Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

A computationally efficient double hybrid density functional based on the random phase approximation

Supporting Information

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1 Computational details

Several density functionals (DF) of each rank in Perdew's picture of Jacob's Ladder[1,2] (except LDA) were tested. From the General Gradient Approximation (GGA) level, the PBE,[3,4] BLYP,[5,6] and B97-d[7] functionals were chosen, whereas for the class of meta-GGAs TPSS[8] was taken. In addition, the hybrid functionals BHLYP,[9] PBE0,[10] and B3LYP[5,6,11,12] and the meta-hybrid PW6B95[13] were used. From the fifth rung, the double hybrid density functionals (DHDF), B2PLYP,[14] PWPB95,[15] PBE0-DH,[16] and the new DHDF PWRB95 were adopted. Additionally, the dRPA method[17] (based on PBE orbitals) was tested, as well. As wavefunction method MP2[18] was chosen.

All calculations for PWRB95 and PBE0-DH were done with a modified version of TURBOMOLE 5.7[19,20] while for the other methods TURBOMOLE 6.6[21] was used. Thereby, in the perturbative treatment of the conventional DHDFs all electrons were taken into account while for the new DHDF PWRB95, dRPA and MP2 the core electrons were kept frozen.

For the calculations of the GMTKN30 database[15,22] we used the (aug-)def2-QZVP[23–25] and def2-TZVP(D)[23,26] basis sets where we used additional diffuse functions for the G21EA (in case of (aug-)def2-QZVP one s- and one p-function for heavy elements and one s-function for hydrogen taken from aug-cc-pVQZ) and WATER27 (in case of (aug-)def2-QZVP one s- and one p-function taken from aug-cc-pVQZ) subsets. For the test sets sHC5, RCx (x=0-5), DBH24, AE6, and NCCE31 we took the def2-QZVP basis set. In case of the Pd/Ni benchmark and the isomerization reaction within the $[Cu_2(en)_2O_2]^{2+}$ complex the single-point calculations were conducted using the def2-QZVPP basis set. In case of Pd the small-core ECP ECP28MWB[27] was applied.

For the two subsets BHPERI and WATER27 in the GMTKN30 database different reference values were used in variance to the original publication. In case of BHPERI we used the new reference data of Karton and Goerigk.[28] For the WATER27 subset we replaced the old reference values of the $(H_2O)_{20}$ complexes by new incremental CCSD(T)(F12) values calculated by Anacker and Friedrich.[29]

In all DF based calculations the grid m4[30] (grid 3 for the SCF and grid 4 for the final energy evaluation) was applied for the numerical quadrature of the exchange-correlation energy. For the RPA part in PWRB95 and dRPA the number of grid points was chosen depending on the HOMO/LUMO gap. For gaps larger than 0.1 a.u. we took 40 grid points for the numerical quadrature. If the gap is between 0.1 a.u. and 0.002 a.u. 150 points were used for the integration and for gaps lower than 0.002 a.u. 1000 grid points were taken. For evaluating the timings we used 40 grid points in all calculations. In case of the cyclacenes the number of RPA grid points was 250. For test purposes we conducted PWRB95 calculations for the GMTKN30 database where all electrons were correlated. Here, a larger number of grid points is required due to a higher frequency interval in the quadrature.

In all calculations the RI for the Coulomb integrals (RI-J)[31] and for the (double) hybrids for the exchange integrals (RI-K)[32] was adopted as well. For the perturbative part of the DHDFs and MP2 and the RPA part in PWRB95 and dRPA the RI approximation[33] was used in all calculations, as well. The corresponding auxiliary basis sets were taken from the TURBOMOLE basis set library.[34] The estimated error of the RI approximation in all variants is completely negligible relative to other sources of error and on the order of 0.1–0.2 kcal mol^{-1} for the considered relative energies.

Additionally, we applied our atom pairwise dispersion correction DFT-D3 (functionals are denoted with "-D3")[35] together with the Becke–Johnson (BJ) damping function[36] as well as the non-local density functional kernel VV10 (functionals are denoted with "-NL").[37]

Within the GMTKN30 database some reactions had to be neglected for the evaluation due to technical problems. In case of PWRB95 these are reaction number 44 of the W4-08 test set, reactions 8 and 11 of the SIE11 set and reaction 10 of the HEAVY28 subset. For dRPA reaction 44 of the W4-08 subset, reaction 11 of the SIE11 test and reactions 10 and 11 of HEAVY28 are discarded.

2 Training set

Table 1: All entries of the PTPSS parameters fit set and their weight factors for the determination of the mean absolute deviations.

system	factor	system	factor	system	factor	system	factor
atomization energies[a]		F_2O	3.0	C_5H_8	1.0	HF + H	1.0
B_2H_6	3.0	BH	3.0	FCH_3F	1.0	O + CH_4	1.0
BF_2H	3.0	BH_3	3.0	FCH_3F	1.0	OH + CH_3	1.0
BF_3	3.0	bnS	3.0	Cl^- + CH_3Cl	1.0	H + PH_3	1.0
C_2H_6	3.0	BF	3.0	CH_3Cl + Cl^-	1.0	H_2 PH_2	1.0
H_2CN	3.0	NH	3.0	$ClCH_3Cl$	1.0	H + OH	1.0
C_2N_2	3.0	NH_2	3.0	$ClCH_3Cl$	1.0	H_2 + O	1.0
CH_2NH_2	3.0	HCN	3.0	F^- + CH_3Cl	1.0	H + H_2S	1.0
CH_3NH	3.0	HOF	3.0	CH_3F + Cl^-	1.0	O + HCl	1.0
CH_3NH_2	3.0	AlH	3.0	FCH_3Cl (complex 1)	1.0	NH_2 + CH_3	1.0
CF_2	3.0	AlH_3	3.0	FCH_3Cl (complex 2)	1.0	NH + CH_4	1.0
N_2H	3.0	AlF	3.0	OH^- + CH_3F	1.0	NH_2 + C_2H_5	1.0
N_2H_2	3.0	bnT	3.0	CH_3OH + F^-	1.0	NH + C_2H_6	1.0
N_2H_4	3.0	CF	3.0	$HOCH_3F$ (complex 1)	1.0	C_2H_6 + NH_2	1.0
FO_2	3.0	BeF_2	3.0	$HOCH_3F$ (complex 2)	1.0	C_2H_5 + NH_3	1.0
F_2O_2	3.0	CH_2C	3.0	H + N_2	1.0	NH_2 + CH_4	1.0
AlF_3	3.0	CH_2CH	3.0	HN_2	1.0	NH_3 + CH_3	1.0
P_4	3.0	C_2H_4	3.0	H +CO	1.0	Pyrrol + C_2H_4	2.0
H_2	3.0	CH_2NH	3.0	HCO	1.0	Cis-triscyclopropacyclohexane	2.0
OH	3.0	HCO	3.0	H + C_2H_4	1.0	1,3-Cyclopentadiene	2.0
HF	3.0	CH_2O	3.0	$C2H_5$	1.0	Thiophene + C_2H_4	2.0
H_2O	3.0	CO_2	3.0	CH_3 + C_2H_4	1.0	**ionization potentials**[c]	
CH	3.0	HNO	3.0	C_3H_7	1.0	H → H^+	2.0
CH_2	3.0	NO_2	3.0	HCN	1.0	Li → Li^+	2.0
CH_3	3.0	N_2O	3.0	HNC	1.0	B → B^+	2.0
CH_4	3.0	O_3	3.0	H + HCl	1.0	C → C^+	2.0
C_2H	3.0	HO_2	3.0	OH + H_2	1.0	N → N^+	2.0
C_2H_2	3.0	**barrier heights**[b]		H_2O + H	1.0	O → O^+	2.0
NH_3	3.0	N_2O + H	1.0	CH_3 + H_2	1.0	F → F^+	2.0
N_2	3.0	OH + N_2	1.0	CH_4 + H	1.0	**non-covalently bound dimers**[d]	
CO	3.0	HF + H	1.0	OH + CH_4	1.0	Ne_2 → 2 Ne	200.0
CN	3.0	H + HF	1.0	H_2O + CH_3	1.0	Ar_2 → 2 Ar	200.0
O_2	3.0	H + HCl	1.0	H + H_2	1.0	Kr_2 → 2 Kr	200.0
NO	3.0	HCl + H	1.0	H + H_2	1.0	$(C_2H_6)_2$	20.0
OF	3.0	H + CH_3F	1.0	OH + NH_3	1.0	$(C_3H_8)_2$	20.0
F_2	3.0	HF + CH_3	1.0	H_2O + NH_2	1.0	$(C_4H_{10})_2$	20.0
PH_3	3.0	H + F_2	1.0	HCl + CH_3	1.0	$(NH_3)_2$	50.0
P_2	3.0	HF + F	1.0	OH + C_2H_6	1.0	$(H_2O)_2$	50.0
Be_2	3.0	CH_3 + F^-	1.0	H_2O + C2H5	1.0	$(HCOOH)_2$	10.0
B_2	3.0	F^- + CH_3	1.0	F + H_2	1.0		
H_2O_2	3.0	C_5H_8	1.0	HF + H	1.0		

[a] taken from the W4-08 set (*J. Phys. Chem. A*, 2008, **112**, 12868). [b] taken from the BH76 set (*J. Phys. Chem. A*, 2004, **108**, 2715;*J. Phys. Chem. A*, 2005, **109**, 2012)) and the BHPERI set (*J. Chem. Theory Comput.*, 2010, **6**, 107). [c] taken from the G21IP set (*J. Chem. Phys.*, 1991, **94**, 7221). [d] taken from the RG6 set and the ADIM6 set (*J. Chem. Phys.*, 2010, **132**, 154104), taken from the S22 set (*Phys. Chem. Chem. Phys.*, 2006, **8**, 1985; *J. Chem. Phys.*, 2010, **132**, 144104)

3 GMTKN30

Table 2: Mean absolute deviations of the complete GMTKN30 database for BLYP(-D3,-NL), B97-D3, PBE(-D3,-NL), and TPSS(-D3,-NL). All values are in kcal/mol and were obtained with the (aug-)def2-QZVP basis.

	BLYP-D3 (-NL)	B97-D3	PBE-D3 (-NL)	TPSS-D3 (-NL)
MB08-165	9.0 (9.1)	9.7	9.8 (10.4)	9.7 (10.1)
W4-08	7.7 (10.5)	4.3	13.5 (14.7)	5.9 (7.7)
G21IP	4.7 (6.3)	3.5	3.9 (4.1)	4.0 (4.7)
G21EA	3.3 (2.9)	2.3	3.4 (2.6)	2.2 (2.8)
PA	2.7 (2.2)	5.7	2.3 (1.9)	4.9 (4.0)
SIE11	12.2 (12.5)	11.2	12.0 (12.1)	9.7 (10.2)
BHPERI	3.6 (4.9)	4.0	6.7 (7.4)	5.5 (7.0)
BH76	9.4 (10.2)	7.4	9.7 (10.1)	9.2 (9.8)
BH76RC	3.2 (3.3)	3.0	4.4 (4.7)	3.7 (3.9)
RSE43	3.2 (3.3)	3.4	3.3 (3.3)	2.4 (2.4)
O3ADD6	6.4 (5.6)	5.8	4.8 (5.3)	4.4 (5.9)
G2RC	4.9 (4.9)	4.6	6.9 (7.5)	7.0 (7.7)
AL2X	3.2 (3.2)	3.8	2.4 (2.5)	3.6 (3.9)
NBPRC	3.1 (2.2)	2.7	2.6 (3.0)	1.5 (2.7)
ISO34	2.6 (2.0)	2.0	1.6 (1.6)	2.0 (2.2)
ISOL22	9.3 (7.1)	8.3	5.2 (4.2)	6.6 (4.7)
DC9	14.2 (9.9)	13.1	11.1 (12.5)	8.8 (10.2)
DARC	13.5 (8.7)	10.4	3.6 (2.7)	5.2 (2.4)
ALK6	3.8 (4.8)	5.6	4.5 (4.2)	4.5 (4.2)
BSR36	3.3 (1.4)	3.4	3.7 (2.2)	4.8 (2.5)
IDISP	5.0 (3.4)	4.7	3.4 (2.1)	3.5 (1.9)
WATER27	2.2 (7.1)	3.7	7.8 (10.3)	3.5 (7.9)
S22	0.25 (0.4)	0.38	0.46 (0.49)	0.30 (0.41)
ADIM6	0.10 (0.16)	0.41	0.24 (0.16)	0.19 (0.26)
RG6	0.07 (0.22)	0.04	0.06 (0.09)	0.04 (0.07)
HEAVY28	0.33 (0.30)	0.28	0.36 (0.33)	0.31 (0.26)
PCONF	0.85 (0.60)	1.16	1.74 (1.37)	1.49 (1.02)
ACONF	0.13 (0.10)	0.07	0.07 (0.06)	0.09 (0.16)
SCONF	0.47 (0.78)	0.51	0.52 (0.81)	0.76 (1.35)
CYCONF	0.47 (0.42)	0.64	0.92 (0.91)	0.91 (0.98)

Table 3: Mean absolute deviations of the complete GMTKN30 database for B3LYP(-D3,-NL), PBE0(-D3,-NL), PW6B95-D3, and BHLYP(-D3,-NL). All values are in kcal/mol and were obtained with the (aug-)def2-QZVP basis.

	B3LYP-D3 (-NL)	PBE0-D3 (-NL)	PW6B95-D3	BHLYP-D3 (-NL)
MB08-165	5.7 (5.9)	8.8 (9.1)	4.8	9.9 (9.9)
W4-08	3.4 (3.6)	3.7 (3.8)	2.4	18.1 (15.6)
G21IP	3.6 (4.3)	3.7 (3.9)	2.8	4.5 (5.8)
G21EA	1.9 (2.5)	2.7 (3.1)	1.5	5.4 (7.1)
PA	2.6 (1.8)	2.9 (2.4)	2.6	3.6 (2.9)
SIE11	8.7 (8.9)	7.7 (7.9)	7.4	5.1 (5.2)
BHPERI	1.2 (1.6)	3.3 (3.9)	1.1	4.2 (2.2)
BH76	5.4 (5.9)	4.5 (4.8)	3.4	2.3 (2.3)
BH76RC	2.2 (2.3)	2.6 (2.8)	1.6	3.9 (3.8)
RSE43	2.1 (2.2)	1.9 (1.8)	2.6	0.8 (0.7)
O3ADD6	3.0 (5.1)	5.7 (7.0)	4.1	6.4 (9.2)
G2RC	2.9 (3.3)	7.0 (7.5)	3.4	5.0 (5.8)
AL2X	1.6 (2.2)	2.8 (2.6)	2.0	0.8 (0.8)
NBPRC	1.9 (1.6)	3.4 (3.8)	1.5	2.3 (2.0)
ISO34	1.8 (1.3)	1.6 (1.7)	1.2	1.4 (1.2)
ISOL22	6.3 (4.8)	2.8 (2.8)	4.5	3.8 (2.1)
DC9	10.0 (7.2)	10.6 (12.6)	6.8	5.9 (4.0)
DARC	7.7 (4.6)	4.1 (6.3)	3.6	2.9 (3.2)
ALK6	3.3 (4.8)	4.4 (3.7)	6.4	3.7 (6.1)
BSR36	3.9 (2.7)	3.8 (2.8)	3.8	5.0 (2.1)
IDISP	4.4 (3.7)	2.5 (2.3)	3.0	4.9 (2.0)
WATER27	3.4 (6.8)	5.3 (7.4)	2.8	3.7 (9.4)
S22	0.31 (0.48)	0.47 (0.57)	0.32	0.52 (1.11)
ADIM6	0.13 (0.24)	0.11 (0.24)	0.35	0.05 (0.81)
RG6	0.05 (0.19)	0.03 (0.07)	0.03	0.02 (0.08)
HEAVY28	0.28 (0.31)	0.26 (0.22)	0.13	0.21 (0.24)
PCONF	0.58 (0.42)	1.16 (1.00)	0.44	0.19 (0.82)
ACONF	0.05 (0.06)	0.06 (0.07)	0.13	0.13 (0.05)
SCONF	0.38 (0.27)	0.26 (0.26)	0.38	0.70 (0.26)
CYCONF	0.28 (0.23)	0.64 (0.67)	0.37	0.21 (0.16)

Table 4: Mean absolute deviations of the complete GMTKN30 database for PWPB95-D3, B2PLYP-D3, and RPA. All values are in kcal/mol and were obtained with the (aug-)def2-QZVP basis (QZ). In case of dRPA the def2-TZVP(D) basis set (TZ) was used, as well.

	PWPB95-D3	B2PLYP-D3	dRPA (QZ)	dRPA (TZ)
MB08-165	2.6	3.4	10.0	14.3
W4-08	2.3	2.3	16.2	22.1
G21IP	2.0	2.3	5.3	3.5
G21EA	1.8	1.4	3.0	2.7
PA	2.0	1.5	4.7	4.3
SIE11	4.2	4.9	6.1	6.2
BHPERI	0.9	1.8	0.7	0.7
BH76	1.7	2.5	2.1	2.9
BH76RC	1.3	1.1	2.6	4.4
RSE43	1.5	1.1	0.6	0.6
O3ADD6	1.5	2.6	2.1	2.8
G2RC	2.5	1.9	3.3	6.7
AL2X	2.8	1.1	1.5	1.9
NBPRC	0.9	1.0	1.9	2.1
ISO34	0.9	1.1	1.0	1.4
ISOL22	2.9	4.3	2.1	2.1
DC9	6.0	5.2	7.4	10.9
DARC	1.7	4.1	0.6	0.6
ALK6	7.4	1.8	6.1	8.6
BSR36	1.8	1.6	1.0	1.5
IDISP	0.7	2.2	1.6	2.4
WATER27	3.3	2.0	5.3	4.4
S22	0.39	0.29	0.37	0.74
ADIM6	0.06	0.14	0.48	0.28
RG6	0.04	0.05	0.38	0.49
HEAVY28	0.17	0.22	0.81	3.81
PCONF	0.47	0.28	0.20	0.68
ACONF	0.14	0.02	0.05	0.06
SCONF	0.31	0.26	0.51	0.42
CYCONF	0.29	0.10	0.19	0.21

Table 5: Mean absolute deviations of the complete GMTKN30 database for PWRB95 with and without the frozen core approximation (noFC). All values are in kcal/mol and were obtained either with the (aug-)def2-QZVP basis (QZ) or the def2-TZVP(D) basis set (TZ).

	PWRB95 (QZ)	PWRB95 (QZ,noFC)	PWRB95 (TZ)	PWRB95 (TZ,noFC)
MB08-165	4.6	4.5	6.5	6.6
W4-08	3.6	3.5	5.0	4.5
G21IP	3.5	3.6	3.0	3.0
G21EA	2.1	2.1	2.7	2.7
PA	2.9	3.1	2.7	2.8
SIE11	6.7	6.7	6.7	6.8
BHPERI	1.3	1.6	1.5	1.6
BH76	3.2	3.2	3.6	3.6
BH76RC	2.1	2.0	3.0	3.0
RSE43	1.9	1.9	1.9	1.9
O3ADD6	2.8	2.9	2.5	2.6
G2RC	2.7	3.0	4.6	4.7
AL2X	1.3	2.2	1.4	2.0
NBPRC	1.2	1.5	1.3	1.5
ISO34	1.1	1.1	1.2	1.3
ISOL22	2.9	2.6	2.8	2.4
DC9	6.4	6.6	5.9	6.5
DARC	1.7	1.4	1.4	1.5
ALK6	3.2	5.7	1.6	2.8
BSR36	2.1	1.1	1.4	0.8
IDISP	0.9	0.6	0.7	0.6
WATER27	1.8	1.4	0.8	0.5
S22	0.24	0.21	0.37	0.42
ADIM6	0.09	0.32	0.12	0.21
RG6	0.18	0.11	0.23	0.17
HEAVY28	0.38	0.20	0.51	0.37
PCONF	0.31	0.44	0.62	0.70
ACONF	0.17	0.26	0.19	0.19
SCONF	0.25	0.22	0.26	0.26
CYCONF	0.35	0.38	0.41	0.44

4 PWRB95 vs. dRPA75

Table 6: Relative electronic energies of CCSDT(Q)/CBS[a] and PWRB95 on the def2-QZVP level together with the mean deviation (MD) and mean absolute deviation (MAD) based on the difference between PWRB95 and the CCSDT(Q) results in kcal mol^{-1} for the sHC5 test set.

System	$E_{CBS}^{CCSDT(Q)}$	PWRB95
C_2H_4 + 2 CH_4 → 2 C_2H_6	-21.32	-21.52
C_2H_2 + 2 CH_4 → C_2H_4 + C_2H_6	-30.82	-32.33
C_3H_8 + CH_4 → 2 C_2H_6	2.08	1.81
C_3H_6 + CH_4 → C_2H_4 + C_2H_6	4.81	4.81
C_4H_6 + 2 CH_4 → 2 C_2H_4 + C_2H_6	13.06	13.11
MD		-0.39
MAD		0.41

[a] taken from dRPA75 publication (*J. Chem. Theory Comput.*, 2015, **11**, 4615).

Table 7: Relative electronic energies of CCSDT(Q)/CBS[a] and PWRB95 on the def2-QZVP level together with the mean deviation (MD) and mean absolute deviation (MAD) based on the difference between PWRB95 and the CCSDT(Q) results in kcal mol^{-1} for the AE6 test set.

System	$E_{CBS}^{CCSDT(Q)}$	PWRB95
$C_2H_2O_2$	636.3	631.1
C_3H_4	706.1	701.4
C_4H_8	1153.7	1148.5
S_2	104.7	105.1
SiH_4	324.9	321.8
SiO	193.9	185.6
MD		-2.85
MAD		3.14

[a] taken from dRPA75 publication (*J. Chem. Theory Comput.*, 2015, **11**, 4615).

Table 8: Mean absolute deviations of PWRB95 for the test sets RCx (x= 0-5), DBH24, BH76, NCCE31, and S22 together with the corresponding subsets in kcal mol^{-1}.

Set	PWRB95	set	PWRB95
RC0	6.35	HB6	0.13
RC1	1.98	CT7	0.65
RC2	1.47	DI6	0.27
RC3	0.33	WI7	0.08
RC4	0.41	PPS5	0.08
RC5	0.33	NCCE31 total	0.25
BH6	2.88	H-bond	0.41
HAT6	3.99	Dispersion	0.16
NS6	3.84	Mixed	0.15
UR6	1.13	S22 total	0.24
DBH24 total	2.96		
NT-BH38	3.58		
HT-BH38	2.88		
BH76 total	3.23		

5 Pd/Ni Benchmark

5.1 Pd subset

Table 9: Relative electronic energies of CCSD(T)/CBS and several DFT methods on the def2-QZVPP level together with the mean deviation (MD), mean absolute deviation (MAD), and root mean square deviation (RMS) based on the difference between a corresponding method and the CCSD(T) reference in kcal mol^{-1} for the Pd subset.

		CCSD(T)	BLYP-D3	BLYP-NL	B97-D3	PBE-D3	PBE-NL	TPSS-D3	TPSS-NL
Benzene	D_e	28.85	30.58	34.02	28.47	36.49	38.76	36.13	39.62
C-H	ΔE_{forw}	23.67	19.47	20.26	19.84	20.11	20.75	21.81	22.68
	ΔE_{back}	1.63	4.70	4.62	3.40	3.24	3.23	3.90	3.82
	ΔE_{reac}	22.04	14.77	15.64	16.44	16.86	17.51	17.91	18.86
BH_3	D_e	32.14	35.02	38.17	33.19	42.88	44.37	39.00	41.54
B-H	ΔE_{forw}	2.32	0.37	0.11	0.72	0.53	0.43	1.13	0.96
	ΔE_{back}	-0.76	3.22	3.32	2.20	2.14	2.19	1.67	1.73
	ΔE_{reac}	3.08	-2.86	-3.20	-1.48	-1.61	-1.76	-0.54	-0.77
C_2H_2	D_e	36.71	40.43	44.55	38.63	48.28	50.36	47.59	50.98
C-H	ΔE_{forw}	25.14	24.18	24.99	24.12	25.09	25.52	26.82	27.49
	ΔE_{back}	0.53	2.64	2.65	1.25	1.30	1.31	2.48	2.47
	ΔE_{reac}	24.61	21.53	22.34	22.86	23.80	24.21	24.34	25.02
C_2H_4	D_e	38.66	40.74	44.88	38.92	48.07	50.24	47.21	50.71
C-H	ΔE_{forw}	33.82	29.17	30.07	29.67	30.45	30.94	32.13	32.83
	ΔE_{back}	1.41	4.54	4.45	3.26	3.00	2.99	3.61	3.54
	ΔE_{reac}	32.42	24.62	25.62	26.41	27.45	27.95	28.52	29.29
C_2H_6	D_e	10.75	11.54	13.69	9.71	15.50	16.72	13.81	15.87
C-C	ΔE_{forw}	26.06	22.82	21.09	23.90	20.44	19.56	20.52	19.09
	ΔE_{back}	21.61	28.69	27.84	26.55	24.80	24.48	26.90	26.22
	ΔE_{reac}	4.45	-5.87	-6.74	-2.65	-4.36	-4.91	-6.39	-7.14
CH_4	D_e	9.92	10.71	13.21	8.96	15.14	16.43	13.27	15.47
C-H	ΔE_{forw}	12.29	8.20	7.42	8.47	6.70	6.37	7.71	7.17
	ΔE_{back}	4.12	8.12	8.04	6.45	6.15	6.15	7.54	7.48
	ΔE_{reac}	8.17	0.08	-0.62	2.02	0.55	0.22	0.17	-0.31
Cyclopropane	D_e	9.66	10.30	12.37	8.38	14.13	15.33	12.67	14.64
C-H	ΔE_{forw}	10.46	5.33	4.36	5.87	3.73	3.22	4.80	3.96
	ΔE_{back}	5.14	9.07	9.01	7.53	7.25	7.28	8.38	8.34
	ΔE_{reac}	5.32	-3.74	-4.65	-1.65	-3.52	-4.07	-3.58	-4.38
H_2	D_e	20.77	23.17	25.52	21.71	28.62	29.60	24.59	26.31
H-H	ΔE_{forw}	3.58	1.92	1.61	2.28	1.35	1.24	1.81	1.62
	ΔE_{back}	-0.74	1.66	1.65	0.71	0.59	0.59	1.23	1.22
	ΔE_{reac}	4.32	0.26	-0.04	1.57	0.77	0.65	0.58	0.40
H_2O	D_e	8.95	12.28	13.72	9.64	13.03	13.87	12.71	14.14
O-H	ΔE_{forw}	26.57	19.82	17.54	21.52	16.90	15.95	16.00	14.55
	ΔE_{back}	9.39	12.29	12.04	10.53	10.50	10.43	12.63	12.46
	ΔE_{reac}	17.18	7.53	5.50	10.98	6.41	5.52	3.38	2.09
C_2H_6	D_e	10.75	11.54	13.69	9.71	15.50	16.72	13.81	15.87
C-H	ΔE_{forw}	12.86	8.40	7.54	8.70	6.89	6.50	8.00	7.36
	ΔE_{back}	4.98	9.35	9.31	7.62	7.44	7.48	8.68	8.67
	ΔE_{reac}	7.88	-0.94	-1.77	1.09	-0.55	-0.98	-0.68	-1.31
NH_3	D_e	23.17	26.78	29.00	24.05	28.86	30.04	28.17	30.20
N-H	ΔE_{forw}	32.04	27.83	26.49	28.52	25.40	24.85	25.37	24.53
	ΔE_{back}	7.85	11.62	11.50	9.97	9.88	9.86	11.50	11.41
	ΔE_{reac}	24.18	16.20	14.99	18.55	15.52	14.98	13.87	13.11
CH_3Cl	D_e	13.96	18.55	20.72	16.03	21.25	22.57	20.47	22.57
C-Cl	ΔE_{forw}	15.77	12.43	11.55	13.51	12.11	11.62	11.46	10.67
OxIn	ΔE_{back}	34.12	34.36	34.37	32.56	33.72	33.71	35.55	35.44
	ΔE_{reac}	-18.35	-21.93	-22.82	-19.06	-21.61	-22.09	-24.09	-24.76
CH_3Cl	D_e	8.49	9.92	12.00	8.02	13.97	15.21	12.07	14.13
C-Cl	ΔE_{forw}	47.52	28.20	30.18	30.88	33.54	34.42	31.56	33.09
S_N2	ΔE_{back}	71.35	58.75	61.71	57.95	62.43	63.87	64.05	66.29
	ΔE_{reac}	-23.83	-30.56	-31.53	-27.07	-28.89	-29.45	-32.49	-33.20
	MAD		4.59	5.38	3.26	5.17	5.60	5.15	5.85
	MD		-1.91	-1.44	-2.03	-0.94	-0.65	-1.10	-0.63
	RMS		5.72	6.21	4.48	6.09	6.64	6.13	6.95

Table 10: Relative electronic energies of CCSD(T)/CBS and several DFT methods on the def2-QZVPP level together with the mean deviation (MD), mean absolute deviation (MAD), and root mean square deviation (RMS) based on the difference between a corresponding method and the CCSD(T) reference in kcal mol^{-1} for the Pd subset.

		CCSD(T)	B3LYP-D3	B3LYP-NL	PBE0-D3	PBE0-NL	PW6B95-D3	BHLYP-D3	BHLYP-NL
Benzene	D_e	28.85	25.09	27.20	28.76	30.50	25.43	16.55	19.49
C-H	ΔE_{forw}	23.67	22.86	23.42	24.19	24.72	25.50	27.92	28.44
	ΔE_{back}	1.63	3.27	3.23	1.53	1.51	1.64	1.78	1.66
	ΔE_{reac}	22.04	19.59	20.19	22.66	23.21	23.86	26.14	26.78
BH_3	D_e	32.14	28.36	30.37	32.92	34.15	29.38	17.67	20.05
B-H	ΔE_{forw}	2.32	2.20	2.01	2.77	2.68	3.42	4.94	4.73
	ΔE_{back}	-0.76	0.86	0.94	-0.80	-0.76	-0.96	-2.28	-2.22
	ΔE_{reac}	3.08	1.34	1.07	3.57	3.43	4.38	7.22	6.95
C_2H_2	D_e	36.71	34.38	37.14	39.34	41.09	35.06	24.35	27.57
C-H	ΔE_{forw}	25.14	24.98	25.59	26.02	26.41	26.17	25.91	26.53
	ΔE_{back}	0.53	0.75	0.77	-0.87	-0.86	-1.13	-1.29	-1.28
	ΔE_{reac}	24.61	24.23	24.82	26.88	27.27	27.30	27.20	27.81
C_2H_4	D_e	38.66	35.30	38.08	39.98	41.80	35.95	26.17	29.45
C-H	ΔE_{forw}	33.82	32.54	33.26	34.43	34.88	35.07	37.02	37.65
	ΔE_{back}	1.41	3.20	3.14	1.40	1.38	1.52	1.82	1.70
	ΔE_{reac}	32.42	29.34	30.11	33.03	33.50	33.55	35.20	35.95
C_2H_6	D_e	10.75	8.18	9.44	10.24	11.19	8.02	2.90	4.76
C-C	ΔE_{forw}	26.06	27.37	26.14	26.34	25.54	26.82	34.34	33.01
	ΔE_{back}	21.61	25.59	25.03	21.62	21.30	21.07	21.87	21.12
	ΔE_{reac}	4.45	1.77	1.11	4.73	4.24	5.75	12.47	11.89
CH_4	D_e	9.92	7.57	9.15	9.99	11.06	7.80	2.47	4.51
C-H	ΔE_{forw}	12.29	12.38	11.81	11.90	11.60	13.74	18.96	18.31
	ΔE_{back}	4.12	6.15	6.12	3.91	3.91	3.89	3.82	3.75
	ΔE_{reac}	8.17	6.23	5.69	7.99	7.70	9.85	15.14	14.57
Cyclopropane	D_e	9.66	6.89	8.11	8.93	9.82	6.90	1.69	3.52
C-H	ΔE_{forw}	10.46	10.50	9.83	10.12	9.65	12.48	18.52	17.71
	ΔE_{back}	5.14	7.54	7.51	5.44	5.46	5.57	5.87	5.75
	ΔE_{reac}	5.32	2.96	2.31	4.67	4.19	6.91	12.65	11.96
H_2	D_e	20.77	19.33	20.90	22.38	23.22	18.42	12.42	14.25
H-H	ΔE_{forw}	3.58	3.83	3.61	3.78	3.68	4.49	6.87	6.63
	ΔE_{back}	-0.74	0.43	0.43	-0.84	-0.84	-0.77	-0.94	-0.95
	ΔE_{reac}	4.32	3.40	3.18	4.62	4.52	5.26	7.81	7.58
H_2O	D_e	8.95	9.25	10.11	8.64	9.32	7.60	5.48	6.69
O-H	ΔE_{forw}	26.57	26.77	25.05	25.95	25.09	27.62	37.39	35.66
	ΔE_{back}	9.39	11.75	11.58	10.05	9.99	10.10	11.94	11.74
	ΔE_{reac}	17.18	15.03	13.46	15.89	15.10	17.52	25.44	23.92
C_2H_6	D_e	10.75	8.18	9.44	10.24	11.19	8.02	2.90	4.76
C-H	ΔE_{forw}	12.86	12.79	12.17	12.35	11.99	14.22	19.62	18.90
	ΔE_{back}	4.98	7.17	7.17	4.89	4.91	4.83	4.48	4.43
	ΔE_{reac}	7.88	5.62	5.00	7.46	7.08	9.39	15.15	14.48
NH_3	D_e	23.17	22.48	23.87	22.60	23.59	20.23	16.26	18.12
N-H	ΔE_{forw}	32.04	32.57	31.54	31.48	30.98	32.55	40.11	39.06
	ΔE_{back}	7.85	10.20	10.12	8.30	8.28	8.25	9.01	8.88
	ΔE_{reac}	24.18	22.37	21.43	23.18	22.70	24.30	31.09	30.18
CH_3Cl	D_e	13.96	14.20	15.47	15.03	16.02	12.77	8.38	10.04
C-Cl	ΔE_{forw}	15.77	15.36	14.69	15.81	15.32	14.88	19.26	18.54
OxIn	ΔE_{back}	34.12	33.48	33.51	32.76	32.71	31.48	31.90	31.80
	ΔE_{reac}	-18.35	-18.13	-18.81	-16.95	-17.39	-16.60	-12.64	-13.26
CH_3Cl	D_e	8.49	6.39	7.60	8.49	9.45	6.25	0.99	2.73
C-Cl	ΔE_{forw}	47.52	37.79	39.21	43.88	44.71	43.75	47.18	48.79
S_N2	ΔE_{back}	71.35	63.72	65.90	67.37	68.66	66.87	67.21	69.36
	ΔE_{reac}	-23.83	-25.93	-26.69	-23.48	-23.96	-23.12	-20.03	-20.57
	MAD		1.87	1.63	0.73	1.01	1.49	5.16	4.40
	MD		-0.91	-0.64	-0.03	0.19	-0.26	0.33	0.71
	RMS		2.56	2.18	1.10	1.37	1.81	6.31	5.24

Table 11: Relative electronic energies of CCSD(T)/CBS, several DFT methods, and dRPA on the def2-QZVPP level together with the mean deviation (MD), mean absolute deviation (MAD), and root mean square deviation (RMS) based on the difference between a corresponding method and the CCSD(T) reference in kcal mol^{-1} for the Pd subset.

		CCSD(T)	PBE0-DH-D3	PWPB95-D3	B2PLYP-D3	PWRB95	dRPA
Benzene	D_e	28.85	29.54	27.67	28.77	26.11	22.19
C-H	ΔE_{forw}	23.67	26.63	25.29	24.00	24.47	22.83
	ΔE_{back}	1.63	0.54	1.65	1.95	2.09	2.91
	ΔE_{reac}	22.04	26.09	23.65	22.05	22.38	19.91
BH_3	D_e	32.14	31.08	30.52	30.37	30.12	25.58
B-H	ΔE_{forw}	2.32	3.44	2.94	2.03	2.68	1.97
	ΔE_{back}	-0.76	-1.95	-0.73	0.33	-0.25	0.30
	ΔE_{reac}	3.08	5.39	3.67	1.70	2.94	1.67
C_2H_2	D_e	36.71	38.32	36.34	37.26	35.58	30.34
C-H	ΔE_{forw}	25.14	26.80	26.41	25.91	26.27	25.77
	ΔE_{back}	0.53	-1.87	-0.52	-0.37	0.15	2.51
	ΔE_{reac}	24.61	28.68	26.93	26.28	26.12	23.27
C_2H_4	D_e	38.66	39.61	37.66	38.77	36.78	32.32
C-H	ΔE_{forw}	33.82	36.42	34.96	34.00	34.39	33.18
	ΔE_{back}	1.41	0.39	1.44	1.68	1.91	2.66
	ΔE_{reac}	32.42	36.02	33.52	32.32	32.49	30.52
C_2H_6	D_e	10.75	9.91	8.79	9.46	7.75	3.87
C-C	ΔE_{forw}	26.06	27.48	26.26	25.91	25.30	26.34
	ΔE_{back}	21.61	19.79	21.80	23.66	22.16	25.02
	ΔE_{reac}	4.45	7.69	4.46	2.25	3.14	1.32
CH_4	D_e	9.92	9.54	8.44	8.92	7.50	3.27
C-H	ΔE_{forw}	12.29	13.68	12.93	11.96	12.01	11.03
	ΔE_{back}	4.12	2.62	4.19	4.63	4.83	6.41
	ΔE_{reac}	8.17	11.06	8.74	7.34	7.17	4.61
Cyclopropane	D_e	9.66	8.53	7.52	8.09	6.29	2.10
C-H	ΔE_{forw}	10.46	11.76	11.04	9.55	10.04	8.34
	ΔE_{back}	5.14	4.32	5.51	5.87	6.06	6.87
	ΔE_{reac}	5.32	7.44	5.52	3.68	3.98	1.47
H_2	D_e	20.77	20.77	19.27	20.69	18.61	15.11
H-H	ΔE_{forw}	3.58	4.74	4.01	3.99	3.40	2.36
	ΔE_{back}	-0.74	-1.76	-0.81	-0.83	-0.20	0.64
	ΔE_{reac}	4.32	6.51	4.82	4.82	3.60	1.72
H_2O	D_e	8.95	8.07	8.20	9.46	7.45	5.64
O-H	ΔE_{forw}	26.57	29.00	26.36	25.79	24.98	24.74
	ΔE_{back}	9.39	9.14	9.63	9.31	10.29	11.33
	ΔE_{reac}	17.18	19.86	16.73	16.48	14.70	13.40
C_2H_6	D_e	10.75	9.91	8.79	9.46	7.75	3.87
C-H	ΔE_{forw}	12.86	14.05	13.31	12.24	12.44	11.51
	ΔE_{back}	4.98	3.54	5.16	5.71	5.74	7.05
	ΔE_{reac}	7.88	10.51	8.15	6.53	6.70	4.46
NH_3	D_e	23.17	21.77	21.44	23.49	20.23	17.32
N-H	ΔE_{forw}	32.04	33.68	31.78	31.86	30.23	29.41
	ΔE_{back}	7.85	7.10	8.07	8.07	8.75	10.01
	ΔE_{reac}	24.18	26.57	23.71	23.79	21.49	19.40
CH_3Cl	D_e	13.96	14.86	13.49	15.09	11.41	6.45
C-Cl	ΔE_{forw}	15.77	16.90	15.15	15.55	13.69	13.79
OxIn	ΔE_{back}	34.12	32.12	32.53	33.05	32.52	34.49
	ΔE_{reac}	-18.35	-15.22	-17.37	-17.50	-18.83	-20.70
CH_3Cl	D_e	8.49	8.17	6.94	7.58	5.67	1.30
C-Cl	ΔE_{forw}	47.52	49.05	44.88	43.80	39.62	31.36
S_N2	ΔE_{back}	71.35	70.97	68.81	68.80	64.19	57.20
	ΔE_{reac}	-23.83	-21.91	-23.93	-25.00	-24.57	-25.84
	MAD		1.64	0.85	0.82	1.53	3.58
	MD		0.78	-0.22	-0.31	-1.09	-2.74
	RMS		1.90	1.12	1.10	2.15	4.79

5.2 $PdCl^-$ subset

Table 12: Relative electronic energies of CCSD(T)/CBS and several DFT methods on the def2-QZVPP level together with the mean deviation (MD), mean absolute deviation (MAD), and root mean square deviation (RMS) based on the difference between a corresponding method and the CCSD(T) reference in kcal mol^{-1} for the $PdCl^-$ subset.

		CCSD(T)	BLYP-D3	BLYP-NL	B97-D3	PBE-D3	PBE-NL	TPSS-D3	TPSS-NL
Benzene	D_e	41.41	36.77	40.44	35.59	43.39	45.80	43.36	46.93
C-H	ΔE_{forw}	14.85	12.88	13.85	13.09	13.53	14.24	14.73	15.69
	ΔE_{back}	0.49	1.36	1.08	0.74	0.27	0.15	1.17	0.93
	ΔE_{reac}	14.36	11.52	12.77	12.34	13.26	14.10	13.56	14.76
C_2H_2	D_e	51.25	47.37	51.40	46.47	55.71	57.77	55.60	58.88
C-H	ΔE_{forw}	11.53	10.37	11.18	10.48	11.07	11.52	12.49	13.17
	ΔE_{back}	1.39	1.73	1.34	0.89	-0.09	-0.24	1.81	1.54
	ΔE_{reac}	10.14	8.64	9.84	9.59	11.16	11.76	10.68	11.63
C_2H_4	D_e	51.99	46.37	50.54	45.45	54.33	56.54	53.95	57.41
C-H	ΔE_{forw}	27.84	23.92	25.11	24.33	25.48	26.11	26.69	27.60
	ΔE_{back}	-0.15	0.83	0.61	0.35	-0.12	-0.20	0.57	0.41
	ΔE_{reac}	27.99	23.09	24.50	23.99	25.60	26.31	26.12	27.19
C_2H_6	D_e	20.78	16.91	19.33	15.70	20.95	22.31	19.79	21.98
C-C	ΔE_{forw}	28.05	26.38	25.07	27.02	24.13	23.42	24.02	22.86
	ΔE_{back}	22.71	25.53	24.23	24.02	21.99	21.50	25.13	24.21
	ΔE_{reac}	5.34	0.85	0.83	3.00	2.15	1.92	-1.11	-1.35
CH_4	D_e	22.05	18.66	21.36	17.33	23.32	24.71	21.59	23.88
C-H	ΔE_{forw}	7.24	6.01	5.52	6.01	4.34	4.13	5.16	4.82
	ΔE_{back}	1.76	3.51	3.13	2.55	1.94	1.80	3.64	3.37
	ΔE_{reac}	5.47	2.50	2.39	3.46	2.40	2.33	1.52	1.45
Cyclopropane	D_e	19.72	16.21	18.49	14.96	19.97	21.28	18.85	20.89
C-H	ΔE_{forw}	4.03	3.50	2.78	3.58	1.41	1.00	2.07	1.41
	ΔE_{back}	2.72	4.34	4.00	3.38	2.80	2.70	4.59	4.36
	ΔE_{reac}	1.30	-0.83	-1.21	0.20	-1.39	-1.71	-2.52	-2.95
H_2O	D_e	17.40	17.02	19.62	15.02	19.35	20.68	18.97	21.08
O-H	ΔE_{forw}	10.87	7.27	6.56	8.71	6.07	5.79	4.68	4.22
	ΔE_{back}	12.83	11.54	11.21	10.66	10.28	10.18	13.16	12.95
	ΔE_{reac}	-1.95	-4.27	-4.65	-1.95	-4.21	-4.39	-8.48	-8.72
C_2H_6	D_e	20.78	16.91	19.33	15.70	20.95	22.31	19.78	21.98
C-H	ΔE_{forw}	8.12	6.94	6.33	6.96	5.18	4.89	5.95	5.47
	ΔE_{back}	2.19	4.06	3.66	3.11	2.46	2.33	4.05	3.78
	ΔE_{reac}	5.93	2.89	2.67	3.85	2.72	2.56	1.90	1.69
NH_3	D_e	25.67	22.69	25.69	20.59	25.39	26.93	25.27	27.74
N-H	ΔE_{forw}	17.48	14.60	14.25	14.73	12.56	12.46	12.47	12.29
	ΔE_{back}	8.65	9.73	9.28	8.72	8.15	8.00	10.68	10.39
	ΔE_{reac}	8.82	4.87	4.97	6.01	4.41	4.46	1.79	1.89
CH_3Cl	D_e	21.97	21.90	24.88	19.93	25.41	27.12	24.81	27.39
C-Cl	ΔE_{forw}	13.27	9.27	9.52	10.24	10.34	10.34	9.01	8.99
OxIn	ΔE_{back}	56.00	49.33	49.07	48.67	49.41	49.34	52.29	52.13
	ΔE_{reac}	-42.73	-40.06	-39.55	-38.43	-39.07	-39.00	-43.28	-43.15
		MAD	2.61	2.01	2.50	2.13	2.56	2.40	2.90
		MD	-1.91	-1.20	-2.06	-1.06	-0.66	-1.08	-0.46
		RMS	3.03	2.47	3.16	2.67	3.13	3.06	3.66

Table 13: Relative electronic energies of CCSD(T)/CBS and several DFT methods on the def2-QZVPP level together with the mean deviation (MD), mean absolute deviation (MAD), and root mean square deviation (RMS) based on the difference between a corresponding method and the CCSD(T) reference in kcal mol^{-1} for the $PdCl^-$ subset.

		CCSD(T)	B3LYP-D3	B3LYP-NL	PBE0-D3	PBE0-NL	PW6B95-D3	BHLYP-D3	BHLYP-NL
Benzene	D_e	41.41	34.51	36.86	39.41	41.24	36.06	29.00	32.28
C-H	ΔE_{forw}	14.85	14.60	15.32	15.56	16.16	16.74	17.11	17.82
	ΔE_{back}	0.49	1.40	1.21	0.48	0.37	0.73	2.28	2.01
	ΔE_{reac}	14.36	13.19	14.11	15.08	15.79	16.02	14.83	15.80
C_2H_2	D_e	51.25	45.77	48.51	52.04	53.76	47.96	40.59	43.85
C-H	ΔE_{forw}	11.53	12.11	12.72	13.12	13.52	13.85	14.24	14.85
	ΔE_{back}	1.39	2.50	2.22	1.15	1.01	1.75	4.76	4.46
	ΔE_{reac}	10.14	9.61	10.50	11.97	12.51	12.10	9.48	10.39
C_2H_4	D_e	51.99	45.30	48.13	51.35	53.19	47.57	40.73	44.15
C-H	ΔE_{forw}	27.84	26.63	27.55	28.56	29.12	29.19	29.84	30.69
	ΔE_{back}	-0.15	0.71	0.54	-0.13	-0.22	0.03	1.17	0.98
	ΔE_{reac}	27.99	25.92	27.01	28.69	29.34	29.16	28.66	29.71
C_2H_6	D_e	20.78	16.27	17.78	18.84	19.90	17.13	13.78	15.95
C-C	ΔE_{forw}	28.05	29.95	29.04	28.66	28.02	29.22	35.57	34.49
	ΔE_{back}	22.71	25.36	24.44	22.52	22.05	22.38	26.22	25.19
	ΔE_{reac}	5.34	4.59	4.60	6.15	5.98	6.84	9.35	9.30
CH_4	D_e	22.05	17.63	19.41	20.62	21.78	18.22	14.48	16.78
C-H	ΔE_{forw}	7.24	8.53	8.18	7.47	7.28	9.44	13.08	12.64
	ΔE_{back}	1.76	3.30	3.01	1.94	1.81	2.15	3.81	3.49
	ΔE_{reac}	5.47	5.24	5.16	5.53	5.47	7.30	9.27	9.15
Cyclopropane	D_e	19.72	15.27	16.69	17.63	18.60	15.85	12.53	14.59
C-H	ΔE_{forw}	4.03	6.11	5.63	4.66	4.30	6.90	10.95	10.31
	ΔE_{back}	2.72	4.36	4.11	3.08	2.97	3.41	5.36	5.04
	ΔE_{reac}	1.30	1.75	1.52	1.59	1.33	3.50	5.59	5.27
H_2O	D_e	17.40	15.68	17.48	16.48	17.62	16.05	13.17	15.28
O-H	ΔE_{forw}	10.87	11.34	10.83	11.18	10.93	12.80	17.93	17.33
	ΔE_{back}	12.83	13.45	13.20	12.86	12.76	13.30	17.40	17.13
	ΔE_{reac}	-1.95	-2.10	-2.37	-1.68	-1.84	-0.50	0.53	0.20
C_2H_6	D_e	20.78	16.26	17.78	18.84	19.90	17.13	13.78	15.94
C-H	ΔE_{forw}	8.12	9.65	9.22	8.54	8.28	10.59	14.50	13.94
	ΔE_{back}	2.19	3.72	3.43	2.32	2.19	2.49	4.04	3.70
	ΔE_{reac}	5.93	5.93	5.78	6.22	6.09	8.10	10.46	10.24
NH_3	D_e	25.67	22.15	24.22	23.39	24.71	21.81	20.09	22.63
N-H	ΔE_{forw}	17.48	18.15	17.93	16.98	16.89	18.24	24.02	23.75
	ΔE_{back}	8.65	10.32	9.98	9.17	9.02	9.51	12.49	12.12
	ΔE_{reac}	8.82	7.83	7.95	7.81	7.87	8.72	11.53	11.63
CH_3Cl	D_e	21.97	19.70	21.68	21.50	22.84	19.44	15.88	18.30
C-Cl	ΔE_{forw}	13.27	11.61	11.82	13.03	13.01	11.83	14.89	14.95
OxIn	ΔE_{back}	56.00	52.39	52.14	53.35	53.24	52.38	56.71	56.44
	ΔE_{reac}	-42.73	-40.78	-40.32	-40.32	-40.23	-40.55	-41.82	-41.49
		MAD	2.01	1.33	0.83	0.73	1.95	4.45	3.71
		MD	-0.84	-0.36	-0.10	0.23	-0.12	0.47	1.04
		RMS	2.67	1.76	1.12	1.07	2.35	5.34	4.26

Table 14: Relative electronic energies of CCSD(T)/CBS, several DFT methods, and dRPA on the def2-QZVPP level together with the mean deviation (MD), mean absolute deviation (MAD), and root mean square deviation (RMS) based on the difference between a corresponding method and the CCSD(T) reference in kcal mol^{-1} for the $PdCl^-$ subset.

		CCSD(T)	PBE0-DH-D3	PWPB95-D3	B2PLYP-D3	PWRB95	dRPA
Benzene	D_e	41.41	41.92	39.48	40.62	38.69	37.51
C-H	ΔE_{forw}	14.85	17.43	16.90	16.33	16.08	14.26
	ΔE_{back}	0.49	0.03	0.20	-0.39	0.52	1.05
	ΔE_{reac}	14.36	17.40	16.70	16.72	15.56	13.21
C_2H_2	D_e	51.25	53.11	50.01	50.46	49.79	46.78
C-H	ΔE_{forw}	11.53	14.08	13.56	12.68	13.17	11.39
	ΔE_{back}	1.39	0.70	0.80	-0.39	1.17	1.70
	ΔE_{reac}	10.14	13.38	12.76	13.08	12.00	9.68
C_2H_4	D_e	51.99	53.15	50.25	50.94	49.84	47.65
C-H	ΔE_{forw}	27.84	30.42	29.39	28.68	28.66	26.97
	ΔE_{back}	-0.15	-0.52	-0.35	-0.71	-0.12	0.30
	ΔE_{reac}	27.99	30.95	29.74	29.39	28.77	26.67
C_2H_6	D_e	20.78	19.70	18.32	18.80	17.88	15.41
C-C	ΔE_{forw}	28.05	29.07	28.42	27.93	27.40	27.45
	ΔE_{back}	22.71	21.63	22.27	22.21	22.50	25.13
	ΔE_{reac}	5.34	7.43	6.14	5.72	4.90	2.32
CH_4	D_e	22.05	20.90	19.57	19.88	19.30	17.21
C-H	ΔE_{forw}	7.24	8.34	8.27	7.46	7.39	5.39
	ΔE_{back}	1.76	1.30	1.76	1.14	2.21	3.32
	ΔE_{reac}	5.47	7.04	6.51	6.32	5.18	2.07
Cyclopropane	D_e	19.72	18.27	16.96	17.67	16.49	14.17
C-H	ΔE_{forw}	4.03	5.02	5.22	4.42	4.31	1.88
	ΔE_{back}	2.72	2.50	2.73	1.92	3.16	3.84
	ΔE_{reac}	1.30	2.52	2.49	2.50	1.15	-1.95
H_2O	D_e	17.40	16.37	16.72	17.02	16.51	14.08
O-H	ΔE_{forw}	10.87	12.88	11.65	10.75	10.46	8.75
	ΔE_{back}	12.83	13.06	12.16	10.68	12.34	12.52
	ΔE_{reac}	-1.95	-0.18	-0.51	0.07	-1.88	-3.77
C_2H_6	D_e	20.78	19.70	18.32	18.80	17.87	15.40
C-H	ΔE_{forw}	8.12	9.27	9.19	8.30	8.31	6.16
	ΔE_{back}	2.19	1.69	2.17	1.70	2.61	3.74
	ΔE_{reac}	5.93	7.59	7.02	6.61	5.70	2.42
NH_3	D_e	25.67	24.06	23.40	24.66	22.51	20.17
N-H	ΔE_{forw}	17.48	18.46	17.61	17.60	16.02	14.38
	ΔE_{back}	8.65	8.67	8.44	7.19	8.91	9.48
	ΔE_{reac}	8.82	9.79	9.17	10.41	7.12	4.90
CH_3Cl	D_e	21.97	22.31	20.75	22.28	19.46	15.89
C-Cl	ΔE_{forw}	13.27	13.99	12.09	12.41	10.48	9.67
OxIn	ΔE_{back}	56.00	54.58	52.81	51.63	51.91	52.88
	ΔE_{reac}	-42.73	-40.58	-40.72	-39.22	-41.43	-43.22
		MAD	1.33	1.27	1.21	1.22	2.51
		MD	0.70	-0.03	-0.13	-0.67	-2.07
		RMS	1.56	1.54	1.54	1.66	3.06

5.3 $PdCl_2$ subset

Table 15: Relative electronic energies of CCSD(T)/CBS and several DFT methods on the def2-QZVPP level together with the mean deviation (MD), mean absolute deviation (MAD), and root mean square deviation (RMS) based on the difference between a corresponding method and the CCSD(T) reference in kcal mol^{-1} for the $PdCl_2$ subset.

		CCSD(T)	BLYP-D3	BLYP-NL	B97-D3	PBE-D3	PBE-NL	TPSS-D3	TPSS-NL
Benzene	D_e	29.96	26.26	27.54	25.38	29.18	30.77	31.05	33.44
C-H	ΔE_{forw}	25.47	21.09	21.17	20.74	19.67	20.08	22.96	23.37
	ΔE_{back}	2.98	4.36	4.32	3.85	3.27	3.28	3.61	3.57
	ΔE_{reac}	22.49	16.73	16.85	16.89	16.41	16.79	19.35	19.80
C_2H_4	D_e	35.04	32.47	35.20	32.00	37.98	39.73	38.00	40.81
C-H	ΔE_{forw}	29.73	28.99	29.84	28.84	29.23	29.79	31.54	32.31
	ΔE_{back}	1.87	5.61	5.65	5.16	4.54	4.63	4.98	5.12
	ΔE_{reac}	27.86	23.38	24.19	23.68	24.69	25.16	26.56	27.18
C_2H_6	D_e	8.06	13.31	15.26	12.78	16.84	18.20	15.68	18.00
C-C	ΔE_{forw}	22.65	30.86	30.82	31.27	30.30	30.19	28.51	28.28
	ΔE_{back}	28.30	32.84	32.53	32.00	29.90	29.84	31.51	31.30
	ΔE_{reac}	-5.65	-1.98	-1.71	-0.73	0.39	0.34	-3.00	-3.02
CH_4	D_e	6.28	2.75	3.85	2.51	6.61	7.35	5.82	7.19
C-H	ΔE_{forw}	6.33	4.98	3.98	4.43	3.37	2.93	4.38	3.66
	ΔE_{back}	5.57	8.83	8.73	7.54	6.61	6.61	7.40	7.37
	ΔE_{reac}	0.77	-3.85	-4.76	-3.10	-3.24	-3.68	-3.03	-3.71
Cyclopropane	D_e	14.40	11.88	12.76	11.38	14.95	15.90	14.82	16.48
C-H	ΔE_{forw}	8.68	7.22	6.18	6.68	5.27	4.81	6.77	6.05
	ΔE_{back}	3.64	7.00	6.77	5.73	4.77	4.71	5.33	5.15
	ΔE_{reac}	5.04	0.21	-0.59	0.95	0.49	0.10	1.44	0.90
H_2	D_e	13.91	11.04	12.62	11.37	16.79	17.37	13.32	14.48
H-H	ΔE_{forw}	0.19	0.23	-0.18	-0.29	-1.03	-1.18	0.23	-0.04
	ΔE_{back}	3.14	4.60	4.84	4.06	4.00	4.10	3.90	4.07
	ΔE_{reac}	-2.95	-4.37	-5.02	-4.34	-5.02	-5.29	-3.66	-4.12
H_2O	D_e	21.12	14.35	16.24	13.46	16.75	17.81	18.77	20.51
O-H	ΔE_{forw}	47.26	37.81	36.00	38.12	34.67	33.90	35.78	34.50
	ΔE_{back}	3.68	8.25	7.92	6.21	5.84	5.74	6.93	6.71
	ΔE_{reac}	43.57	29.56	28.08	31.91	28.83	28.16	28.85	27.78
C_2H_6	D_e	8.06	6.04	6.44	5.46	8.73	9.27	8.25	9.29
C-H	ΔE_{forw}	4.98	4.56	3.33	3.84	2.52	1.96	3.67	2.75
	ΔE_{back}	7.27	10.48	10.50	9.39	8.59	8.68	9.10	9.20
	ΔE_{reac}	-2.29	-5.92	-7.18	-5.54	-6.07	-6.72	-5.44	-6.44
CH_3Cl	D_e	20.64	16.03	17.38	15.25	18.78	19.97	19.80	21.64
C-Cl	ΔE_{forw}	30.71	24.06	22.99	24.89	23.50	22.84	22.69	21.58
OxIn	ΔE_{back}	18.78	21.21	21.23	20.29	20.05	20.07	20.37	20.32
	ΔE_{reac}	11.93	2.85	1.76	4.60	3.45	2.77	2.33	1.27
		MAD	3.71	3.74	3.42	3.26	3.49	2.83	3.31
		MD	-1.96	-1.91	-2.16	-1.74	-1.59	-1.27	-1.04
		RMS	4.65	4.89	4.24	4.56	4.84	4.24	4.80

Table 16: Relative electronic energies of CCSD(T)/CBS and several DFT methods on the def2-QZVPP level together with the mean deviation (MD), mean absolute deviation (MAD), and root mean square deviation (RMS) based on the difference between a corresponding method and the CCSD(T) reference in kcal mol^{-1} for the $PdCl_2$ subset.

		CCSD(T)	B3LYP-D3	B3LYP-NL	PBE0-D3	PBE0-NL	PW6B95-D3	BHLYP-D3	BHLYP-NL
Benzene	D_e	29.96	25.43	25.89	28.08	29.06	26.19	24.34	26.64
C-H	ΔE_{forw}	25.47	25.61	25.64	25.73	25.97	27.82	33.89	34.09
	ΔE_{back}	2.98	3.44	3.44	2.13	2.13	2.29	1.74	1.70
	ΔE_{reac}	22.49	22.17	22.20	23.60	23.83	25.53	32.15	32.39
C_2H_4	D_e	35.04	31.28	32.99	35.46	36.86	32.41	28.44	31.13
C-H	ΔE_{forw}	29.73	32.93	33.58	34.01	34.51	35.31	39.03	39.54
	ΔE_{back}	1.87	5.00	5.03	3.76	3.85	4.09	3.60	3.71
	ΔE_{reac}	27.86	27.93	28.55	30.25	30.66	31.22	35.44	35.84
C_2H_6	D_e	8.06	8.64	9.74	10.14	11.18	6.42	-0.16	2.31
C-C	ΔE_{forw}	22.65	27.87	27.90	26.33	26.24	24.37	21.31	21.27
	ΔE_{back}	28.30	28.65	28.50	24.91	24.86	24.32	21.08	20.87
	ΔE_{reac}	-5.65	-0.78	-0.60	1.42	1.38	0.04	0.24	0.40
CH_4	D_e	6.28	3.58	4.07	6.77	7.32	4.39	4.81	6.18
C-H	ΔE_{forw}	6.33	8.02	7.25	7.35	6.93	8.70	13.70	12.83
	ΔE_{back}	5.57	6.04	6.02	3.32	3.33	3.51	1.42	1.43
	ΔE_{reac}	0.77	1.98	1.23	4.03	3.60	5.20	12.28	11.40
Cyclopropane	D_e	14.40	11.34	11.55	13.83	14.44	11.51	10.63	12.26
C-H	ΔE_{forw}	8.68	10.65	9.85	9.85	9.42	11.30	17.18	16.30
	ΔE_{back}	3.64	5.12	5.00	2.56	2.50	2.90	2.13	1.94
	ΔE_{reac}	5.04	5.53	4.85	7.28	6.92	8.40	15.05	14.36
H_2	D_e	13.91	11.65	12.64	16.17	16.67	12.48	11.33	12.71
H-H	ΔE_{forw}	0.19	1.42	1.11	0.68	0.53	1.59	4.30	3.93
	ΔE_{back}	3.14	2.88	3.08	1.81	1.92	1.62	-0.34	-0.09
	ΔE_{reac}	-2.95	-1.46	-1.97	-1.13	-1.39	-0.03	4.63	4.02
H_2O	D_e	21.12	17.96	19.18	20.30	21.18	19.26	23.65	25.41
O-H	ΔE_{forw}	47.26	47.10	45.75	46.53	45.81	48.54	61.72	60.20
	ΔE_{back}	3.68	5.66	5.46	2.86	2.78	3.01	1.67	1.46
	ΔE_{reac}	43.57	41.44	40.29	43.67	43.03	45.53	60.05	58.73
C_2H_6	D_e	8.06	6.13	6.04	8.29	8.59	6.03	6.66	7.73
C-H	ΔE_{forw}	4.98	7.14	6.22	6.05	5.53	7.35	12.22	11.17
	ΔE_{back}	7.27	7.66	7.70	5.19	5.27	5.24	2.78	2.89
	ΔE_{reac}	-2.29	-0.51	-1.49	0.86	0.26	2.10	9.44	8.28
CH_3Cl	D_e	20.64	18.11	18.73	20.66	21.48	19.30	21.48	22.98
C-Cl	ΔE_{forw}	30.71	30.08	29.33	30.93	30.32	30.81	38.32	37.25
OxIn	ΔE_{back}	18.78	19.07	19.15	17.30	17.32	16.29	13.95	14.01
	ΔE_{reac}	11.93	11.01	10.18	13.64	13.00	14.52	24.37	23.24
		MAD	1.58	1.39	1.48	1.45	2.47	6.38	5.85
		MD	-0.24	-0.28	0.29	0.36	0.15	2.51	2.67
		RMS	2.03	1.77	1.80	1.77	2.82	7.60	7.00

Table 17: Relative electronic energies of CCSD(T)/CBS, several DFT methods and dRPA on the def2-QZVPP level together with the mean deviation (MD), mean absolute deviation (MAD), and root mean square deviation (RMS) based on the difference between a corresponding method and the CCSD(T) reference in kcal mol^{-1} for the $PdCl_2$ subset.

		CCSD(T)	PBE0-DH-D3	PWPB95-D3	B2PLYP-D3	PWRB95	dRPA
Benzene	D_e	29.96	31.27	28.12	28.39	26.23	24.18
C-H	ΔE_{forw}	25.47	28.12	26.85	24.09	26.32	26.33
	ΔE_{back}	2.98	1.72	3.05	3.73	2.69	3.06
	ΔE_{reac}	22.49	26.40	23.80	20.36	23.63	23.27
C_2H_4	D_e	35.04	37.31	33.78	34.58	33.04	29.86
C-H	ΔE_{forw}	29.73	35.99	34.61	32.72	34.76	34.39
	ΔE_{back}	1.87	3.67	4.97	5.49	4.61	4.87
	ΔE_{reac}	27.86	32.32	29.64	27.23	30.15	29.52
C_2H_6	D_e	8.06	10.44	9.59	12.64	8.25	6.17
C-C	ΔE_{forw}	22.65	25.24	26.96	30.60	26.01	27.17
	ΔE_{back}	28.30	24.23	27.71	32.23	26.38	28.33
	ΔE_{reac}	-5.65	1.00	-0.76	-1.63	-0.37	-1.16
CH_4	D_e	6.28	7.92	4.15	3.51	3.64	0.84
C-H	ΔE_{forw}	6.33	8.11	7.36	5.74	7.33	7.40
	ΔE_{back}	5.57	2.42	5.33	7.25	5.00	6.57
	ΔE_{reac}	0.77	5.69	2.04	-1.51	2.33	0.83
Cyclopropane	D_e	14.40	15.43	11.93	12.17	10.89	7.82
C-H	ΔE_{forw}	8.68	10.65	9.50	7.75	9.47	9.16
	ΔE_{back}	3.64	1.60	3.83	5.18	3.67	4.58
	ΔE_{reac}	5.04	9.05	5.68	2.57	5.81	4.58
H_2	D_e	13.91	16.45	12.38	12.65	12.02	9.00
H-H	ΔE_{forw}	0.19	0.97	0.70	-0.02	0.74	0.58
	ΔE_{back}	3.14	1.14	2.66	3.63	2.61	3.14
	ΔE_{reac}	-2.95	-0.17	-1.96	-3.66	-1.87	-2.55
H_2O	D_e	21.12	22.21	18.74	17.45	18.10	15.85
O-H	ΔE_{forw}	47.26	49.64	46.50	44.01	45.24	45.10
	ΔE_{back}	3.68	1.57	4.31	5.73	4.16	5.50
	ΔE_{reac}	43.57	48.07	42.19	38.27	41.08	39.61
C_2H_6	D_e	8.06	9.25	5.83	5.63	5.22	2.77
C-H	ΔE_{forw}	4.98	6.43	6.01	4.59	6.13	6.66
	ΔE_{back}	7.27	4.43	7.20	9.19	6.67	7.82
	ΔE_{reac}	-2.29	2.00	-1.19	-4.61	-0.54	-1.17
CH_3Cl	D_e	20.64	23.50	19.30	18.67	17.57	13.69
C-Cl	ΔE_{forw}	30.71	32.27	30.14	28.97	28.88	28.93
OxIn	ΔE_{back}	18.78	16.59	18.72	21.59	18.07	19.56
	ΔE_{reac}	11.93	15.67	11.42	7.38	10.81	9.36
		MAD	2.59	1.24	1.98	1.74	2.37
		MD	1.23	-0.09	-0.60	-0.54	-1.18
		RMS	2.88	1.62	2.34	2.13	3.27

5.4 Ni subset

Table 18: Relative electronic energies of CCSD(T)/CBS and several DFT methods on the def2-QZVPP level together with the mean deviation (MD), mean absolute deviation (MAD), and root mean square deviation (RMS) based on the difference between a corresponding method and the CCSD(T) reference in kcal mol^{-1} for the Ni subset.

		CCSD(T)	BLYP-D3	BLYP-NL	B97-D3	PBE-D3	PBE-NL	TPSS-D3	TPSS-NL
Benzene	ΔE_{forw}	18.18	14.37	15.81	15.16	16.79	17.71	17.84	19.18
C-H	ΔE_{back}	4.62	5.00	4.65	2.78	2.78	2.65	4.38	4.11
	ΔE_{reac}	13.56	9.37	11.16	12.38	14.02	15.05	13.46	15.07
BH_3	ΔE_{forw}	11.38	5.02	5.15	6.32	6.50	6.55	6.33	6.43
B-H	ΔE_{back}	2.19	3.23	3.39	1.26	1.96	2.05	2.74	2.85
	ΔE_{reac}	9.19	1.79	1.76	5.06	4.54	4.50	3.59	3.58
C_2H_4	ΔE_{forw}	30.44	25.97	26.96	26.42	27.87	28.38	29.01	29.73
C-H	ΔE_{back}	4.08	4.43	4.19	2.29	2.27	2.21	3.74	3.56
	ΔE_{reac}	26.36	21.53	22.77	24.13	25.60	26.17	25.27	26.17
C_2H_6	ΔE_{forw}	10.43	5.11	5.34	6.46	7.04	7.11	6.37	6.53
C-C	ΔE_{back}	27.03	29.34	27.88	25.96	24.05	23.47	27.14	26.01
	ΔE_{reac}	-16.60	-24.24	-22.54	-19.50	-17.01	-16.36	-20.77	-19.49
CH_4	ΔE_{forw}	4.09	3.57	3.42	3.84	3.24	3.18	3.13	3.05
C-H	ΔE_{back}	9.43	10.60	10.16	7.81	7.71	7.57	10.43	10.12
	ΔE_{reac}	-5.34	-7.03	-6.74	-3.96	-4.47	-4.39	-7.29	-7.07
Cyclopropane	ΔE_{forw}	-0.31	-1.09	-1.30	-0.62	-1.27	-1.43	-1.56	-1.83
C-H	ΔE_{back}	7.25	8.78	8.34	5.97	6.01	5.84	8.45	8.08
	ΔE_{reac}	-7.56	-9.87	-9.64	-6.59	-7.27	-7.27	-10.02	-9.92
H_2	ΔE_{forw}	0.60	0.16	0.12	0.39	0.12	0.10	-0.08	-0.11
H-H	ΔE_{back}	2.29	2.45	2.37	0.45	0.86	0.85	2.66	2.60
	ΔE_{reac}	-1.69	-2.29	-2.25	-0.06	-0.74	-0.74	-2.74	-2.70
C_2H_6	ΔE_{forw}	4.28	3.78	3.56	4.16	3.41	3.31	3.37	3.21
C-H	ΔE_{back}	10.34	11.97	11.58	9.09	9.13	9.01	11.54	11.25
	ΔE_{reac}	-6.06	-8.19	-8.02	-4.93	-5.71	-5.70	-8.17	-8.04
NH_3	ΔE_{forw}	25.74	19.54	18.70	19.64	17.31	16.99	17.07	16.56
N-H	ΔE_{back}	14.87	15.20	14.84	12.45	12.78	12.67	15.92	15.67
	ΔE_{reac}	10.88	4.34	3.86	7.19	4.53	4.31	1.15	0.90
		MAD	2.76	2.40	2.08	1.98	2.01	2.13	2.13
		MD	-2.10	-2.00	-1.71	-1.76	-1.70	-1.73	-1.63
		RMS	3.68	3.37	2.58	2.78	2.86	3.26	3.26

Table 19: Relative electronic energies of CCSD(T)/CBS and several DFT methods on the def2-QZVPP level together with the mean deviation (MD), mean absolute deviation (MAD), and root mean square deviation (RMS) based on the difference between a corresponding method and the CCSD(T) reference in kcal mol^{-1} for the Ni subset.

		CCSD(T)	B3LYP-D3	B3LYP-NL	PBE0-D3	PBE0-NL	PW6B95-D3	BHLYP-D3	BHLYP-NL
Benzene	ΔE_{forw}	18.18	15.94	16.96	18.22	19.01	19.08	16.75	17.70
C-H	ΔE_{back}	4.62	5.78	5.53	4.20	4.08	4.95	10.34	9.99
	ΔE_{reac}	13.56	10.16	11.43	14.02	14.93	14.13	6.41	7.71
BH_3	ΔE_{forw}	11.38	8.15	8.25	10.10	10.15	10.51	11.95	12.07
B-H	ΔE_{back}	2.19	1.77	1.91	0.25	0.32	0.50	1.24	1.34
	ΔE_{reac}	9.19	6.38	6.34	9.85	9.82	10.02	10.71	10.73
C_2H_4	ΔE_{forw}	30.44	28.64	29.42	30.99	31.45	31.13	31.19	31.89
C-H	ΔE_{back}	4.08	5.34	5.16	3.81	3.73	4.57	10.04	9.77
	ΔE_{reac}	26.36	23.30	24.26	27.18	27.71	26.56	21.14	22.12
C_2H_6	ΔE_{forw}	10.43	7.24	7.40	9.39	9.47	8.60	9.55	9.77
C-C	ΔE_{back}	27.03	30.44	29.42	26.95	26.38	27.32	37.59	36.28
	ΔE_{reac}	-16.60	-23.20	-22.02	-17.56	-16.92	-18.72	-28.04	-26.51
CH_4	ΔE_{forw}	4.09	6.01	5.91	6.01	5.96	6.94	9.55	9.45
C-H	ΔE_{back}	9.43	11.16	10.84	9.24	9.09	9.80	16.18	15.77
	ΔE_{reac}	-5.34	-5.15	-4.94	-3.23	-3.13	-2.86	-6.63	-6.32
Cyclopropane	ΔE_{forw}	-0.31	1.74	1.63	1.88	1.73	3.11	5.59	5.45
C-H	ΔE_{back}	7.25	9.51	9.22	7.64	7.47	8.31	14.89	14.49
	ΔE_{reac}	-7.56	-7.77	-7.59	-5.76	-5.74	-5.19	-9.29	-9.04
H_2	ΔE_{forw}	0.60	0.39	0.37	0.35	0.34	0.42	0.40	0.38
H-H	ΔE_{back}	2.29	3.25	3.19	2.28	2.26	2.89	7.51	7.39
	ΔE_{reac}	-1.69	-2.86	-2.82	-1.93	-1.92	-2.47	-7.11	-7.01
C_2H_6	ΔE_{forw}	4.28	6.43	6.27	6.45	6.37	7.38	10.21	10.05
C-H	ΔE_{back}	10.34	12.11	11.82	10.07	9.94	10.56	16.52	16.11
	ΔE_{reac}	-6.06	-5.68	-5.55	-3.61	-3.57	-3.17	-6.31	-6.06
NH_3	ΔE_{forw}	25.74	22.73	22.12	21.34	21.07	22.12	28.67	28.09
N-H	ΔE_{back}	14.87	15.98	15.70	14.57	14.45	15.07	21.77	21.37
	ΔE_{reac}	10.88	6.75	6.42	6.77	6.62	7.05	6.90	6.72
		MAD	2.06	1.78	1.16	1.27	1.43	4.36	4.01
		MD	-0.56	-0.48	0.00	0.06	0.33	1.41	1.49
		RMS	2.50	2.20	1.63	1.71	1.86	5.34	4.89

Table 20: Relative electronic energies of CCSD(T)/CBS, several DFT methods, and dRPA on the def2-QZVPP level together with the mean deviation (MD), mean absolute deviation (MAD), and root mean square deviation (RMS) based on the difference between a corresponding method and the CCSD(T) reference in kcal mol^{-1} for the Ni subset.

		CCSD(T)	PBE0-DH-D3	PWPB95-D3	B2PLYP-D3	PWRB95	dRPA
Benzene	ΔE_{forw}	18.18	21.80	22.13	23.97	19.84	19.20
C-H	ΔE_{back}	4.62	0.77	-0.27	-5.81	3.80	4.31
	ΔE_{reac}	13.56	21.03	22.41	29.78	16.05	14.89
BH_3	ΔE_{forw}	11.38	11.54	10.30	9.71	9.54	8.20
B-H	ΔE_{back}	2.19	-1.21	-0.16	-2.17	1.57	3.21
	ΔE_{reac}	9.19	12.76	10.46	11.88	7.97	4.99
C_2H_4	ΔE_{forw}	30.44	33.15	32.48	32.17	31.01	29.85
C-H	ΔE_{back}	4.08	0.47	-0.68	-6.04	3.32	3.66
	ΔE_{reac}	26.36	32.68	33.16	38.20	27.69	26.18
C_2H_6	ΔE_{forw}	10.43	11.14	9.78	9.86	9.09	9.94
C-C	ΔE_{back}	27.03	21.01	19.20	10.74	25.28	27.02
	ΔE_{reac}	-16.60	-9.87	-9.42	-0.88	-16.18	-17.08
CH_4	ΔE_{forw}	4.09	7.02	6.65	5.66	6.38	6.14
C-H	ΔE_{back}	9.43	4.69	3.54	-3.54	8.84	10.14
	ΔE_{reac}	-5.34	2.34	3.11	9.20	-2.47	-4.00
Cyclopropane	ΔE_{forw}	-0.31	2.84	2.38	1.19	1.79	0.30
C-H	ΔE_{back}	7.25	2.89	1.52	-5.78	6.87	7.42
	ΔE_{reac}	-7.56	-0.06	0.86	6.97	-5.07	-7.12
H_2	ΔE_{forw}	0.60	0.96	0.89	1.99	0.39	0.27
H-H	ΔE_{back}	2.29	-1.39	-2.33	-8.80	2.01	2.46
	ΔE_{reac}	-1.69	2.35	3.22	10.79	-1.61	-2.19
C_2H_6	ΔE_{forw}	4.28	7.47	7.02	5.89	6.77	6.56
C-H	ΔE_{back}	10.34	5.48	4.47	-2.21	9.53	10.48
	ΔE_{reac}	-6.06	1.99	2.55	8.10	-2.76	-3.92
NH_3	ΔE_{forw}	25.74	21.31	20.21	17.16	20.68	20.72
N-H	ΔE_{back}	14.87	10.84	8.89	3.53	14.13	15.93
	ΔE_{reac}	10.88	10.46	11.31	13.63	6.56	4.78
		MAD	4.13	4.61	8.58	1.58	1.34
		MD	0.92	0.52	0.21	0.05	-0.27
		RMS	4.68	5.32	10.20	2.01	2.04

6 $[Cu_2(en)O_2]^{2+}$ isomerization

Table 21: Relative electronic energies of CCSD(T)/def2-TZVPP, different DFT methods, and dRPA on the def2-QZVPP level for the isomerization reaction in the $[Cu_2(en)O_2]^{2+}$ complex at defined oxygen-oxygen distances in kcal mol^{-1} where the energy at 1.9 Å was used as zero point.

distance	CCSD(T)	PBE-D3	PWPB95-D3	PWRB95	dRPA
1.30	4.91	6.06	-1.25	-1.38	4.42
1.35	-0.73	1.04	-6.31	-5.42	-0.63
1.40	-4.33	-1.87	-9.30	-7.44	-3.64
1.45	-6.41	-3.18	-10.74	-7.97	-5.11
1.50	-7.34	-3.34	-11.01	-7.42	-5.44
1.55	-7.40	-2.70	-10.37	-6.14	-4.91
1.60	-6.79	-1.58	-9.01	-4.38	-3.74
1.65	-5.65	-0.31	-7.09	-2.46	-2.20
1.70	-4.13	0.77	-4.80	-0.72	-0.67
1.75	-2.46	1.39	-2.59	0.49	0.43
1.80	-1.03	1.43	-0.98	0.96	0.84
1.85	-0.16	0.92	-0.17	0.74	0.65
1.90	0.00	0.00	0.00	0.00	0.00
1.95	-0.49	-1.20	-0.23	-1.06	-0.91
2.00	-1.42	-2.53	-0.67	-2.29	-1.97
2.05	-2.45	-3.90	-1.20	-3.54	-3.02
2.10	-3.46	-5.19	-1.73	-4.72	-4.02
2.15	-4.24	-6.33	-2.17	-5.71	-4.84
2.20	-4.80	-7.27	-2.49	-6.49	-5.49
2.25	-5.05	-7.97	-2.62	-6.97	-5.87
2.30	-5.02	-8.39	-2.54	-7.17	-6.03
2.35	-4.66	-8.50	-2.21	-7.06	-5.88
2.40	-3.97	-8.30	-1.61	-6.59	-5.45

7 $[5.5.6]_n$cyclacenes

Table 22: Adiabatic energy differences between triplets and closed-shell singlets for several density functionals, dRPA and MP2 in kcal/mol of $[5.5.6]_n$cyclacenes 6_n.

n	3	4	5	6	7	8
TPSS-D3[a]	16.4	5.6	4.9	2.5	3.4	0.8
PW6B95-D3[a]	25.3	-1.6	23.9	-10.5	30.5	-16.3
B2PLYP-D3[a]	19.5	12.7	8.9	14.0	8.1	16.4
PWPB95-D3[b]	27.0	4.0	24.9	-0.9	30.3	-3.1
PWRB95[b]	13.4	0.9	21.1	-6.4	25.9	-11.1
MP2[b]	20.6	51.0	-9.0	65.3	-23.8	74.3
dRPA[b]	27.8	1.1	24.2	-5.8	29.7	-10.5

[a] using the def2-QZVP basis set, taken from *Phys. Chem. Chem. Phys.*, 2015, **17**, 7366. [b] using the def2-TZVP basis set.

8 PWRB95 total energies for testing and implementation purposes

Table 23 shows SCF energies, NL and RPA correlation contributions and the total absolute energies in Eh of PWRB95 for three systems. In case the functional is implemented into other electronic structure codes, these values can be used for testing the correct implementation. The calculations were carried out with the def2-QZVP basis set. The SCF and NL energies were obtained with TURBOMOLE's large grid 'm5' which is the largest grid for using the VV10 impelentation. The RI-J approximation was used for the SCF treatment. The SCF energy convergence criterion was set to 10. To ensure converged RPA correlation energies we used 5000 grid points in the rirpa module.

Table 23: SCF energies (E^{SCF}), scaled NL correlation (E^{NL}), scaled RPA correlation contributions (E^{RPA}), and the total absolute energies (E^{tot}) in E_h of PWRB95 for three systems. E^{SCF}, E^{NL}, and E^{RPA} were rounded to seven devimal places. E^{tot} is the sum of these three rounded values.

	Ne	H_2O^a	Benzene^b
E^{SCF}	-128.9378326	-76.4028848	-232.0836191
E^{NL}	0.0132684	0.0129481	0.0499749
E^{RPA}	-0.1526599	-0.1558435	-0.5765266
E^{tot}	-129.0772241	-76.5457802	-232.6101706

[a] The structure was taken from the WATER27 set. [b] The structure was taken from the SIE11 set.

References

[1] J. P. Perdew, A. Ruzsinszky, J. Tao, V. Staroverov, G. E. Scuseria, and G. Csonka. *J. Chem. Phys.*, 123:062201, 2005.

[2] S. Kurth, J. P. Perdew, and P. Blaha. *Int. J. Quant. Chem.*, 75:889, 1999.

[3] J. P. Perdew, K. Burke, and M. Ernzerhof. *Phys. Rev. Lett.*, 77:3865, 1996.

[4] J. P. Perdew, K. Burke, and M. Ernzerhof. *Phys. Rev. Lett.*, 78:196, 1997.

[5] A. D. Becke. *Phys. Rev. A*, 38:3098, 1988.

[6] C. Lee, W. Yang, and R. G. Parr. *Phys Rev. B*, 37:785, 1988.

[7] S. Grimme. *J. Comput. Chem.*, 27:1787, 2006.

[8] J. Tao, J. P. Perdew, V. N. Staroverov, and G. E. Scuseria. *Phys. Rev. Lett.*, 91:146401, 2003.

[9] A. D. Becke. *J. Chem. Phys.*, 98:1372, 1993.

[10] M. Ernzerhof and G. E. Scuseria. *J. Chem. Phys.*, 110:5029, 1999.

[11] A. D. Becke. *J. Chem. Phys.*, 98:5648, 1993.

[12] P. J. Stephens, F. J. Devlin, C. F. Chabalowski, and M. J. Frisch. *J. Phys. Chem.*, 98:11623, 1994.

[13] Y. Zhao and D. G. Truhlar. *J. Phys. Chem. A*, 109:5656, 2005.

[14] S. Grimme. *J. Chem. Phys.*, 124:034108, 2006.

[15] L. Goerigk and S. Grimme. *J. Chem. Theory Comput.*, 7:291, 2011.

[16] E. Brémond and C. Adamo. *J. Chem. Phys.*, 135:024106, 2011.

[17] F. Furche. *J. Chem. Phys.*, 129:114105, 2008.

[18] C. Møller and M. S. Plesset. *Phys. Rev.*, 46:618, 1934.

[19] R. Ahlrichs, M. Bär, M. Häser, and et al. TUROMOLE:Version 5.7, http://www.turbomole.com, 2004.

[20] R. Ahlrichs, M. Bär, M. Häser, H. Horn, and C. Kölmel. *Chem. Phys. Lett.*, 162:165, 1989.

[21] TURBOMOLE 6.6: R. Ahlrichs et al., Universität Karlsruhe 2014. See http://www.turbomole.com.

[22] L. Goerigk and S. Grimme. *Phys. Chem. Chem. Phys*, 13:6670, 2011.

[23] F. Weigend and R. Ahlrichs. *Phys. Chem. Chem. Phys.*, 7:3297, 2005.

[24] Jr. Dunning, T. H. *J. Chem. Phys.*, 90:1007, 1989.

[25] R. A. Kendall, Jr. Dunning, T. H., and R. J. Harrison. *J. Chem. Phys.*, 96:6796, 1992.

[26] D. Rappoport and F. Furche. *J. Chem. Phys.*, 133:134105, 2010.

[27] D. Andrae, U. Haeussermann, M. Dolg, H. Stoll, and H. Preuss. *Theor. Chim. Acta*, 77:123, 1990.

[28] A. Karton and L. Goerigk. *J. Comput. Chem.*, 36:622, 2015.

[29] T. Anacker and J. Friedrich. *J. Comput. Chem.*, 35:634, 2014.

[30] K. Eichkorn, F. Weigend, O. Treutler, and R. Ahlrichs. *Theor. Chem. Acc.*, 97:119, 1997.

[31] S. Vahtras, J. Almlöf, and M.W. Feyereisen. *Chem. Phys. Lett.*, 213:514, 1993.

[32] F. Weigend. *Phys. Chem. Chem. Phys.*, 4:4285, 2002.

[33] F. Weigend and M. Häser. *Theo. Chem. Acc.*, 97:331, 1997.

[34] F. Weigend. *Phys. Chem. Chem. Phys.*, 8:1057, 2006.

[35] S. Grimme, J. Antony, S. Ehrlich, and H. Krieg. *J. Chem. Phys.*, 132:154104, 2010.

[36] S. Grimme, S. Ehrlich, and L. Goerigk. *J. Comput. Chem.*, 32:1456, 2011.

[37] O. A. Vydrov and T. Van Voorhis. *J. Chem. Phys.*, 133:244103, 2010.