	5.92	6.74	-4.84
PWPB95	2.36	3.58	1.88	2.91	0.48
B2-PLYP	2.60	3.61	2.15	2.96	0.45
B2IP-PLYP	2.78	3.81	2.23	3.08	0.55
DSD-PBEP86	2.94	4.40	2.98	4.02	-0.04
B2GP-PLYP	3.16	4.44	2.62	3.79	0.54
PW6B95	3.85	6.03	2.68	4.19	1.17
M06-2X	4.01	6.84	3.02	4.90	0.99
ωB97X	4.27	7.34	3.82	6.02	0.45
CAM-B3LYP	4.30	7.27	3.53	6.17	0.76
B3LYP	4.33	6.43	4.55	6.43	-0.21
M06	4.65	6.63	4.46	5.73	0.19
O3LYP	4.92	6.72	17.13	20.16	-12.20
PBE0	4.95	7.27	3.88	5.65	1.08
CAM-QTP01	5.04	8.61	5.28	7.71	-0.24
BLYP	5.84	7.81	7.22	10.28	-1.38
OLYP	5.92	7.71	5.59	8.27	0.33
TPSSh	5.97	7.96	4.76	6.58	1.21
BP86	6.01	7.89	12.43	15.12	-6.41
PBE	6.21	8.08	14.41	18.11	-8.21
TPSS	6.70	8.72	4.89	6.49	1.82

Tab. S2: Mean absolute deviations (MAD) and root mean square deviations (RMSD) of different electronic structure methods for the reaction energies (RE) of the W4-11-1stRow set. All values given in kcal mol^{-1}.

Method	**MAD**	**RMSD**
CCSD(T)	0.77	1.00
ΛCCSD(T)	0.94	1.29
PWPB95	2.31	3.57
B2-PLYP	2.60	3.64
B2IP-PLYP	2.78	3.82
MBPT(4)	2.78	4.02
DSD-PBEP86	2.92	4.39
B2GP-PLYP	3.19	4.49
MP2.5	3.63	5.31
PW6B95	3.81	6.10
M06-2X	3.92	6.93
CAM-B3LYP	4.20	7.37
ωB97X	4.22	7.48
B3LYP	4.23	6.41
Pade[2,3]	4.36	6.84
MBPT(3)	4.48	7.25
M06	4.73	6.76
PBE0	4.89	7.29
O3LYP	4.90	6.72
CAM-QTP01	5.00	8.79
MBPT(2)	5.17	6.97
BLYP	5.76	7.69
OLYP	5.85	7.61
TPSSh	5.95	7.99
BP86	5.98	7.83
PBE	6.18	8.02
TPSS	6.70	8.73

Tab. S3: Mean absolute deviations (MAD) and root mean square deviations (RMSD) of different electronic structure methods for the reaction energies (RE) of the W4-11-1stRow-noMR set. All values given in kcal mol^{-1}.

Method	**MAD**	**RMSD**
CCSD(T)	0.67	0.86
ΛCCSD(T)	0.73	0.95
PWPB95	1.67	2.13
MBPT(4)	2.05	2.75
DSD-PBEP86	2.11	2.77
M06-2X	2.12	2.69
B2-PLYP	2.18	2.77
B2IP-PLYP	2.25	2.86
MP2.5	2.29	2.93
B2GP-PLYP	2.34	2.94
MBPT(3)	2.64	3.53
Pade[2,3]	2.69	3.55
PW6B95	2.80	3.58
ωB97X	2.84	3.74
CAM-B3LYP	2.87	3.79
CAM-QTP01	3.13	4.08
B3LYP	3.25	4.16
M06	3.69	4.70
PBE0	3.97	5.17
MBPT(2)	4.25	5.42
O3LYP	4.33	5.51
BLYP	4.42	5.56
BP86	4.87	6.19
OLYP	4.92	6.31
TPSSh	5.01	6.42
PBE	5.16	6.55
TPSS	5.53	7.01