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

Performance of a nonempirical exchange functional from the density matrix expansion: Comparative study with different correlation

February 2, 2017

Yuxiang Mo, Guocai Tian, and Jianmin Tao

Supplemental Material

CONTENTS

Table S1: 148 G2 standard enthalpies of formation $\Delta_f H^{o}_{298}$ (ZPE-corrected) of the TMTPSS functional evaluated self-consistently using the modified Gaussian 09 with the 6-311++G(3*df*, 3*pd*) basis set. Experimental values are from Ref. [S1]. All values are in kcal/mol.

Molecule	Name	Expt.	TMTPSS
$AlCl_3$	Aluminum trichloride	-139.7	-135.3
AlF_3	Aluminum trifluoride	-289.0	-272.6
BCl_3	Boron trichloride	-96.3	-95.9
BF_3	Boron trifluoride	-271.4	-261.9
BeH	Beryllium monohydride	81.7	72.0
CCl_4	Tetrachloromethane	-22.9	-26.4
CF_4	Tetrafluoromethane	-223.0	-224.2
CH	Methylidyne radical	142.5	139.1
CH_2Cl_2	Dichloromethane	-22.8	-26.7
CH_2F_2	Difluoromethane	-107.7	-112.0
CH_2O_2	Formic acid	-90.5	-90.4
CH_2O	Formaldehyde	-26.0	-28.7
CH_2	Singlet carbene	102.8	102.6
CH_2	Triplet carbene	93.7	87.7
CH_3Cl	Chloromethane	-19.6	-23.5
CH_3	Methyl radical	35.0	30.0
CH_3O	Hydroxymethyl radical	-4.1	-7.0
CH_3O	Methoxy radical	4.1	-3.4
CH_3S	Methylthio radical	29.8	24.9
CH_4	Methane	-17.9	-21.0
CH_4O	Methanol	-48.0	-48.5
CH_4S	Thiomethanol	-5.5	-9.3
$CHCl_3$	Trichloromethane	-24.7	-28.3
CHF_3	Trifluoromethane	-166.6	-169.5
CHO	Formyl radical	10.0	5.0
CN	Cyano radical	104.9	101.2
CNH	Hydrogen cyanide	31.5	28.4
CNH_3O_2	Methyl nitrite	-15.9	-32.8
CNH_3O_2	Nitromethane	-17.8	-34.5
CNH_5	Methylamine	-5.5	-9.8
C_2Cl_4	Tetrachloroethylene	-3.0	-9.4
C_2F_4	Tetrafluoroethylene	-157.4	-167.6
C_2H	Ethynyl radical	135.1	135.8
C_2H_2	Acetylene	54.2	55.3
$C_2H_2O_2$	Glyoxal	-50.7	-53.5
C_2H_2O	Ketene	-11.4	-16.3
C_2H_3Cl	Vinyl chloride	8.9	1.5
C_2H_3	Vinyl radical	71.6	65.5
C_2H_3F	Vinyl fluoride	-33.2	-38.2
C_2H_3O	Carbonyl methane	-2.4	-8.6
C_2H_3OCl	Acetyl chloride	-58.0	-62.9
C_2H_3OF	Acetyl fluoride	-105.7	-108.7

C_2H_4	Ethylene	12.5	9.6
$C_2H_4O_2$	Acetic acid	-103.4	-103.0
$C_2H_4O_2$	Methyl formate	-85.0	-91.3
C_2H_4O	Acetaldehyde	-39.7	-42.9
C_2H_4O	Oxirane	-12.6	-21.0
C_2H_4S	Thiirane	19.6	11.3
C_2H_5Cl	Ethyl chloride	-26.8	-31.3
C_2H_5	Ethyl radical	28.9	22.6
C_2H_5O	Ethoxy radical	-3.7	-12.7
C_2H_6	Ethane	-20.1	-24.1
C_2H_6O	Dimethyl ether	-44.0	-50.1
C_2H_6O	Ethanol	-56.2	-60.3
C_2H_6OS	Dimethyl sulfoxide	-36.2	-41.2
C_2H_6S	Dimethyl sulfide	-8.9	-14.6
C_2H_6S	Thioethanol	-11.1	-18.8
C_2N_2	Cyanogen	73.3	66.0
C_2NF_3	Trifluoroacetonitril	-118.4	-123.8
C_2NH_3	Acetonitrile	18.0	13.4
C_2NH_5	Aziridine	30.2	19.8
C_2NH_5O	Acetamide	-57.0	-61.0
C_2NH_7	Dimethylamine	-4.4	-11.8
C_2NH_7	Ethylamine	-11.3	-17.7
C_3H_4	Allene	45.5	40.4
C_3H_4	Cyclopropene	66.2	61.7
C_3H_4	Propyne	44.2	43.5
C_3H_6	Cyclopropane	12.7	6.1
C_3H_6O	Acetone	-51.9	-55.2
C_3H_6	Propene	4.8	1.1
C_3H_7Cl	1-Chloropropane	-31.5	-36.6
C_3H_7	Isopropyl radical	21.5	14.2
C_3H_8O	Methoxyethane	-51.7	-58.5
C_3H_8O	Isopropyl alcohol	-65.2	-66.2
C_3H_8	Propane	-25.0	-29.5
C_3NH_3	Acrylonitrile	43.2	39.6
C_3NH_9	Trimethylamine	-5.7	-16.5
C_4H_{10}	Isobutane	-32.1	-36.5
C_4H_{10}	n-Butane	-30.0	-34.9
C_4H_4O	Furan	-8.3	-13.9
C_4H_4S	Thiophene	27.5	22.8
C_4H_6	1,3-Butadiene	26.3	22.2
C_4H_6	2-Butyne	34.8	33.2
C_4H_6	Bicyclo[S1.1.0]butane	51.9	43.5
C_4H_6	Cyclobutene	37.4	33.1
C_4H_6	Methylenecyclopropane	47.9	38.5
C_4H_8	Cyclobutane	6.8	0.6
C_4H_8	Isobutene	-4.0	-7.8
C_4H_9	tert-Butyl radical	12.3	5.1

C_4NH_5	Pyrrole	25.9	18.4
C_5H_8	Spiropentane	44.3	33.7
C_5NH_5	Pyridine	33.6	24.0
C_6H_6	Benzene	19.7	15.7
Cl_2	Dichlorine	0.0	-2.2
CO	Carbon monoxide	-26.4	-23.4
CO_2	Carbon dioxide	-94.1	-96.1
COF_2	Carbonyl fluoride	-152.7	-147.4
COS	Carbonyl sulfide	-33.1	-38.8
CS	Carbon monosulfide	66.9	68.0
CS_2	Carbon disulfide	28.0	20.4
FCl	Chlorine monofluoride	-13.2	-17.4
F_2	Difluorine	0.0	-6.0
F_3Cl	Chlorine trifluoride	-38.0	-58.2
HCl	Hydrogen chloride	-22.1	-21.6
HF	Hydrogen fluoride	-65.1	-60.9
HOCl	Hypochlorous acid	-17.8	-19.0
HO	Hydroxyl radical	9.4	9.1
HS	Mercapto radical	34.2	31.7
H_2	Dihydrogen	0.0	-2.4
H_2O_2	Hydrogen peroxide	-32.5	-31.7
H_2O	Water	-57.8	-51.9
H_2S	Hydrogen sulfide	-4.9	-6.8
LiF	Lithium fluoride	-80.1	-76.3
LiH	Lithium hydride	33.3	32.2
Li_2	Dilithium	51.6	54.0
Na_2	Disodium	34.0	33.5
NaCl	Sodium chloride	-43.6	-40.4
NF_3	Trifluoroamine	-31.6	-52.3
NH_2	Amino radical	45.1	38.5
NH_3	Ammonia	-11.0	-12.0
NH	Imidogen	85.2	78.0
NO_2	Nitrogen dioxide	7.9	-10.1
NOCl	Nitrosyl chloride	12.4	-3.2
NO	Nitric oxide	21.6	14.0
N_2	Dinitrogen	0.0	-4.6
N_2H_4	Hydrazine	22.8	17.0
N_2O	Nitrous oxide	19.6	3.1
OCl	Monochlorine monoxide	24.2	16.6
OF_2	Difluorine monoxide	5.9	-8.8
OS	Sulfur monoxide	1.2	-3.9
O_2	Dioxygen	0.0	-8.5
O_2S	Sulfur dioxide	-71.0	-69.9
O_3	Ozone	34.1	21.6
P_2	Diphosphorus	34.3	32.3
PF_3	Phosphorus trifluoride	-229.1	-223.9
PH_2	Phosphino radical	33.1	23.9

PH_3	Phosphane	1.3	-6.9
S_2	Disulfur	30.7	23.7
$SiCH_6$	Methylsilane	-7.0	-15.0
$SiCl_4$	Silicon tetrachloride	-158.4	-152.2
SiF_4	Silicon tetrafluoride	-386.0	-362.6
SiH_2	Singlet silylene	65.2	59.7
SiH_2	Triplet silylene	86.2	77.2
SiH_3	Silyl radical	47.9	37.2
SiH_4	Silane	8.2	-2.8
SiO	Silicon monoxide	-24.6	-18.5
Si_2H_6	Disilane	-12.2	2.5
Si_2	Disilicon	139.9	138.4

Table S2: 75 G3 subset standard enthalpies of formation $\Delta_f H^{\circ}_{298}$ (ZPE-corrected) of the TMTPSS functional evaluated self-consistently using modified Gaussian 09 with the 6-311++G(3*df*, 3*pd*) basis set. Experimental values are from Ref. [S1]. All values are in kcal/mol.

Molecule	Name	Expt.	TMTPSS
C_4H_6	Methyl allene	38.8	33.4
C_5H_8	Isoprene	18.0	14.2
C_5H_{10}	Cyclopentane	-18.3	-21.6
C_5H_{12}	*n*-Pentane	-35.1	-40.1
C_5H_{12}	Neo pentane	-40.2	-43.9
C_6H_8	1,3 Cyclohexadiene	25.4	23.8
C_6H_8	1,4 Cyclohexadiene	25.0	24.6
C_6H_{12}	Cyclohexane	-29.5	-31.9
C_6H_{14}	*n*-Hexane	-39.9	-45.5
C_6H_{14}	3-Methyl pentane	-41.1	-45.3
$C_6H_5CH_3$	Toluene	12.0	8.0
C_7H_{16}	*n*-Heptane	-44.9	-50.7
C_8H_8	Cyclooctatetraene	70.7	70.6
C_8H_{18}	*n*-Octane	-49.9	-56.0
$C_{10}H_8$	Naphthalene	35.9	31.2
$C_{10}H_8$	Azulene	69.1	62.0
CH_3COOCH_3	Acetic acid methyl ester	-98.4	-103.4
$(CH_3)_3COH$	*t*-Butanol	-74.7	-75.3
$C_6H_5NH_2$	Aniline	20.8	14.8
C_6H_5OH	Phenol	-23.0	-23.9
C_4H_6O	Divinyl ether	-3.3	-8.9
C_4H_8O	Tetrahydrofuran	-44.0	-48.7
C_5H_8O	Cyclopentanone	-45.9	-49.3
$C_6H_4O_2$	Benzoquinone	-29.4	-31.0
$C_4H_4N_2$	Pyrimidine	46.8	30.6
$C_2H_6O_2S$	Dimethyl sulphone	-89.2	-89.3
C_6H_5Cl	Chlorobenzene	12.4	7.7
$NC\text{-}CH_2\text{-}CH_2\text{-}CN$	Butanedinitrile	46.9	34.3
$C_4H_4N_2$	Pyrazine	50.1	44.5

CH_3-C(=O)-CCH	Acetyl acetylene	15.6	16.7
CH_3-CH=CH-CHO	Crotonaldehyde	-24.0	-29.8
CH_3-C(=O)-O-C(=O)-CH_3	Acetic anhydride	-136.8	-141.8
C_4H_6S	2,5-Dihydrothiophene	20.8	16.5
$(CH_3)_2$CH-CN	Isobutane nitrile	5.6	8.4
CH_3-CO-CH_2-CH_3	Methyl ethyl ketone	-57.1	-61.5
$(CH_3)_2$CH-CHO	Isobutanal	-51.6	-54.4
$C_4H_8O_2$	1,4-Dioxane	-75.5	-81.7
C_4H_8S	Tetrahydrothiophene	-8.2	-12.4
$(CH_3)_3$C-Cl	*t*-Butyl chloride	-43.5	-48.4
CH_3-CH_2-CH_2-CH_2-Cl	*n*-Butyl chloride	-37.0	-41.9
C_4H_8NH	Tetrahydropyrrole	-0.8	-7.8
CH_3-CH_2-CH(CH_3)-NO_2	Nitro-*s*-butane	-39.1	-55.5
CH_3-CH_2-O-CH_2-CH_3	Diethyl ether	-60.3	-66.7
CH_3-CH(OCH_3)$_2$	Dimethyl acetal	-93.1	-100.5
$(CH_3)_3$C-SH	*t*-Butanethiol	-26.2	-30.6
CH_3-CH_2-S-S-CH_2-CH_3	Diethyl disulfide	-17.9	-25.3
$(CH_3)_3$C-NH_2	*t*-Butylamine	-28.9	-33.6
Si(CH_3)$_4$	Tetramethylsilane	-55.7	-53.6
C_5H_6S	2-Methyl thiophene	20.0	15.1
cyc-C_4H_4N-CH_3	*n*-methyl pyrrole	24.6	14.7
$C_5H_{10}O$	Tetrahydropyran	-53.4	-57.5
CH_3-CH_2-CO-CH_2-CH_3	Diethyl ketone	-61.6	-66.2
CH_3-C(=O)-O-CH(CH_3)$_2$	Isopropyl acetate	-115.1	-120.0
$C_5H_{10}S$	Tetrahydrothiopyran	-15.2	-18.8
cyc-C_5H_{10}NH	Piperidine	-11.3	-16.8
$(CH_3)_3$C-O-CH_3	*t*-Butyl methyl ether	-67.8	-73.2
$C_6H_4F_2$	1,3-Difluorobenzene	-73.9	-80.3
$C_6H_4F_2$	1,4-Difluorobenzene	-73.3	-79.6
C_6H_5F	Fluorobenzene	-27.7	-32.7
$(CH_3)_2$CH-O-CH(CH_3)$_2$	Di-isopropyl ether	-76.3	-82.1
PF_5	Phosphorus pentafluoride	-381.0	-368.2
SF_6	Sulfur hexafluoride	-291.7	-294.0
P_4	Tetraphosphorus	14.1	-1.7
SO_3	Sulfite	-94.6	-93.5
SCl_2	Sulfur dichloride	-4.2	-9.1
$POCl_3$	Phosphoryl chloride	-133.8	-133.1
PCl_5	Phosphorus pentachloride	-86.1	-94.9
Cl_2O_2S	Sulfuryl chloride	-84.8	-86.5
PCl_3	Phosphorus trichloride	-69.0	-73.4
Cl_2S_2	Disulfur dichloride	-4.0	-16.2
$SiCl_2$	Singlet dichlorosilylene	-40.3	-39.1
CF_3Cl	Chlorotrifluoromethane	-169.5	-173.2
C_2F_6	Hexafluoroethane	-321.3	-324.6
CF_3	Trifluoromethyl	-111.3	-118.3
C_6H_5	Phenyl radical	81.2	73.1

Table S3: W4-08 atomization energies of the TMTPSS functional evaluated self-consistently using modified Gaussian 09 with the 6-311++G(3*df*, 3*pd*) basis set. The reference values are from high-level calculations [S2]. All values are in kcal/mol.

Molecule	Ref.	TMTPSS	Molecule	Ref.	TMTPSS	Molecule	Ref.	TMTPSS
B_2H_6	607.02	621.10	OH	107.21	106.75	BF	182.52	177.88
BHF_2	410.97	407.59	HF	141.64	136.87	NH	83.10	90.75
BF_3	470.97	460.82	H_2O	232.97	226.76	NH_2	182.59	188.39
C_2H_6	713.08	716.23	CH	84.22	87.31	HCN	313.42	315.90
H_2CN	343.75	352.85	CH_2	190.74	181.07	HOF	158.65	161.64
NCCN	502.04	509.72	CH_3	307.87	312.43	AlH	73.57	73.93
CH_2NH_2	482.28	489.25	CH_4	420.42	423.25	AlH_3	213.17	219.19
CH_3NH	474.63	484.36	C_2H	266.16	264.83	AlF	163.78	156.75
CH_3NH_2	582.30	586.49	C_2H_2	405.52	404.44	AlCl	122.62	117.83
CF_2	258.78	261.17	NH_3	298.02	299.01	SiH	73.92	76.35
N_2H	224.86	236.97	C_2	147.02	128.24	SiH_4	324.95	332.93
N_2H_2	296.53	305.22	N_2	228.48	233.09	SiO	193.05	186.24
N_2H_4	438.28	444.20	CO	259.73	256.25	SiF	142.71	139.75
FO_2	134.72	153.81	CN	181.35	185.15	CS	172.22	170.22
F_2O_2	152.37	180.64	NO	152.75	160.34	BN ($^3\Pi$)	105.82	114.12
AlF_3	430.97	410.50	O_2	120.82	128.94	CF	132.72	136.98
Si_2H_6	535.89	546.91	OF	53.08	62.97	BeF_2	309.10	303.68
P_4	290.58	305.55	F_2	39.04	44.75	CH_2C	359.93	360.80
SO_2	260.62	257.25	PH_3	242.27	250.08	CH_2CH	446.08	450.91
SO_3	346.94	342.43	HS	87.73	89.39	C_2H_4	564.10	566.43
OCS	335.75	339.26	H_2S	183.91	184.31	CH_2NH	439.44	444.78
CS_2	280.78	285.38	HCl	107.50	105.95	HCO	279.42	283.75
S_2O	208.78	209.97	SO	126.47	130.16	H_2CO	374.66	376.51
S_3	168.36	171.94	ClO	65.45	72.15	CO_2	390.14	391.33
S_4	234.35	240.57	ClF	62.80	65.57	HNO	205.89	211.53
$BeCl_2$	225.27	225.19	P_2	117.59	119.19	NO_2	227.88	245.48
CCl_2	177.36	181.36	S_2	104.25	108.66	N_2O	270.85	287.23
$AlCl_3$	312.65	301.84	Cl_2	59.75	60.20	O_3	147.43	159.70
ClCN	285.45	289.29	Be_2	2.67	6.52	HO_2	175.53	181.76
OClO	128.12	138.35	B_2	67.46	66.39	H_2O_2	269.09	268.12
ClOO	126.39	142.82	BH	84.99	84.23	F_2O	93.78	108.10
Cl_2O	101.46	107.54	BH_3	281.29	287.75	HOCl	166.23	165.63
H_2	109.49	112.01	BN ($^1\Sigma^+$)	105.24	97.94	S_2H	165.13	169.44

Table S4: 58 electron affinities (ZPE-corrected) of TMTPSS. Experimental values are from Ref. [S1]. Results of the TMTPSS functional were obtained self-consistently using modified Gaussian 09 with the 6-311++G(3*df*,3*pd*) basis set. All values are in eV.

Molecule	Expt.	TMTPSS
C (^{3}P) → C$^-$ (^{4}S)	1.26	1.35
O (^{3}P) → O$^-$ (^{2}P)	1.46	1.42
F (^{2}P) → F$^-$ (^{1}S)	3.40	3.24
Si (^{3}P) → Si$^-$ (^{4}S)	1.39	1.35
P (^{4}S) → P$^-$ (^{3}P)	0.75	0.84
S (^{3}P) → S$^-$ (^{2}P)	2.08	2.06
Cl (^{2}P) → Cl$^-$ (^{1}S)	3.61	3.52
CH ($^2\Pi$) → CH$^-$ ($^3\Sigma^-$)	1.24	1.31
CH_2 ($^3B_1$) → CH_2^- ($^2B_1$)	0.65	0.58
CH_3 ($^2A_2''$) → CH_3^- ($^1A_1$, C_{3v})	0.08	-0.07
NH ($^3\Sigma^-$) → NH$^-$ ($^2\Pi$)	0.37	0.22
NH_2 ($^2B_1$) → NH_2^- ($^1A_1$, C_{2v})	0.77	0.51
OH ($^2\Pi$) → OH$^-$ ($^1\Sigma^+$)	1.83	1.56
SiH ($^2\Pi$) → SiH$^-$ ($^3\Sigma^-$)	1.28	1.28
SiH_2 ($^1A_1$) → SiH_2^- ($^2B_1$, C_{2v})	1.12	1.19
SiH_3 ($^2A_1$) → SiH_3^- ($^1A_1$, C_{3v})	1.41	1.32
PH ($^3\Sigma^-$) → PH$^-$ ($^2\Pi$)	1.03	0.97
PH_2 ($^2B_1$) → PH_2^- ($^1A_1$, C_{2v})	1.27	1.14
SH ($^2\Pi$) → SH$^-$ ($^1\Sigma^+$)	2.31	2.19
O_2 ($^3\Sigma_g^-$) → O_2^- ($^2\Pi_g$)	0.45	0.34
NO ($^2\Pi$) → NO$^-$ ($^3\Sigma^-$)	0.03	0.12
CN ($^2\Sigma^+$) → CN$^-$ ($^1\Sigma^+$)	3.86	3.72
PO ($^2\Pi$) → PO$^-$ ($^3\Sigma^-$)	1.09	1.14
S_2 ($^3\Sigma_g^-$) → S_2^- ($^2\Pi_g$)	1.67	1.52
Cl_2 ($^1\Sigma_g^+$) → Cl_2^- ($^2\Sigma_u^+$)	2.38	2.62
Li (^{2}S) → Li$^-$ (^{1}S)	0.62	0.57
B (^{2}P) → B$^-$ (^{3}P)	0.28	0.38
Na (^{2}S) → Na$^-$ (^{1}S)	0.55	0.56
Al (^{2}P) → Al$^-$ (^{3}P)	0.44	0.42
C_2 ($^1\Sigma_g^+$) → C_2^- ($^2\Sigma_g^+$)	3.27	4.08
C=C=O ($^3\Sigma^-$) → C=C=O$^-$ ($^2\Pi$, $C_{\infty v}$)	2.29	2.08
CF_2 ($^1A_1$) → CF_2^- ($^2B_1$, C_{2v})	0.17	0.35
NCO ($^2\Pi$) → NCO$^-$ ($^1\Sigma^+$, $C_{\infty v}$)	3.61	3.27
NO_2 ($^2A_1$) → NO_2^- ($^1A_1$, C_{2v})	2.27	1.94
O_3 ($^1A_1$) → O_3^- ($^2B_1$, C_{2v})	2.10	2.23

OF ($^2\Pi$) → OF^- ($^1\Sigma^-$)	2.27	2.00
SO_2 ($^1A_1$) → SO_2^- ($^2B_1$, C_{2v})	1.11	1.21
S_2O ($^1A'$) → S_2O^- ($^2A''$, C_s)	1.88	1.92
HC≡C ($^2\Sigma^+$) → HC≡C^- ($^1\Sigma^+$, $C_{\infty v}$)	2.97	2.90
CH_2=CH ($^2A'$) → CH_2=CH^- ($^1A'$, C_s)	0.67	0.55
CH_2=C=C ($^1A_1$) → CH_2=C=C^- ($^2B_1$, C_{2v})	1.79	1.81
CH_2=C=CH ($^2A'$) → CH_2=C=CH^- ($^1A'$, C_s)	0.89	0.83
CH_2=$CHCH_2$ ($^2A_2$) → CH_2=$CHCH_2^-$ ($^1A_1$, C_{2v})	0.48	0.37
HC=O ($^2A'$) → HC=O^- ($^1A'$, C_s)	0.31	0.24
CHF ($^1A'$) → CHF^- ($^2A''$, C_s)	0.54	0.71
CH_3O ($^2A'$) → CH_3O^- ($^1A'$, C_s)	1.57	1.39
CH_3S ($^2A'$) → CH_3S^- ($^1A'$, C_{3v})	1.87	1.70
CH_2S ($^1A_1$) → CH_2S^- ($^2A'$, C_s)	0.47	0.56
CH_2CN ($^2B_1$) → CH_2CN^- ($^1A'$, C_s)	1.54	1.37
CH_2NC ($^2B_1$) → CH_2NC^- ($^1A'$, C_s)	1.06	1.01
HC≡CO ($^2A''$) → HC≡CO^- ($^1A'$, C_s)	2.35	2.06
CH_2CHO ($^2A''$) → CH_2CHO^- ($^1A'$, C_s)	1.82	1.68
CH_3CO ($^2A'$) → CH_3CO^- ($^1A'$, C_s)	0.42	0.34
CH_3CH_2O ($^2A''$) → $CH_3CH_2O^-$ ($^1A'$, C_s)	1.71	1.53
CH_3CH_2S ($^2A''$) → $CH_3CH_2S^-$ ($^1A'$, C_s)	1.95	1.79
LiH ($^1\Sigma^+$) → LiH^- ($^2\Sigma^+$)	0.34	0.40
HNO ($^1A'$) → HNO^- ($^2A''$, C_s)	0.34	0.48
HOO ($^2A''$) → HOO^- ($^1A'$, C_s)	1.08	0.75

Table S5. Proton affinities (ZPE-corrected) for the G3/99 (8 species) test set evaluated with TMTPSS using the 6-311++G(3*df*,3*pd*) basis set. Experimental values are from Ref. [S1]. All values are in kcal/mol.

Molecule	Expt.	TMTPSS
NH_3	202.5	203.5
H_2O	165.1	163.8
C_2H_2	152.3	157.2
SiH_4	154.0	155.0
PH_3	187.1	189.1
H_2S	168.8	171.0
HCl	133.6	135.8
H_2	100.8	100.9

Table S6. Equilibrium bond lengths (r_e) in Å for the T-96R (96 diatomic molecules) test set computed with the M06L and TMTPSS functionals using the 6-311++G(3*df*,3*pd*) basis set. Experimental values are from Ref. [S1].

Molecule	Expt.	M06L	TMTPSS	Molecule	Expt.	M06L	TMTP	Molecule	Expt.	M06L	TMTP
H_2	0.741	0.744	0.743	CS	1.535	1.535	1.543	AlCl	2.130	2.137	2.153
Li_2	2.673	2.657	2.733	CS_2	1.553	1.550	1.560	AlO	1.618	1.625	1.634
LiH	1.595	1.594	1.597	N_2	1.098	1.097	1.101	AlS	2.029	2.021	2.043
LiF	1.564	1.571	1.582	N_2^+	1.116	1.109	1.114	Si_2	2.246	2.146	2.271
LiCl	2.021	2.025	2.027	NH	1.036	1.046	1.045	SiH	1.520	1.520	1.531
LiO	1.688	1.692	1.704	NH^+	1.070	1.084	1.083	SiH_4	1.480	1.475	1.482
Be_2	2.440	2.503	2.444	NF	1.317	1.311	1.329	SiF	1.601	1.621	1.635
BeH	1.343	1.339	1.352	NCl	1.611	1.604	1.623	SiF_4	1.553	1.562	1.578
BeF	1.361	1.365	1.373	NO	1.151	1.148	1.157	SiCl	2.058	2.061	2.081
BeO	1.331	1.318	1.335	NO^+	1.063	1.062	1.067	$SiCl_4$	2.019	2.015	2.032
BeS	1.742	1.728	1.746	NS	1.494	1.492	1.503	SiN	1.572	1.563	1.576
B_2	1.590	1.608	1.620	O_2	1.208	1.205	1.218	SiO	1.510	1.512	1.525
BH	1.232	1.226	1.237	O_2^+	1.116	1.109	1.120	SiS	1.929	1.932	1.944
BF	1.263	1.257	1.270	OH	0.970	0.971	0.982	P_2	1.893	1.885	1.896
BF_3	1.313	1.306	1.319	OH^+	1.029	1.032	1.039	P_4	2.210	2.179	2.201
BCl	1.715	1.715	1.726	OF	1.358	1.343	1.363	PH	1.421	1.421	1.430
BCl_3	1.742	1.734	1.745	F_2	1.412	1.404	1.415	PF	1.589	1.605	1.620
BN	1.281	1.316	1.330	F_2^+	1.322	1.293	1.315	PCl	2.015	2.006	2.030
BO	1.204	1.201	1.212	HF	0.917	0.917	0.930	PN	1.491	1.486	1.494
BS	1.609	1.608	1.619	HF^+	1.001	1.007	1.019	PO	1.476	1.478	1.491
C_2	1.242	1.251	1.255	Na_2	3.079	3.064	3.099	S_2	1.889	1.890	1.908
CH	1.120	1.125	1.130	NaH	1.887	1.899	1.891	SH	1.341	1.340	1.350
CH_4	1.087	1.085	1.092	NaF	1.926	1.932	1.944	SF	1.601	1.609	1.627
CF	1.272	1.270	1.286	NaCl	2.361	2.374	2.375	SF_6	1.561	1.568	1.591
CF_4	1.323	1.318	1.333	NaO	2.052	2.057	2.071	SO	1.481	1.487	1.502
CCl	1.645	1.645	1.663	MgH	1.730	1.738	1.746	SO_3	1.420	1.422	1.440
CCl_4	1.767	1.767	1.778	MgF	1.750	1.762	1.779	Cl_2	1.988	1.974	2.009
CN	1.172	1.164	1.173	MgCl	2.196	2.203	2.220	Cl_2^+	1.891	1.882	1.913
CO	1.128	1.128	1.134	MgO	1.748	1.734	1.749	HCl	1.275	1.275	1.285
CO^+	1.115	1.111	1.120	Al_2	2.466	2.442	2.478	HCl^+	1.315	1.317	1.326
CO_2	1.160	1.159	1.169	AlH	1.648	1.647	1.660	ClF	1.628	1.636	1.656
CP	1.562	1.550	1.562	AlF	1.654	1.673	1.686	ClO	1.570	1.565	1.589

Table S7. Harmonic vibrational frequencies (ω_e) in cm^{-1} of the T-82F (82 diatomic molecules) test set computed with the M06L and TMTPSS functionals using the 6-311++G(3*df*,3*pd*) basis set. Experimental values are from Ref. [S1].

Molecule	Expt.	M06L	TMTPSS	Molecule	Expt.	M06L	TMTPSS
H_2	4401.2	4386.3	4403.1	F_2	916.6	997.7	988.2
Li_2	351.4	334.8	335.5	F_2^+	1073.3	1164.7	1153.6
LiH	1405.7	1400.2	1405.4	HF	4138.3	3993.1	3981.3
LiF	910.6	890.1	888.7	HF^+	3090.5	2947.1	2942.4
LiCl	643.0	635.9	633.9	Na_2	159.1	156.9	155.6
LiO	814.6	794.4	793.5	NaH	1172.2	1153.5	1156.4
LiNa	256.8	248.5	246.8	NaF	535.7	519.5	518.8
Be_2	267.9	337.1	315.1	NaO	492.3	471.4	471.2
BeH	2060.8	2022.6	2020.1	MgH	1495.2	1449.2	1455.4
BeH^+	2221.7	2188.9	2206.1	MgH^+	1699.1	1699.1	1710.9
BeF	1247.4	1226.1	1222.3	MgO	784.8	805.4	802.1
BeCl	846.7	833.0	827.0	MgS	528.7	535.5	532.4
BeO	1487.3	1492.3	1491.5	Al_2	350.0	352.4	346.9
BeS	997.9	996.1	993.9	AlH	1682.6	1638.6	1658.9
B_2	1051.3	1019.9	1008.9	AlF	802.3	750.5	750.8
BH	2366.9	2313.4	2350.0	AlCl	481.3	466.9	465.4
BF	1402.1	1368.6	1366.9	AlO	979.2	954.0	950.0
BCl	840.3	824.3	822.1	AlS	617.1	611.4	607.7
BN	1514.6	1532.0	1525.0	Si_2	511.0	550.8	499.5
BO	1885.7	1867.2	1858.2	SiH	2041.8	2003.3	2013.1
BS	1180.2	1171.2	1163.7	SiH^+	2157.2	2105.0	2128.4
C_2	1854.7	1850.9	1840.0	SiF	857.2	799.7	797.8
CH	2858.5	2792.7	2794.3	SiCl	535.6	520.4	515.5
CF	1308.1	1258.1	1248.1	SiN	1151.4	1161.3	1158.8
CN	2068.6	2097.6	2092.7	SiO	1241.5	1209.8	1209.9
CO	2169.8	2151.4	2149.6	SiS	749.6	738.0	737.2
CO^+	2214.2	2224.4	2215.7	P_2	780.8	799.8	799.2
CP	1239.7	1265.3	1261.3	P_2^+	672.2	690.3	689.5
CS	1285.2	1281.4	1280.4	PH	2365.2	2349.5	2347.5
N_2	2358.6	2371.4	2370.2	PF	846.8	804.3	799.5
N_2^+	2207.0	2269.9	2264.1	PCl	551.4	546.3	539.0
NH	3282.3	3250.0	3237.5	PN	1337.2	1364.2	1363.6
NF	1141.4	1137.3	1123.1	PO	1233.3	1214.4	1211.4
NCl	828.0	839.8	825.7	S_2	725.6	715.7	709.5
NO	1904.2	1911.2	1903.4	SO	1149.2	1124.0	1116.3
NO^+	2376.4	2395.9	2393.6	Cl_2	559.7	547.9	539.2
NS	1218.7	1229.7	1224.2	Cl_2^+	645.6	635.6	627.1
O_2	1580.2	1583.7	1570.7	HCl	2990.9	2929.3	2920.9
O_2^+	1904.8	1967.6	1958.3	HCl^+	2673.7	2617.6	2615.4
OH	3737.8	3623.8	3610.8	ClF	786.1	766.4	758.2
OH^+	3113.4	3034.2	3028.6	ClO	853.8	859.5	847.2

Table S8. Bond lengths (Å) and ZPE-corrected dissociation energies D_0 (kcal/mol) of 10 hydrogen-bonded complexes. The 6-311++G(3*df*,3*pd*) basis set was used in the calculations of both the geometry and ZPE. BSSE corrections are not included in the calculations. Illustration of hydrogen bonds is available in Fig. 1 of Ref. [S3]. MP2 values are from Ref. [S1].

	MP2	M06L	TMTPSS
HF/HF			
D_0	3.0	2.9	3.0
r(F....F)	2.731	2.714	2.743
HCl/HCl			
D_0	1.5	0.9	0.9
r(Cl....Cl)	3.742	3.666	3.783
H_2O/H_2O			
D_0	3.2	2.8	2.8
r(O....O)	2.895	2.906	2.936
HF/HCN			
D_0	6.2	5.6	5.4
r(H....N)	1.814	1.831	1.843
HF/H_2O			
D_0	6.4	6.2	6.2
r(F....O)	2.635	2.647	2.667
CN^-/H_2O			
D_0	14.7	14.3	14.0
r(N....H)	1.767	1.807	1.814
OH^-/H_2O'			
D_0	28.2	27.7	27.3
r(O....H)	1.344	1.225	1.448
r(O'-H)	1.117	1.225	1.093
HCC^-/H_2O			
D_0	17.7	16.6	16.8
r(C....H)	1.818	1.883	1.876
H_3O^+/H_2O			
D_0	34.2	34.1	33.2
r(H....O)	1.192	1.202	1.216
NH_4^+/H_2O			
D_0	19.3	19.5	18.5
r(H....O)	1.629	1.630	1.667

References:

[S1] V. N. Staroverov, G. E. Scuseria, J. Tao, and J. P. Perdew, J. Chem. Phys. **119**, 12129 (2003).

[S2] A. Karton, A. Tarnopolsky, J.-F. Lamère, G.C. Schatz, and J. M. L. Martin, J. Phys. Chem. A **112**, 12868 (2008).

[S3] A. D. Rabuck and G. E. Scuseria, Theor. Chem. Acc. **104**, 439 (2000).