Supplementary information for: Long-range Corrected Density Functional Through The Density Matrix Expansion Based Semilocal Exchange Hole

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REFERENCES

[1]R. Peverati, D. G. Truhlar, Phil. Trans. R. Soc. A, **372**, 20120476, (2014).
[2]S. J. Chakravorty, S. R. Gwaltney, E. R. Davidson, F. A. Parpia, and C. F. Fischer, Phys. Rev. A 47, 3649 (1993).
[3]L. A. Curtiss, K. Raghavachari, P. C. Redfern, and J. A. Pople, J. Chem. Phys. **106**, 1063 (1997).
[4]R. Haunschild and W. klopper, J. Chem. Phys. **136**, 164102 (2012).
[5]B. J. Lynch, Y. Zhao, and D. G. Truhlar, J. Phys. Chem. A. **107**, 1384 (2003).
[6]B. J. Lynch, Y. Zhao, and D. G. Truhlar, see http://t1.chem.umn.edu/db/ for the Minnesota databases for chemistry and solid state physics.
[7]Y. Zhao, N. E. Schultz, and D. G. Truhlar, J. Chem. Theory Comput. **2**, 364 (2006).
[8]S. Parthiban and J. M. L. Martin, J. Chem. Phys. **114**, 6014 (2001).
[9]Y. Zhao and D. G. Truhlar, J. Phys. Chem. A. **110**, 10478 (2006).
[10]Y. Zhao, B. J. Lynch, and D. G. Truhlar, J. Phys. Chem. A. **108**, 2715 (2004).
[11]Y. Zhao, N. Gonzlez-Garca, and D. G. Truhlar, J. Phys. Chem. A. **109**, 2012 (2005).
[12]CRC Handbook of Chemistry and Physics, 85th ed., edited by D. R. Lide (CRC, Boca Raton, 2004).

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TABLE I: Total energies of atoms of the AE17 test set. All quantities are in Hartree.

Atom	Accurate	LC-TMLYP	CAM-B3LYP	LC-wPBE	LC-wPBEh	HSE06
H	-0.500	-0.498	-0.498	-0.506	-0.503	-0.504
He	-2.904	-2.904	-2.901	-2.904	-2.897	-2.902
Li	-7.478	-7.479	-7.470	-7.469	-7.468	-7.475
Be	-14.667	-14.659	-14.649	-14.637	-14.639	-14.647
B	-24.654	-24.650	-24.640	-24.624	-24.622	-24.631
C	-37.845	-37.846	-37.836	-37.816	-37.809	-37.819
N	-54.589	-54.592	-54.580	-54.559	-54.547	-54.558
O	-75.067	-75.082	-75.070	-75.038	-75.021	-75.034
F	-99.734	-99.755	-99.741	-99.698	-99.676	-99.691
Ne	-128.938	-128.958	-128.941	-128.887	-128.861	-128.877
Na	-162.255	-162.284	-162.266	-162.191	-162.176	-162.196
Mg	-200.053	-200.085	-200.071	-199.968	-199.964	-199.987
Al	-242.346	-242.378	-242.368	-242.251	-242.252	-242.275
Si	-289.359	-289.386	-289.380	-289.254	-289.255	-289.279
P	-341.259	-341.274	-341.274	-341.140	-341.141	-341.166
S	-398.110	-398.124	-398.130	-397.981	-397.981	-398.006
Cl	-460.148	-460.156	-460.170	-460.007	-460.006	-460.031
MAE:		0.014	0.012	0.058	0.064	0.049

TABLE II: Atomization energies of the G2/97 test set computed using 6-311++G(3df,3pd) basis set. All quantities are in kcal/mol.

Molecule	Name	CCSD(T)	LC-TMLYP	CAM-B3LYP	HSE06	LC-wPBEh	LC-wPBE
$AlCl_3$	Aluminum trichloride	313.454	296.554	298.340	299.901	304.697	304.700
AlF_3	Aluminum trifluoride	432.192	423.120	421.851	405.461	412.407	423.887
BCl_3	Boron trichloride	323.172	311.653	316.831	322.862	328.117	327.386
BF_3	Boron trifluoride	469.403	469.250	472.731	460.220	468.020	477.027
BeH	Berilium monohydride	50.789	59.041	57.878	55.750	55.646	56.307
CCl_4	Tetrachloromethane	313.633	290.760	300.516	309.732	317.961	318.900
CF_4	Tetrafluoromethane	478.081	474.318	481.322	470.480	483.696	497.207
CH	Methylidyne radical	83.869	84.181	84.581	82.540	82.594	82.757
CH_2Cl_2	Dichloromethane	370.105	360.856	366.374	367.093	372.443	372.825
CH_2F_2	Difluoromethane	436.843	436.682	440.984	431.319	438.860	446.088
CH_2O_2	Formic acid	500.306	496.773	502.809	494.101	502.523	512.239
CH_2O	Formaldehyde	373.210	370.842	374.573	368.344	373.126	378.865
CH_2	Singlet carbene	180.619	179.036	180.093	175.104	175.887	176.129
CH_2	Triplet carbene	189.742	192.908	192.265	191.974	193.319	193.458
CH_3Cl	Chloromethane	394.518	390.557	394.303	390.860	395.017	398.384
CH_3	Methyl radical	306.590	309.872	310.393	305.975	308.004	308.348
CH_3O	Hydroxymethyl radical	408.552	410.225	413.731	406.111	411.653	416.408
CH_3O	Methoxy radical	398.894	401.810	405.650	398.684	403.463	406.868
CH_3S	Methylthio radical	381.246	379.860	383.621	379.825	383.831	384.327
CH_4	Methane	418.872	419.442	421.728	414.313	417.339	417.786
CH_4O	Methanol	511.829	510.393	514.948	504.527	510.723	515.107
CH_4S	Thiomethanol	473.495	468.435	473.454	467.683	472.529	472.759
$CHCl_3$	Trichloromethane	343.726	328.171	335.715	340.673	347.343	347.890
CHF_3	Trifluromethane	458.777	457.111	462.677	452.278	462.583	473.031
CHO	Formyl radical	278.282	277.952	281.141	277.208	281.601	288.076
CN	Cyano radical	180.065	171.734	175.903	175.782	178.319	184.040
CNH	Hydrogen cyanide	311.523	306.806	311.321	306.873	310.709	316.849
CNH_3O_2	Methyl nitrite	597.491	591.807	601.318	590.089	601.927	617.609
CNH_3O_2	Nitromethane	599.632	594.796	604.178	594.946	606.578	621.793
CNH_5	Methylamine	580.082	581.265	586.523	575.203	581.506	584.945
C_2Cl_4	Tetrachloroethylene	469.319	443.444	456.156	468.158	478.089	480.002
C_2F_4	Tetrafluroethylene	587.668	585.044	595.207	586.173	601.051	617.058
C_2H	Ethynyl radical	263.659	259.285	262.065	262.499	265.939	268.874

Molecule	Name	CCSD(T)	LC-TMLYP	CAM-B3LYP	HSE06	LC-wPBEh	LC-wPBE
C_2H_2	Acetylene	402.763	398.238	402.701	399.415	403.514	406.538
$C_2H_2O_2$	Glyoxal	632.360	626.469	634.166	626.661	636.828	648.482
C_2H_2O	Ketene	530.603	528.160	534.752	531.175	538.034	545.063
C_2H_3Cl	Vinyl Chloride	541.516	534.758	541.256	539.475	545.621	547.159
C_2H_3	Vinyl radical	443.495	444.270	447.813	444.680	448.901	450.463
$C2H_3F$	Vinyl fluoride	571.223	569.888	575.789	568.530	575.961	581.167
C_2H_3O	Carbonyl methane	579.876	579.815	585.270	579.183	587.150	594.057
C_2H_3OCl	Acetyl chloride	666.141	658.682	666.763	663.092	672.548	678.736
C_2H_3OF	Acetyl fluoride	704.174	702.133	709.060	699.579	710.908	720.984
C_2H_4	Ethylene	561.341	559.677	564.289	557.978	563.004	564.509
$C_2H_4O_2$	Acetic acid	800.868	796.975	805.365	793.934	806.334	816.580
$C_2H_4O_2$	Methyl formate	784.033	780.283	789.027	776.512	788.607	799.134
C_2H_4O	Acetaldehyde	675.005	672.836	678.961	670.378	678.919	685.164
C_2H_4O	Oxirane	648.827	645.662	652.701	646.203	656.000	662.551
C_2H_4S	Thiirane	623.588	614.840	622.588	621.626	629.740	631.147
C_2H_5Cl	Ethyl chloride	690.032	684.990	691.046	685.149	693.159	694.073
C_2H_5	Ethyl radical	601.427	604.575	607.667	601.067	606.814	607.768
C_2H_5O	Ethoxy radical	695.120	693.990	700.091	690.434	699.163	703.176
C_2H_6	Ethane	710.204	710.151	714.620	704.925	711.685	712.706
C_2H_6O	Dimethyl ether	796.040	794.452	801.834	787.867	797.713	802.781
C_2H_6O	Ethanol	808.220	805.832	812.692	799.593	809.705	814.681
C_2H_6OS	Dimethyl sulfoxide	854.413	843.593	852.509	842.449	854.015	859.579
C_2H_6S	Dimethyl sulfide	766.299	760.892	768.210	760.057	768.776	769.579
C_2H_6S	Thioethanol	769.393	759.898	767.017	759.297	767.755	768.611
C_2N_2	Cyanogen	498.280	487.112	497.502	496.298	502.497	514.202
C_2NF_3	Trifluroacetonitril	639.494	631.856	642.309	633.152	647.912	664.825
C_2NH_3	Acetonitrile	613.275	609.358	616.337	610.098	617.372	623.798
C_2NH_5	Aziridine	717.130	716.099	723.957	716.847	726.913	732.204
C_2NH_5O	Acetamide	864.915	864.443	873.626	861.004	873.234	882.334
C_2NH_7	Dimethylamine	867.075	867.478	875.413	861.192	871.286	875.357
C_2NH_7	Ethaylamine	875.261	875.268	882.824	868.988	879.212	883.262
C_3H_4	Allene	699.982	697.512	705.195	701.089	707.791	710.593
C_3H_4	Cyclopropene	678.007	674.397	681.646	680.022	689.009	692.702
C_3H_4	Propyne	701.358	697.075	704.110	699.154	706.664	710.064
C_3H_6	Cyclopropane	849.824	848.357	855.192	849.312	860.093	862.855
C_3H_6O	Acetone	975.379	972.549	980.961	969.788	982.347	989.206
C_3H_6	Propene	857.410	854.948	862.011	853.583	862.342	864.388
C_3H_7Cl	1-Chloropropane	983.574	977.152	985.451	977.104	989.047	990.570
C_3H_7	Isopropyl radical	897.482	899.901	905.525	896.684	906.246	907.776
C_3H_8O	Methoxyethane	1092.532	1089.835	1099.506	1082.889	1096.657	1102.325
C_3H_8O	Isopropyl alcohol	1105.317	1101.272	1110.470	1094.582	1108.848	1114.490
C_3H_8	Propane	1003.629	1002.364	1009.091	996.926	1007.614	1009.234
C_3NH_3	Acrylontrile	758.512	751.581	761.326	756.828	765.428	772.666
C_3NH_9	Trimethylamine	1156.873	1155.466	1166.209	1148.850	1162.998	1167.702
C_4H_{10}	Isobutane	1298.551	1295.316	1304.362	1289.524	1304.387	1306.648
C_4H_{10}	n-Butane	1297.126	1294.485	1303.464	1288.831	1303.453	1305.675
C_4H_4O	Furan	990.051	981.675	995.093	991.347	1006.657	1014.983
C_4H_4S	Thiophene	959.884	944.312	958.029	961.15	974.128	977.119
C_4H_6	1,3-Butadiene	1007.991	1002.335	1012.399	1005.956	1015.762	1018.334
C_4H_6	2-Butyne	999.002	994.597	1004.196	997.597	1008.527	1012.329
C_4H_6	Bicyclobutane	981.134	976.271	986.084	984.928	999.515	1003.833
C_4H_6	Cyclobutene	996.655	990.395	1000.312	996.705	1009.852	1013.538
C_4H_6	Methylenecyclopropane	988.022	984.755	994.524	990.587	1002.946	1006.814
C_4H_8	Cyclobutane	1145.231	1141.000	1150.321	1142.278	1157.472	1160.748
C_4H_8	Isobutene	1154.236	1150.227	1159.713	1148.937	1161.638	1164.266
C_4H_9	tert-Butyl radical	1194.236	1195.266	1203.398	1192.221	1205.737	1207.839
C_4NH_5	Pyrrole	1067.054	1061.231	1075.519	1071.433	1086.773	1093.563
C_5H_8	Spiropentane	1278.794	1274.912	1286.697	1282.710	1301.015	1306.116
C_5NH_5	Pyridine	1232.274	1224.520	1240.976	1238.408	1254.591	1261.301
C_6H_6	Benzene	1361.588	1351.847	1367.589	1366.772	1383.255	1386.980
Cl_2	Dichlorine	59.073	49.717	53.787	56.549	57.519	57.429
CO	Carbon monoxide	258.877	253.099	256.086	252.342	256.640	263.594
CO_2	Carbon dioxide	388.592	383.819	388.878	386.141	393.027	403.906
COF_2	Carbonyl fluoride	419.501	416.439	422.309	415.439	425.550	438.358

Molecule	Name	CCSD(T)	LC-TMLYP	CAM-B3LYP	HSE06	LC-wPBEh	LC-wPBE
COS	Carbonyl sulfide	334.288	323.917	331.236	332.961	337.283	343.087
CS	Carbon monosulfide	170.985	158.193	163.580	165.487	167.115	168.542
CS_2	Carbon disulphide	278.664	260.900	271.232	278.778	279.226	279.065
FCl	Chlorine monofluoride	62.572	57.789	60.464	57.794	60.496	65.211
F_2	Difluorine	38.755	33.653	35.726	30.987	34.537	43.543
F_3Cl	Chlorine trifluoride	128.346	122.527	127.762	121.252	121.818	143.144
HCl	Hydrogen Chloride	107.199	103.705	105.245	103.977	104.929	104.806
HF	Hydrogen fluoride	141.513	139.731	140.472	135.855	137.636	140.632
HOCl	Hypochlorus acid	165.791	158.940	163.131	159.040	162.544	167.201
HO	Hydroxyl radical	106.955	107.885	108.536	104.853	106.067	108.169
HS	Mercapto radical	87.390	86.586	88.021	85.894	86.494	86.382
H_2	Dihydrgen	109.400	108.551	109.030	104.526	104.157	104.167
H_2O_2	Hydrogen peroxide	268.655	263.737	268.362	258.406	264.039	273.121
H_2O	Water	232.565	230.243	232.150	225.021	227.760	231.398
H_2S	Hydrogen sulphide	183.298	179.011	181.995	178.065	179.500	179.142
LiF	Lithium fluoride	139.369	138.674	138.748	130.852	132.306	137.425
LiH	Lithium hydride	57.904	58.156	58.767	52.894	52.924	54.056
Li_2	Dilithium	24.197	20.473	20.790	19.195	18.779	18.702
Na_2	Disodium	17.101	14.835	15.760	16.007	14.253	13.629
NaCl	Sodium chloride	98.466	93.802	94.101	93.059	94.203	95.107
NF_3	Trifluoroamine	206.212	205.920	211.849	202.826	212.749	229.797
NH_2	Amino radical	181.955	185.884	187.201	181.752	183.030	185.079
NH_3	Ammonia	297.070	298.266	301.017	292.418	295.099	297.855
NH	Imidogen	82.787	86.614	87.129	84.779	85.099	86.250
NO_2	Nitrogen dioxide	227.058	223.792	229.708	227.199	234.332	249.950
NOCl	Nitrosyl chloride	191.468	179.285	186.936	187.652	190.566	200.173
NO	Nitric oxide	152.187	152.076	155.553	151.083	155.645	165.033
N_2	Dinitrogen	227.436	221.004	225.375	220.155	224.120	233.383
N_2H_4	Hydrazine	436.699	439.305	445.302	432.631	438.648	444.844
N_2O	Nitrous oxide	269.474	260.391	268.310	266.965	272.736	286.787
OCl	Monochlorine monoxide	64.532	60.782	64.414	63.911	66.317	70.850
OF_2	Diflourine monoxide	93.772	88.454	92.717	85.333	91.996	107.134
OS	Sulpher monoxide	125.796	121.753	124.850	122.695	125.781	131.371
O_2	Dioxygen	120.545	120.211	122.247	119.053	123.945	134.354
O_2S	Sulpher dioxide	259.766	242.447	247.926	243.384	250.050	261.909
O_3	Ozone	146.819	127.518	133.319	130.192	137.357	157.302
P_2	Diphosphorus	115.951	101.715	109.368	108.139	106.800	105.249
PF_3	Phosphorus trifluoride	365.156	358.945	363.138	346.160	354.900	366.277
PH_2	Phosphino radical	153.970	156.048	158.111	151.768	152.437	152.210
PH_3	Phosphane	241.475	241.074	244.408	235.193	236.549	236.101
S_2	Disulpher	103.112	94.086	99.540	103.470	103.745	102.838
$SiCH_6$	Methylsilane	627.656	626.056	628.950	615.066	620.848	621.521
$SiCl_4$	Silicon tetrachloride	388.483	363.085	368.207	372.984	380.505	379.385
SiF_4	Silicon tetrafluoride	577.546	561.266	563.563	542.041	552.638	565.454
SiH_2	Singlet silylene	153.678	151.544	153.158	146.142	146.497	146.237
SiH_2	Triplet silylene	133.260	133.435	133.272	131.065	132.283	132.398
SiH_3	Silyl radical	228.083	228.742	229.201	221.869	223.400	223.457
SiH_4	Silane	324.589	323.886	324.989	313.063	315.062	315.038
SiO	Silicon monoxide	192.359	184.530	187.015	179.053	182.238	188.634
Si_2H_6	Disilane	535.471	531.535	533.434	517.718	522.240	522.039
Si_2	Disilicon	73.411	57.596	63.290	69.760	66.661	63.634
MAE:			5.099	4.329	5.195	5.735	5.36

TABLE III: Ionization potential for the test set IP13/3 for the exchange-correlation functional shown in each column using 6-311++G(3df,3pd) basis set. All quantities are in kcal/mol.

Molecule	Expt	LC-TMLYP	CAM-B3LYP	HSE06	LC-wPBEh	LC-wPBE
C	259.74	266.26	266.59	265.53	262.77	269.24
S	238.34	239.71	242.58	239.84	240.52	242.13
SH	238.36	238.06	241.07	238.63	239.51	240.76
Cl	299.31	298.53	301.29	298.79	299.68	301.26
Cl_2	265.30	262.75	264.08	261.28	262.37	266.15
OH	298.90	303.99	305.66	300.63	301.81	305.61
O	313.67	323.58	325.29	320.15	320.84	325.35
O_2	278.90	288.71	290.08	286.64	286.48	287.09
P	242.80	237.60	239.33	242.63	243.77	244.83
PH	234.10	232.80	234.44	237.00	238.13	239.44
PH_2	226.30	227.27	228.91	230.70	231.76	233.20
S_2	216.00	220.35	221.13	221.07	221.98	224.95
Si	188.05	185.25	186.95	189.51	190.70	191.83
MAE:		3.92	4.56	3.24	3.88	5.55

TABLE IV: Electron affinity for the test set EA13/03 for the exchange-correlation functional shown in each column using 6-311++G(3df,3pd) basis set. All quantities are in kcal/mol.

Molecule	Expt	LC-TMLYP	CAM-B3LYP	HSE06	LC-wPBEh	LC-wPBE
C	29.19	28.50	30.45	31.95	33.05	33.37
S	47.91	46.64	49.38	47.15	47.52	47.39
SH	53.84	49.60	52.54	51.03	51.44	51.01
Cl	84.24	81.77	84.12	82.09	82.73	82.83
Cl_2	55.60	61.44	62.66	59.93	58.33	58.18
OH	42.30	38.25	40.19	35.16	36.67	39.12
O	33.77	35.32	36.49	30.46	31.99	35.40
O_2	10.80	8.48	10.73	5.29	5.52	7.58
P	16.92	17.19	19.96	17.57	17.49	17.09
PH	23.20	20.59	23.65	21.69	21.78	21.12
PH_2	29.40	24.05	27.30	26.04	26.28	25.56
S_2	38.50	36.07	38.05	36.10	36.34	38.06
Si	32.33	26.79	29.05	32.92	33.24	33.06
MAE:		2.97	1.96	2.87	2.44	2.06

TABLE V: Proton affinities for the test set PA8 for the exchange-correlation functional shown in each column using 6-311++G(3df,3pd) basis set. All quantities are in kcal/mol

Molecule	Expt	LC-TMLYP	CAM-B3LYP	HSE06	LC-wPBEh	LC-wPBE
NH_3	211.90	211.43	209.91	213.10	224.43	213.47
H_2O	171.80	170.69	169.94	172.88	181.24	173.07
C_2H_2	156.60	158.89	157.71	161.51	170.00	162.25
SiH_4	156.50	156.39	154.97	157.65	165.54	156.50
PH_3	193.10	195.40	192.48	193.81	208.02	195.66
H_2S	173.70	174.74	173.26	175.85	186.08	175.87
HCl	137.10	137.34	136.40	139.48	146.56	139.28
H_2	105.90	103.95	103.18	106.62	112.24	106.57
MAE:		1.19	1.37	1.79	10.94	2.01

TABLE VI: FORWARD barrier heights of hydrogen transfer reactions for the HTBH38/04 test set for the exchange-correlation functional shown in each column using 6-311++G(3df,3pd) basis set. All quantities are in kcal/mol.

	Molecule	Expt	LC-TMLYP	CAM-B3LYP	HSE06	LC-wPBEh	LC-wPBE
1.	$H + HCl \rightarrow H_2 + Cl$	5.70	2.15	0.98	2.87	4.05	5.81
2.	$OH + H_2 \rightarrow H_2O + H$	4.90	3.10	0.84	1.38	0.65	2.75
3.	$CH_3 + H_2 \rightarrow CH_4 + H$	12.10	11.17	8.80	8.14	7.70	9.92
4.	$OH + CH_4 \rightarrow H_2O + CH_3$	6.50	5.18	2.30	2.99	2.66	4.95
5.	$H + H_2 \rightarrow H_2 + H$	9.60	6.23	4.83	6.04	6.26	7.87
6.	$OH + NH_3 \rightarrow H_2O + NH_2$	3.00	2.40	-0.31	-0.94	-0.73	2.95
7.	$HCl + CH_3 \rightarrow CH_4 + Cl$	1.70	1.66	-0.55	-1.35	-1.02	1.38
8.	$OH + C_2H_6 \rightarrow H_2O + C_2H_5$	3.20	2.57	0.24	0.12	-0.02	2.48
9.	$F + H_2 \rightarrow HF + H$	1.42	-3.49	-5.16	-3.67	-4.23	-2.71
10.	$O + CH_4 \rightarrow OH + CH_3$	13.47	9.52	8.23	8.52	8.28	10.06
11.	$H + PH_3 \rightarrow H_2 + PH_2$	3.10	1.49	0.10	0.69	1.44	2.99
12.	$H + HO \rightarrow H_2 + O$	10.50	7.18	5.68	7.22	7.89	10.47
13.	$H + H_2S \rightarrow H_2 + HS$	3.50	2.06	0.63	1.40	2.13	3.83
14	$O + HCl \rightarrow OH + Cl$	9.57	6.87	4.31	3.54	4.23	8.02
15.	$CH_3 + NH_2 \rightarrow CH_4 + NH$	8.00	9.76	7.15	6.17	6.26	9.24
16.	$C_2H_5 + NH_2 \rightarrow C_2H_6 + NH$	7.50	11.41	9.04	8.03	8.10	10.84
17.	$NH_2 + C_2H_6 \rightarrow NH_3 + C_2H_5$	10.40	12.29	9.74	8.62	8.53	11.31
18.	$NH_2 + CH_4 \rightarrow NH_3 + CH_3$	14.50	14.65	12.22	11.20	11.04	13.70
19.	s-trans cis-$C_5H_8 \rightarrow$ s-trans cis-C_5H_8	38.40	43.17	40.42	36.62	36.19	39.99
	MAE:		2.24	3.37	3.18	3.09	1.38

TABLE VII: BACKWARD barrier heights of hydrogen transfer reactions for the HTBH38/04 test set for the exchange-correlation functional shown in each column using 6-311++G(3df,3pd) basis set. All quantities are in kcal/mol.

	Molecule	Expt	LC-TMLYP	CAM-B3LYP	HSE06	LC-wPBEh	LC-wPBE
1.	$H + HCl \rightarrow H_2 + Cl$	7.86	6.98	4.79	3.45	3.30	6.16
2.	$OH + H_2 \rightarrow H_2O + H$	21.20	17.00	15.47	17.09	18.23	21.05
3.	$CH_3 + H_2 \rightarrow CH_4 + H$	15.30	12.20	11.09	11.93	12.85	14.82
4.	$OH + CH_4 \rightarrow H_2O + CH_3$	19.60	18.05	15.33	14.90	15.09	18.36
5.	$H + H_2 \rightarrow H_2 + H$	9.60	6.22	4.83	6.04	6.26	7.87
6.	$OH + NH_3 \rightarrow H_2O + NH_2$	12.70	12.39	9.50	8.62	8.95	12.98
7.	$HCl + CH_3 \rightarrow CH_4 + Cl$	7.06	7.52	5.55	3.01	3.39	6.63
8.	$OH + C_2H_6 \rightarrow H_2O + C_2H_5$	19.90	19.48	17.00	16.55	16.92	20.03
9.	$F + H_2 \rightarrow HF + H$	33.40	27.80	26.32	27.79	29.35	32.62
10.	$O + CH_4 \rightarrow OH + CH_3$	7.90	7.85	5.42	5.06	5.03	7.98
11.	$H + PH_3 \rightarrow H_2 + PH_2$	23.20	25.01	22.83	21.77	21.47	23.37
12.	$H + HO \rightarrow H_2 + O$	12.87	7.81	6.18	6.89	5.99	7.62
13.	$H + H_2S \rightarrow H_2 + HS$	16.76	18.19	15.71	13.76	13.30	15.85
14	$O + HCl \rightarrow OH + Cl$	9.36	11.07	7.61	4.45	5.39	11.20
15.	$CH_3 + NH_2 \rightarrow CH_4 + NH$	22.40	20.06	18.42	17.53	17.67	20.22
16.	$C_2H_5 + NH_2 \rightarrow C_2H_6 + NH$	18.30	17.67	15.88	14.88	15.01	17.67
17.	$NH_2 + C_2H_6 \rightarrow NH_3 + C_2H_5$	17.40	19.21	16.69	15.48	15.79	18.83
18.	$NH_2 + CH_4 \rightarrow NH_3 + CH_3$	17.80	17.53	14.74	13.54	13.79	17.08
19.	s-trans cis-$C_5H_8 \rightarrow$ s-trans cis-C_5H_8	38.40	43.17	40.42	36.62	36.19	39.99
	MAE:		2.09	3.22	3.77	3.53	1.14

TABLE VIII: FORWARD barrier heights of non-hydrogen transfer reactions for the NHTBH38/04 test set for the exchange-correlation functional shown in each column using 6-311++G(3df,3pd) basis set. All quantities are in kcal/mol

	Molecule	Expt	LC-TMLYP	CAM-B3LYP	HSE06	LC-wPBEh	LC-wPBE
1.	$H + N_2O \rightarrow OH + N_2$	17.13	14.92	12.73	14.38	15.19	17.81
2.	$H + HF \rightarrow HF + H$	42.18	36.88	33.38	34.28	35.74	40.35
3.	$H + ClH \rightarrow HCl + H$	18.00	16.91	14.47	14.05	15.17	18.39
4.	$H + FCH_3 \rightarrow HF + CH_3$	30.38	27.53	25.43	25.80	28.12	32.56
5.	$H + F_2 \rightarrow HF + F$	2.27	-3.51	-5.22	47.03	-2.70	0.57
6.	$CH_3 + FCl \rightarrow CH_3F + Cl$	6.75	5.75	3.00	1.64	4.76	9.86
7.	$F^- + CH_3F \rightarrow FCH_3 + F^-$	-0.34	-2.37	-2.66	-1.75	-1.30	1.07
8.	$F^-...CH_3F \rightarrow FCH_3...F^-$	13.38	12.34	12.04	11.88	12.46	14.36
9.	$Cl^- + CH_3Cl \rightarrow ClCH_3 + Cl^-$	3.10	4.95	2.85	1.42	4.30	8.56
10.	$Cl^-...CH_3Cl \rightarrow ClCH_3...Cl^-$	13.41	14.90	12.74	11.21	13.88	17.75
11.	$F^- + CH_3Cl \rightarrow FCH_3 + Cl^-$	-12.54	-13.01	-14.56	-14.71	-13.07	-9.33
12.	$F^-...CH_3Cl \rightarrow FCH_3...Cl^-$	3.44	3.36	2.19	1.65	2.95	5.38
13.	$OH^- + CH_3F \rightarrow HOCH_3 + F^-$	-2.44	-3.93	-4.29	-4.12	-3.44	-1.11
14	$OH^-...CH_3F \rightarrow HOCH_3...F^-$	10.96	10.38	9.88	8.94	9.79	11.84
15.	$H + N_2 \rightarrow HN_2$	14.36	10.41	8.88	9.04	9.55	12.11
16.	$H + CO \rightarrow HCO$	3.17	1.06	0.11	0.75	0.99	2.33
17.	$H + C_2H_4 \rightarrow CH_3CH_2$	1.72	0.88	0.15	1.05	1.28	2.03
18.	$CH_3 + C_2H_4 \rightarrow CH_3CH_2CH_2$	6.85	7.84	6.49	5.12	5.25	6.91
19.	$HCN \rightarrow CNH$	48.07	47.95	46.99	46.49	45.88	46.53
	MAE:		1.85	2.91	5.01	2.02	1.81

TABLE IX: BACKWARD barrier heights of non-hydrogen transfer reactions for the NHTBH38/04 test set for the exchange-correlation functional shown in each column using 6-311++G(3df,3pd) basis set. All quantities are in kcal/mol

	Molecule	Expt	LC-TMLYP	CAM-B3LYP	HSE06	LC-wPBEh	LC-wPBE
1.	$H + N_2O \rightarrow OH + N_2$	82.27	81.77	76.76	71.89	71.14	77.41
2.	$H + HF \rightarrow HF + H$	42.18	36.88	33.38	34.28	35.74	40.35
3.	$H + ClH \rightarrow HCl + H$	18.00	16.91	14.47	14.05	15.17	18.39
4.	$H + FCH_3 \rightarrow HF + CH_3$	57.02	55.03	50.86	50.97	51.98	56.64
5.	$H + F_2 \rightarrow HF + F$	105.80	102.14	98.95	151.38	99.75	102.53
6.	$CH_3 + FCl \rightarrow CH_3F + Cl$	59.16	60.00	57.28	54.30	57.66	63.91
7.	$F^- + CH_3F \rightarrow FCH_3 + F^-$	-0.34	-2.37	-2.66	-1.75	-1.30	1.07
8.	$F^-...CH_3F \rightarrow FCH_3...F^-$	13.38	12.34	12.04	11.88	12.46	14.36
9.	$Cl^- + CH_3Cl \rightarrow ClCH_3 + Cl^-$	3.10	4.95	2.85	1.42	4.30	8.56
10.	$Cl^-...CH_3Cl \rightarrow ClCH_3...Cl^-$	13.41	14.90	12.74	11.21	13.88	17.75
11.	$F^- + CH_3Cl \rightarrow FCH_3 + Cl^-$	20.11	21.14	20.91	20.22	21.48	23.78
12.	$F^-...CH_3Cl \rightarrow FCH_3...Cl^-$	29.42	30.21	29.72	28.50	29.82	32.16
13.	$OH^- + CH_3F \rightarrow HOCH_3 + F^-$	17.66	17.51	16.40	16.79	17.84	21.49
14	$OH^-...CH_3F \rightarrow HOCH_3...F^-$	47.20	48.42	48.59	48.63	50.16	52.45
15.	$H + N_2 \rightarrow HN_2$	10.61	12.89	11.81	11.49	11.95	13.05
16.	$H + CO \rightarrow HCO$	22.68	25.38	24.57	25.14	25.47	25.87
17.	$H + C_2H_4 \rightarrow CH_3CH_2$	41.75	45.76	43.49	44.12	45.06	47.60
18.	$CH_3 + C_2H_4 \rightarrow CH_3CH_2CH_2$	32.97	34.46	33.27	33.69	36.31	39.48
19.	$HCN \rightarrow CNH$	32.82	34.79	33.80	32.63	32.23	33.19
	MAE:		1.86	2.48	5.06	2.78	3.24

TABLE X: Binding energies for the 31 weakly interacting systems for the exchange-correlation functional shown in each column. All quantities are in kcal/mol.

Molecule	Expt	LC-TMLYP	CAM-B3LYP	HSE06	LC-wPBEh	LC-wPBE
$(NH_3)_2$	3.15	3.00	2.95	2.68	2.70	2.51
$(HF)_2$	4.57	5.18	5.26	4.47	4.55	4.27
$(H_2O)_2$	4.97	5.36	5.41	4.73	4.85	4.62
NH_3-H_2	6.41	6.64	6.74	6.19	6.32	6.06
$(HCONH_2)_2$	14.94	14.14	14.58	13.20	13.71	13.04
$(HCOOH)_2$	16.15	16.45	17.12	15.32	16.09	15.57
C_2H_4-F_2	1.06	1.29	1.27	1.40	1.01	0.57
NH_3-F_2	1.81	2.18	2.31	2.35	1.84	1.09
C_2H_2-ClF	3.81	3.14	3.63	3.93	3.51	2.52
HCN-ClF	4.86	4.66	4.92	4.22	4.12	3.55
NH_3-Cl_2	4.88	4.38	5.04	5.41	4.65	3.40
H_2O-ClF	5.36	5.55	5.90	5.31	5.20	4.47
NH_3-ClF	10.62	10.75	11.91	12.63	11.96	9.82
$(H_2S)_2$	1.66	1.23	1.15	1.26	1.16	1.00
$(HCl)_2$	2.01	1.67	1.62	1.50	1.45	1.23
HCl-H_2S	3.35	3.00	3.10	3.25	3.14	2.76
CH_3Cl-HCl	3.55	2.80	2.79	2.52	2.59	2.26
HCN-CH_3SH	3.59	3.21	3.10	3.01	3.07	2.86
CH_3SH-HCl	4.16	4.07	4.23	4.40	4.42	3.90
HeNe	0.04	0.09	0.02	0.06	0.01	-0.02
HeAr	0.06	0.07	0.001	0.05	-0.005	-0.03
Ne_2	0.08	0.20	0.12	0.12	0.07	0.01
NeAr	0.13	0.19	0.08	0.10	0.03	-0.03
CH_4-Ne	0.22	0.26	0.13	0.16	0.09	0.03
C_6H_6-Ne	0.47	0.55	0.27	0.13	0.16	0.09
$(CH_4)_2$	0.51	0.22	-0.08	-0.15	-0.14	-0.16
$(C_2H_2)_2$	1.34	1.06	0.82	0.80	0.81	0.77
$(C_2H_4)_2$	1.42	0.73	0.33	0.06	0.26	0.27
Sandwich C_6H_6	1.81	-0.26	-0.92	-1.22	-0.78	-0.42
T-Shaped C_6H_6	2.74	1.68	1.32	0.85	1.35	1.73
Parrallel C_6H_6	2.78	0.63	-0.09	-0.54	0.13	0.58
MAE		0.45	0.58	0.71	0.56	0.78

TABLE XI: Thermochemistry of π system for the πTC13 test set for functional shown in each column using 6-311++G(3df,3pd) basis set. All quantities are in kcal/mol.

Molecule	Expt	LC-TMLYP	CAM-B3LYP	HSE06	LC-wPBEh	LC-wPBE
E2-E1	-1.40	-0.54	-1.17	-1.99	-1.20	0.28
E4-E3	-8.80	-7.34	-5.53	-2.84	-5.43	-8.74
E6-E5	-14.30	-13.63	-10.68	-6.04	-10.69	-15.53
P-2	167.81	169.20	167.72	171.29	171.28	172.33
P-4	193.45	198.7	196.52	199.21	198.25	198.09
P-6	209.68	215.59	213.74	216.79	215.28	214.55
P-8	219.67	225.96	224.48	228.01	225.85	224.65
P-10	225.95	233.09	231.99	236.04	233.16	231.52
SB-2	214.46	216.81	214.78	216.97	216.71	218.10
SB-4	226.15	230.32	228.55	231.15	230.47	231.08
SB-6	233.44	238.86	237.51	240.69	239.32	239.19
SB-8	238.16	244.44	243.55	247.38	245.20	244.40
SB-10	240.97	248.33	247.90	252.42	249.39	247.97
MAE		4.19	3.41	6.54	4.79	4.24

TABLE XII: Alkyl Bond Dissociation Energies for the ABDE12 test set for functional shown in each column using 6-311++G(3df,3pd) basis set. All quantities are in kcal/mol.

Molecule	Expt	LC-TMLYP	CAM-B3LYP	HSE06	LC-wPBEh	LC-wPBE
C_2H_6	97.39	90.41	93.81	92.94	95.62	95.07
iPr-CH_3	95.00	85.57	88.35	86.79	89.98	90.25
C_2H_6O	89.79	82.77	85.67	83.02	86.01	87.11
iPr-OCH_3	91.51	82.11	84.39	80.66	84.22	86.20
Et-H	108.92	105.54	106.89	103.80	104.80	104.90
Et-CH_3	95.89	87.90	90.94	89.80	92.66	92.51
Et-OCH_3	95.26	83.47	86.04	82.93	86.10	87.60
Et-OH	100.29	93.41	96.49	93.69	96.82	97.61
tBu-H	103.86	100.10	100.94	97.28	98.59	99.33
tBu-CH_3	93.67	83.18	85.77	83.69	87.34	88.07
tBu-OCH_3	89.27	79.44	81.49	77.07	81.19	83.74
tBu-OH	115.02	92.92	95.55	91.59	95.47	97.17
MAE		9.08	6.63	9.38	6.42	5.52

TABLE XIII: Difficult Cases for the DC9/12 test set for functional shown in each column using 6-311++G(3df,3pd) basis set. All quantities are in kcal/mol.

Molecule	Expt	LC-TMLYP	CAM-B3LYP	HSE06	LC-wPBEh	LC-wPBE
$HCN...BF_3 \rightarrow HCN+BF_3$	5.70	5.01	4.91	3.83	4.33	4.34
$C_6Cl_6+6HCl \rightarrow 6Cl_2+C_6H_6$	148.30	144.97	141.91	144.80	153.28	160.61
$P_4 \rightarrow 4P$	289.90	256.60	271.77	283.76	285.53	272.48
$SF_6 \rightarrow S+6F$	477.50	463.46	472.76	453.70	474.63	485.38
$PF_5 \rightarrow P+5F$	556.40	545.51	552.07	528.06	543.83	555.82
$P_4O_{10} \rightarrow P_4+5O_2$	719.70	689.83	691.38	642.16	662.23	689.52
$C_6F_6 \rightarrow 6C+6F$	1388.10	1377.73	1402.08	1396.46	1427.31	1428.70
$Si(OCH_3)_4 \rightarrow Si+4C+4O+12H$	2023.50	2008.65	2026.92	1982.47	2012.26	2024.38
urotropin $\rightarrow$ 6C+4N+12H	2151.10	2127.14	2156.80	2134.04	2174.88	2178.84
MAE		15.69	9.53	23.07	17.54	15.44

TABLE XIV: Isomerization Energies for the IsoL6/11 test set for functional shown in each column using 6-311++G(3df,3pd) basis set. All quantities are in kcal/mol.

	Expt	LC-TMLYP	CAM-B3LYP	HSE06	LC-wPBEh	LC-wPBE
10-	6.82	3.17	3.09	5.31	6.11	6.24
13-	33.52	30.29	29.86	31.34	30.11	30.71
14-	5.30	3.19	3.75	5.14	4.54	5.13
20-	4.66	4.21	4.37	5.04	5.10	5.22
3-	9.77	9.67	10.47	10.27	11.21	11.97
9-	21.66	19.51	19.49	17.96	18.47	18.65
MAE		1.96	2.03	1.42	1.67	1.57

TABLE XV: Reaction Energies for the HC7/11 test set for functional shown in each columni using 6-311++G(3df,3pd) basis set. All quantities are in kcal/mol.

Reaction	Expt	LC-TMLYP	CAM-B3LYP	HSE06	LC-wPBEh	LC-wPBE
E22 - E1	14.34	11.42	10.73	20.58	31.36	41.38
E31 - E1	25.02	19.66	18.02	28.22	42.93	57.50
$(CH_3)_3CC(CH_3)_3 \rightarrow$ n-C_8H_18	1.90	-5.39	-4.94	-6.45	-3.73	-2.79
n-C_6H_14 + 4 $CH_4 \rightarrow 5C_2H_6$	9.81	5.60	5.89	5.15	5.96	6.15
n-C_8H_18 + 6 $CH_4 \rightarrow 7C_2H_6$	14.84	8.31	8.74	7.63	8.83	9.14
adamantane $\rightarrow$ 3 C_2H_4 + 2 C_2H_2	193.99	188.20	189.13	201.95	221.14	233.46
biclo[2.2.2]octane $\rightarrow$ 3 C_2H_4 + C_2H_2	127.22	121.71	122.06	131.04	145.21	154.63
MAE		5.37	5.35	5.92	13.65	20.07