Supplementary material to: Long-range corrected hybrid meta-generalized-gradient approximations with dispersion corrections

You-Sheng Lin,[1] Chen-Wei Tsai,[1] Guan-De Li,[1] and Jeng-Da Chai[1,2,*]

[1] *Department of Physics, National Taiwan University, Taipei 10617, Taiwan*

[2] *Center for Theoretical Sciences and Center for Quantum Science and Engineering, National Taiwan University, Taipei 10617, Taiwan*

* Author to whom correspondence should be addressed. Electronic mail: jdchai@phys.ntu.edu.tw.

TABLE S1: -$\epsilon_N(N)$ (in eV) of IP131 database. Most experimental reference values are collected from the NIST database, [1] while other publications [2–14] are adopted for the molecules marked.

Molecule	Reference	ωM05-D	M05-2X	ωB97X-D
H (Hydrogen atom)	13.60	11.10	10.44	11.04
He (Helium atom)	24.59	20.75	20.75	20.18
Li (Lithium atom)	5.39	5.06	4.19	5.22
Be (Beryllium atom) [2]	9.32	8.19	7.29	8.27
B (Boron atom)	8.30	7.21	6.39	7.24
C (Carbon atom)	11.26	9.74	9.11	9.57
N (Nitrogen atom)	14.53	12.46	12.02	12.13
O (Oxygen atom)	13.62	11.80	11.51	11.48
F (Fluorine atom)	17.42	15.15	15.10	14.63
Ne (Neon atom)	21.57	18.77	18.93	18.06
Na (Sodium atom)	5.14	4.92	4.08	4.87
Mg (Magnesium atom)	7.65	7.15	6.36	7.07
Al (Aluminum atom)	5.99	5.33	4.43	5.47
Si (Silicon atom)	8.15	7.29	6.42	7.29
P (Phosphorus atom)	10.49	9.33	8.51	9.25
S (Sulfur atom)	10.36	9.33	8.65	9.30
Cl (Chlorine atom)	12.97	11.70	11.12	11.56
Ar (Argon atom)	15.76	14.17	13.68	13.93
CH_3 (Methyl radical)	9.84	8.79	7.92	8.60
CH_4 (Methane)	13.60	13.16	12.59	12.97
NH (Imidogen) ($^3\Sigma^-$)	13.49	11.97	11.51	11.64
NH_2 (Amino radical)	12.00	10.99	10.47	10.74
NH_3 (Ammonia)	10.82	10.01	9.41	9.74
OH (Hydroxyl radical)	13.02	11.64	11.32	11.26
H_2O (Water) [3]	12.62	11.51	11.10	11.10
HF (Hydrogen fluoride)	16.12	14.42	14.28	13.90

SiH_3 (Silyl)	8.74	8.19	7.32	8.16
SiH_4 (Silane)	12.30	11.86	11.18	11.80
PH_3 (Phosphine)	10.59	9.79	9.03	9.76
H_2S (Hydrogen sulfide)	10.50	9.57	8.84	9.47
HCl (Hydrogen sulfide) [4]	12.77	11.64	11.02	11.45
C_2H_2 (Acetylene)	11.49	10.61	9.85	10.36
C_2H_4 (Ethylene)	10.68	10.01	9.17	9.74
C_2H_6 (Ethane)	11.99	11.70	11.15	11.59
HCN (Hydrogen cyanide)	13.61	12.62	11.97	12.35
CO (Carbon monoxide)	14.01	12.97	12.51	12.81
HCO (Formyl radical)	9.31	8.81	8.30	8.62
H_2CO (Formaldehyde)	10.89	10.09	9.60	9.82
CH_3OH (Methyl alcohol)	10.96	10.23	9.76	9.93
N_2 (Nitrogen diatomic)	15.58	14.58	14.25	14.28
N_2H_4 (Hydrazine)	8.98	9.03	8.46	8.79
NO (Nitric oxide)	9.26	8.70	8.35	8.35
O_2 (Oxygen diatomic) ($^3\Sigma_g$)	12.30	11.48	11.26	11.02
H_2O_2 (Hydrogen peroxide)	11.70	10.77	10.42	10.36
F_2 (Fluorine diatomic)	15.70	14.44	14.39	13.90
CO_2 (Carbon dioxide)	13.78	12.97	12.54	12.65
P_2 (Phosphorus diatomic)	10.62	9.93	9.14	9.90
S_2 (Sulfur diatomic) ($^3\Sigma_g$)	9.55	8.95	8.30	8.87
Cl_2 (Chlorine diatomic)	11.49	10.77	10.17	10.64
NaCl (Sodium Chloride)	9.80	8.60	7.94	8.40
SiO (Silicon monoxide) [5]	11.61	10.88	10.20	10.77
CS (Carbon monosulfide) [6]	11.34	10.99	10.42	10.91
ClO (Monochlorine monoxide)	11.01	10.12	9.71	9.90
ClF (Chlorine monofluoride)	12.77	11.67	11.18	11.45
Si_2H_6 (Disilane)	10.53	10.15	9.41	10.12
CH_3Cl (Methyl chloride)	11.29	10.61	9.98	10.42
CH_3SH (Methanethiol)	9.44	8.79	8.05	8.68

SO_2 (Sulfur dioxide)	12.50	11.78	11.29	11.59
BF_3 (Borane, trifluoro-)	15.96	14.82	14.72	14.28
BCl_3 (Borane, trichloro-)	11.64	11.18	10.58	11.02
$AlCl_3$ (Aluminum trichloride)	12.01	11.48	10.85	11.29
CF_4 (Carbon tetrafluoride)	16.20	15.23	15.15	14.69
CCl_4 (Carbon tetrachloride)	11.69	11.15	10.58	10.99
OCS (Carbonyl sulfide)	11.19	10.64	9.96	10.53
CS_2 (Carbon disulfide)	10.09	9.57	8.89	9.57
CF_2O (Carbonic difluoride)	13.60	12.78	12.43	12.38
SiF_4 (Silicon tetrafluoride)	16.40	15.37	15.26	14.85
N_2O (Nitrous oxide)	12.89	12.00	11.51	11.75
NF_3 (Nitrogen trifluoride)	13.60	12.62	12.35	12.32
PF_3 (Phosphorus trifluoride)	12.20	10.74	10.17	10.69
O_3 (Ozone)	12.73	12.35	11.91	11.97
F_2O (Difluorine monoxide)	13.26	12.51	12.40	12.02
ClF_3 (Chlorine trifluoride)	13.05	12.19	11.86	11.86
C_2F_4 (Tetrafluoroethylene)	10.69	9.93	9.41	9.71
CF_3CN (Acetonitrile, trifluoro-)	14.30	13.30	12.73	13.00
CH_3CCH (Propyne)	10.37	9.82	9.08	9.60
CH_2CCH_2 (Allene)	10.20	9.79	9.06	9.60
C_3H_4 (Cyclopropene)	9.86	9.33	8.60	9.11
C_3H_6 (Cyclopropane)	10.54	10.47	9.74	10.28
C_3H_8 (Propane)	11.51	11.21	10.66	11.10
CH_3CCCH_3 (2-Butyne)	9.79	9.19	8.46	8.98
C_4H_6 (Cyclobutene)	9.43	9.19	8.43	8.98
$CH_3CH(CH_3)CH_3$ (Isobutane)	11.13	10.99	10.42	10.85
C_6H_6 (Benzene)	9.25	9.28	8.49	9.06
CH_2F_2 (Methane, difluoro-)	13.27	12.27	11.97	11.97
CHF_3 (Methane, trifluoro-)	15.50	13.52	13.27	13.22
CH_2Cl_2 (Methylene chloride)	11.40	10.85	10.28	10.72
$CHCl_3$ (Chloroform)	11.50	10.85	10.28	10.72

CH_3NO_2 (Methane, nitro-)	11.29	11.12	10.77	10.72
CH_3SiH_3 (Methyl silane)	11.60	11.23	10.50	11.12
HCOOH (Formic acid)	11.50	10.69	10.23	10.36
CH_3CONH_2 (Acetamide)	10.00	9.66	9.17	9.36
C_2H_5N (Aziridine)	9.85	9.36	8.73	9.11
C_2N_2 (Cyanogen)	13.51	12.78	12.19	12.54
CH_3NHCH_3 (Dimethylamine)	8.95	8.60	7.97	8.38
CH_2CO (Ketene)	9.64	9.19	8.49	9.00
C_2H_4O (Ethylene oxide)	10.57	10.25	9.79	9.90
$C_2H_2O_2$ (Ethanedial)	10.60	10.12	9.63	9.87
CH_3CH_2OH (Ethanol)	10.64	10.09	9.63	9.79
CH_3OCH_3 (Dimethyl ether)	10.10	9.66	9.14	9.36
C_2H_4S (Thiirane)	9.05	8.57	7.86	8.46
CH_3SOCH_3 (Dimethyl sulfoxide)	9.10	8.76	8.16	8.57
CH_2CHF (Ethene, fluoro-)	10.63	9.90	9.17	9.66
CH_3CH_2Cl (Ethyl chloride)	11.06	10.44	9.85	10.28
CH_2CHCl (Ethene, chloro-)	10.20	9.60	8.87	9.41
CH_3COCl (Acetyl Chloride)	11.03	10.77	10.23	10.53
$CH_2ClCH_2CH_3$ (Propane, 1-chloro-)	10.88	10.42	9.76	10.25
$N(CH_3)_3$ (Trimethylamine)	8.54	8.27	7.62	8.05
C_4H_4O (Furan)	8.90	8.70	7.92	8.51
C_4H_5N (Pyrrole)	8.23	8.13	7.32	7.92
NO_2 (Nitrogen dioxide)	11.23	10.72	10.42	10.36
SF_6 (Sulfur Hexafluoride) [7]	15.70	14.96	14.91	14.42
$CFCl_3$ (Trichloromonofluoromethane)	11.76	11.23	10.66	11.07
CF_3Cl (Methane, chlorotrifluoro-)	13.08	12.27	11.75	12.05
CF_3Br (Bromotrifluoromethane) [8]	12.08	11.29	10.74	11.12
HCCF (Fluoroacetylene) [9]	11.50	10.53	9.85	10.28
HCCCN (Cyanoacetylene) [10]	11.75	11.07	10.42	10.85
C_4N_2 (2-Butynedinitrile) [13]	11.84	11.56	10.96	11.34
C_2N_2 (Cyanogen)	13.51	12.78	12.19	12.54

C_3O_2 (Carbon suboxide) [11]	10.80	10.39	9.82	10.23
FCN (Cyanogen fluoride) [12]	13.65	12.46	11.89	12.16
C_4H_2 (Diacetylene)	10.30	9.71	9.00	9.52
H_2CS (Thioformaldehyde)	9.38	8.73	8.02	8.62
$CHONH_2$ (Formamide) [12]	10.40	9.90	9.44	9.57
CH_2CHCHO (Acrolein) [14]	10.10	9.90	9.38	9.57
CH_2CCl_2 (Ethene, 1,1-dichloro-)	10.00	9.57	8.87	9.41
C_2HF_3 (Trifluoroethylene) [9]	10.62	9.74	9.14	9.52
CH_2CF_2 (Ethene, 1,1-difluoro-) [9]	10.70	10.01	9.33	9.76
CH_3F (Methyl fluoride)	13.04	12.21	11.86	11.91
CF_2Cl_2 (Difluorodichloromethane)	12.24	11.61	11.07	11.45
SiF_2 (Silicon difluoride)	11.08	10.25	9.52	10.23
MSE		-0.79	-1.34	-1.02
MAE		0.79	1.34	1.02
rms		0.96	1.43	1.18

TABLE S2: $-\epsilon_{N+1}(N+1)$ and $-\epsilon_{N+1}(N)$ (in eV) of EA115 database. Reference values are calculated by the CCSD(T) theory.

	reference	ωM05-D		M05-2X		ωB97X-D	
molecule		$-\epsilon_{N+1}(N+1)$	$-\epsilon_{N+1}(N)$	$-\epsilon_{N+1}(N+1)$	$-\epsilon_{N+1}(N)$	$-\epsilon_{N+1}(N+1)$	$-\epsilon_{N+1}(N)$
H (Hydrogen atom)	0.75	0.84	-0.52	-0.08	-0.53	0.84	-0.53
He (Helium atom)	-2.63	-4.35	-4.76	-5.17	-3.89	-4.27	-4.30
Li (Lithium atom)	0.62	0.68	-0.44	0.00	0.14	0.71	-0.19
Be (Beryllium atom)	-0.36	-0.46	-0.52	-1.20	0.35	-0.41	-0.30
B (Boron atom)	0.25	0.19	0.38	-0.65	1.28	0.16	0.57
C (Carbon atom)	1.25	0.87	1.69	0.08	2.42	0.73	1.99
N (Nitrogen atom)	-0.22	-0.60	0.49	-1.39	1.55	-0.63	0.52
O (Oxygen atom)	1.45	0.76	2.18	0.16	2.96	0.54	2.48
F (Fluorine atom)	3.44	2.28	4.30	1.90	4.81	1.93	4.90
Ne (Neon atom)	-5.31	-7.18	-7.07	-8.16	-5.82	-7.53	-6.83

Na (Sodium atom)	0.54	0.68	-0.49	0.05	-0.03	0.68	-0.24
Mg (Magnesium atom)	-0.23	-0.41	-0.65	-0.98	0.11	-0.30	-0.38
Al (Aluminum atom)	0.45	0.27	0.22	-0.54	1.12	0.33	0.35
Si (Silicon atom)	1.42	1.09	1.41	0.22	2.31	1.06	1.55
P (Phosphorus atom)	0.74	0.57	0.98	-0.24	2.20	0.63	1.20
S (Sulfur atom)	2.10	1.77	2.53	1.01	3.64	1.71	2.77
Cl (Chlorine atom)	3.69	3.05	4.27	2.34	5.22	2.91	4.57
Ar (Argon atom)	-2.81	-3.18	-3.78	-4.03	-2.53	-3.48	-3.40
CH_3 (Methyl radical)	-0.07	-0.08	-0.08	-0.92	1.09	-0.16	-0.05
CH_4 (Methane)	-0.62	-1.01	-1.52	-1.58	-0.92	-0.92	-1.17
NH (Imidogen)	0.33	-0.03	0.65	-0.79	1.66	-0.14	0.84
NH_2 (Amino radical)	0.74	0.44	0.90	-0.33	1.85	0.27	1.12
NH_3 (Ammonia)	-0.56	-0.98	-1.52	-1.63	-0.76	-0.90	-1.12
OH (Hydroxyl radical)	1.83	1.22	2.15	0.63	2.91	0.95	2.53
H_2O (Water)	-0.56	-1.03	-1.50	-1.80	-0.68	-0.95	-1.09
HF (Hydrogen fluoride)	-0.63	-1.14	-1.47	-1.85	-0.73	-1.01	-1.12
SiH_3 (Silyl)	0.93	0.79	1.14	-0.03	2.53	0.82	1.31
SiH_4 (Silane)	-1.11	-1.09	-1.69	-1.60	-0.95	-1.06	-1.28
PH_3 (Phosphine)	-1.21	-0.90	-1.50	-1.44	-0.71	-0.90	-1.09
SH_2 (Hydrogen sulfide)	-0.49	-1.85	-1.41	-2.39	-0.63	-1.69	-1.03
HCl (Hydrogen chloride)	-0.52	-0.92	-1.36	-1.63	-0.54	-0.84	-0.98
C_2H_2 (Acetylene)	-1.90	-2.50	-1.52	-3.24	-1.09	-2.56	-1.22
C_2H_4 (Ethylene)	-1.86	-2.07	-1.74	-2.86	-0.92	-2.12	-1.33
C_2H_6 (Ethane)	-0.62	-1.03	-1.55	-1.55	-0.90	-0.95	-1.17
HCN (Hydrogen cyanide)	-0.48	-2.07	-1.41	-2.83	-0.92	-2.01	-1.09
CO (Carbon monoxide)	-1.50	-1.90	-1.33	-2.67	-0.46	-1.93	-1.09
HCO (Formyl radical)	0.02	-0.27	0.44	-1.01	1.39	-0.33	0.57
CH_2O (Formaldehyde)	-0.55	-1.31	-0.63	-2.09	0.19	-1.41	-0.46
CH_3OH (Methyl alcohol)	-0.55	-0.95	-1.44	-1.50	-0.79	-0.84	-1.09
N_2 (Nitrogen diatomic)	-2.24	-2.80	-1.55	-3.56	-0.71	-2.88	-1.28
N_2H_4 (Hydrazine)	-0.45	-1.52	-1.41	-1.99	-0.57	-1.39	-1.01

NO (Nitric oxide)	-0.42	-0.92	0.60	-1.52	1.44	-1.12	0.87
O_2 (Oxygen diatomic)	-0.08	-0.87	0.79	-1.36	1.60	-1.09	1.12
H_2O_2 (Hydrogen peroxide)	-0.92	-1.47	-1.63	-2.04	-0.82	-1.33	-1.25
F_2 (Fluorine diatomic)	0.42	-0.38	1.69	-0.57	2.42	-0.73	2.15
CO_2 (Carbon dioxide)	-0.65	-4.49	-1.69	-5.11	-0.73	-4.68	-1.31
P_2 (Phosphorus diatomic)	0.48	0.33	0.73	-0.46	1.71	0.35	0.95
S_2 (Sulfur diatomic)	1.53	1.12	1.69	0.44	2.72	1.12	1.93
Cl_2 (Chlorine diatomic)	0.75	0.38	1.06	-0.33	1.99	0.27	1.33
NaCl (Sodium Chloride)	0.65	0.52	0.16	-0.16	0.79	0.65	0.46
SiO (Silicon monoxide)	0.03	-0.33	0.11	-1.12	1.09	-0.24	0.33
CS (Carbon monosulfide)	-0.09	-0.30	0.33	-1.03	1.25	-0.33	0.54
ClO (Monochlorine monoxide)	2.19	1.60	2.58	1.06	3.37	1.41	2.77
ClF (Chlorine monofluoride)	0.44	-0.14	0.92	-0.79	1.85	-0.22	1.28
Si_2H_6 (Disilane)	-0.69	-1.22	-1.58	-1.69	-0.76	-1.17	-1.20
CH_3Cl (Methyl chloride)	-0.51	-0.84	-1.39	-1.47	-0.68	-0.76	-1.01
CH_3SH (Methanethiol)	-0.50	-0.87	-1.41	-1.44	-0.63	-0.79	-1.03
SO_2 (Sulfur dioxide)	0.81	0.41	1.41	-0.19	2.42	0.30	1.66
BF_3 (Borane, trifluoro-)	-1.04	-1.25	-1.71	-1.88	-0.82	-1.17	-1.31
BCl_3 (Borane, trichloro-)	-0.17	-1.01	-0.16	-1.52	0.76	-0.98	-0.03
$AlCl_3$ (Aluminum trichloride)	0.06	-0.08	-0.35	-0.79	0.73	-0.11	-0.19
CF_4 (Carbon tetrafluoride)	-1.33	-1.96	-2.48	-2.53	-1.52	-1.82	-2.04
CCl_4 Carbon tetrachloride)	-0.46	-0.35	-0.41	-1.01	0.57	-0.35	-0.14
OCS (Carbonyl sulfide)	-0.74	-1.58	-1.03	-2.26	-0.08	-1.58	-0.82
CS_2 (Carbon disulfide)	0.01	-0.11	0.16	-0.79	1.12	-0.11	0.35
CF_2O (Carbonic difluoride)	-2.37	-2.50	-1.55	-3.40	-0.65	-2.42	-1.36
SiF_4 (Silicon tetrafluoride)	-0.81	-1.25	-1.66	-1.88	-0.63	-1.22	-1.22
N_2O (Nitrous oxide)	-2.01	-2.58	-1.58	-3.26	-0.65	-2.75	-1.36
NF_3 (Nitrogen trifluoride)	-2.06	-2.88	-2.67	-3.64	-1.82	-2.86	-2.37
PF_3 (Phosphorus trifluoride)	-1.23	-1.58	-1.88	-2.12	-0.98	-1.50	-1.55
O_3 (Ozone)	1.93	1.90	3.24	1.58	4.22	1.55	3.48
F_2O (Difluorine monoxide)	-0.31	-1.01	0.44	-1.36	1.22	-1.17	0.82

ClF_3 (Chlorine trifluoride)	1.20	0.63	1.60	0.14	2.56	0.52	1.90
C_2F_4 (Tetrafluoroethylene)	-1.65	-2.42	-2.07	-2.94	-1.03	-2.34	-1.66
CH_3CCH (Propyne)	-1.13	-1.77	-1.41	-2.23	-0.82	-1.60	-1.06
CH_2CCH_2 (Allene)	-0.56	-1.55	-1.60	-2.04	-0.92	-1.41	-1.22
C_3H_4 (Cyclopropene)	-1.82	-2.01	-1.66	-2.80	-0.92	-2.07	-1.31
C_3H_6 (Cyclopropane)	-0.65	-1.17	-1.71	-1.63	-1.03	-1.09	-1.33
CH_2F_2 (Methane, difluoro-)	-0.58	-1.06	-1.52	-1.63	-0.95	-0.90	-1.20
CF_3H (Methane, trifluoro-)	-0.60	-1.17	-1.58	-1.85	-1.01	-1.01	-1.25
CH_2Cl_2 (Methylene chloride)	-0.49	-0.82	-1.31	-1.50	-0.49	-0.73	-0.98
$CHCl_3$ (Chloroform)	-0.83	-0.79	-1.01	-1.52	-0.05	-0.73	-0.76
CH_3NO_2 (Methane, nitro-)	-0.37	-0.49	0.05	-1.06	0.98	-0.65	0.27
CH_3SiH_3 (Methyl silane)	-0.53	-0.92	-1.47	-1.47	-0.73	-0.84	-1.09
HCOOH (Formic acid)	-0.57	-2.15	-1.63	-2.88	-0.87	-2.18	-1.25
CH_3CONH_2 (Acetamide)	-0.31	-1.60	-1.22	-2.09	-0.49	-1.44	-0.84
C_2N_2 (Cyanogen)	-0.19	-0.33	0.52	-1.03	1.47	-0.38	0.68
CH_2CO (Ketene)	-0.51	-1.41	-1.03	-1.96	-0.16	-1.28	-0.87
C_2H_4O (Ethylene oxide)	-0.86	-1.03	-1.60	-1.55	-0.95	-0.95	-1.22
$C_2H_2O_2$ (Ethanedial)	0.69	0.63	1.28	-0.11	2.18	0.49	1.41
CH_3CH_2OH (Ethanol)	-0.53	-0.92	-1.44	-1.47	-0.76	-0.82	-1.09
CH_3OCH_3 (Dimethyl ether)	-0.58	-1.01	-1.52	-1.47	-0.84	-0.90	-1.14
C_2H_4S (Thiirane)	-0.78	-1.25	-1.60	-1.69	-0.87	-1.14	-1.20
CH_2CHF (Ethene, fluoro-)	-0.88	-2.18	-1.66	-2.91	-1.01	-2.23	-1.28
CH_3CH_2Cl (Ethyl chloride)	-0.51	-0.90	-1.47	-1.44	-0.73	-0.79	-1.09
CH_2CHCl (Ethene, chloro-)	-1.11	-1.60	-1.41	-2.39	-0.52	-1.66	-1.20
CH_3CClO (Acetyl Chloride)	-0.85	-1.12	-0.79	-1.80	0.11	-1.14	-0.65
NO_2 (Nitrogen dioxide)	1.44	0.90	1.99	0.38	3.02	0.76	2.18
$CFCl_3$ (Trichloromonofluoromethane)	-0.68	-0.76	-0.65	-1.39	0.33	-0.73	-0.41
CF_3Cl (Methane, chlorotrifluoro-)	-1.06	-1.63	-1.82	-2.28	-0.84	-1.55	-1.52
HCCF (Fluoroacetylene)	-0.55	-0.95	-1.39	-1.47	-0.82	-0.82	-1.09
HCCCN (Cyanoacetylene)	-0.36	-0.76	-0.19	-1.52	0.71	-0.79	-0.08
C_4N_2 (2-Butynedinitrile)	0.68	0.76	1.25	0.05	2.20	0.71	1.36

C_2N_2 (Cyanogen)	-0.19	-0.33	0.52	-1.03	1.47	-0.38	0.68
C_3O_2 (Carbon suboxide)	-0.74	-1.01	-0.19	-1.66	0.76	-1.12	-0.05
FCN (Cyanogen fluoride)	-0.66	-4.08	-1.31	-4.81	-0.33	-4.22	-0.95
C_4N_2 (Diacetylene)	-0.64	-1.28	-0.92	-2.01	-0.03	-1.28	-0.82
H_2CS (Thioformaldehyde)	0.28	0.11	0.68	-0.68	1.55	0.05	0.82
$CHONH_2$ (Formamide)	-0.35	-2.48	-1.33	-3.21	-0.63	-2.45	-0.95
CH_2CCl_2 (Ethene, 1,1-dichloro-)	-1.07	-1.01	-1.12	-1.58	-0.19	-0.90	-0.98
C_2HF_3 (Trifluoroethylene)	-0.54	-1.14	-1.60	-1.74	-0.92	-0.98	-1.25
CH_2CF_2 (Ethene, 1,1-difluoro-)	-1.03	-2.26	-1.66	-2.96	-0.95	-2.31	-1.28
CH_3F (Methyl fluoride)	-0.58	-0.98	-1.50	-1.55	-0.90	-0.87	-1.14
CF_2Cl_2 (Difluorodichloromethane)	-0.90	-1.31	-1.20	-1.90	-0.22	-1.28	-0.92
SiF_2 (Silicon difluoride)	0.10	-0.27	0.22	-1.06	1.20	-0.19	0.44
MSE		-0.53	-0.24	-1.18	0.60	-0.54	0.04
MAE		0.55	0.62	1.18	0.79	0.56	0.55
rms		0.79	0.73	1.32	0.97	0.82	0.65

TABLE S3: Reference values of FG115 database calculated by the CCSD(T) theory, compared with HOMO-LUMO gap results by DFT methods.

Molecule	Reference	ωM05-D	M05-2X	ωB97X-D
H (Hydrogen atom)	12.86	11.62	10.98	11.57
He (Helium atom)	27.23	25.57	24.70	24.56
Li (Lithium atom)	4.22	5.49	4.05	5.41
Be (Beryllium atom)	9.66	8.70	6.94	8.57
B (Boron atom)	7.99	6.83	5.11	6.66
C (Carbon atom)	9.97	8.05	6.69	7.59
N (Nitrogen atom)	14.74	11.97	10.47	11.61
O (Oxygen atom)	12.14	9.63	8.54	9.00
F (Fluorine atom)	13.98	10.88	10.28	9.74
Ne (Neon atom)	26.91	25.84	24.75	24.89
Na (Sodium atom)	4.14	5.41	4.11	5.11

Mg (Magnesium atom)	7.76	7.81	6.26	7.45
Al (Aluminum atom)	5.53	5.11	3.32	5.11
Si (Silicon atom)	6.73	5.88	4.11	5.74
P (Phosphorus atom)	9.78	8.35	6.31	8.05
S (Sulfur atom)	8.23	6.80	5.00	6.53
Cl (Chlorine atom)	9.30	7.43	5.90	6.99
Ar (Argon atom)	18.65	17.95	16.21	17.33
CH_3 (Methyl radical)	9.86	8.87	6.83	8.54
CH_4 (Methane)	15.06	14.69	13.52	14.14
NH (Imidogen) ($^3\Sigma^-$)	13.17	11.32	9.85	10.80
NH_2 (Amino radical)	11.34	10.09	8.62	9.63
NH_3 (Ammonia)	11.54	11.53	10.17	10.85
OH (Hydroxyl radical)	11.27	9.49	8.40	8.73
H_2O (Water)	13.35	13.00	11.78	12.19
HF (Hydrogen fluoride)	16.91	15.88	15.01	15.01
SiH_3 (Silyl)	7.95	7.04	4.79	6.85
SiH_4 (Silane)	14.03	13.55	12.13	13.08
PH_3 (Phosphine)	11.82	11.29	9.74	10.85
H_2S (Hydrogen sulfide)	11.00	10.99	9.47	10.50
HCl (Hydrogen chloride)	13.36	13.00	11.56	12.43
C_2H_2 (Acetylene)	13.43	12.13	10.93	11.59
C_2H_4 (Ethylene)	12.57	11.75	10.09	11.07
C_2H_6 (Ethane)	13.41	13.25	12.05	12.76
HCN (Hydrogen cyanide)	14.31	14.04	12.89	13.44
CO (Carbon monoxide)	15.57	14.31	12.97	13.90
HCO (Formyl radical)	9.56	8.38	6.91	8.05
CH_2O (Formaldehyde)	11.56	10.72	9.41	10.28
CH_3OH (Methyl alcohol)	11.67	11.67	10.55	11.02
N_2 (Nitrogen diatomic)	17.88	16.13	14.96	15.56
N_2H_4 (Hydrazine)	10.29	10.44	9.03	9.79
NO (Nitric oxide)	10.11	8.11	6.91	7.48

O_2 (Oxygen diatomic) ($^3\Sigma_g$)	12.52	10.69	9.66	9.90
H_2O_2 (Hydrogen peroxide)	12.65	12.40	11.23	11.61
F_2 (Fluorine diatomic)	15.53	12.76	11.97	11.75
CO_2 (Carbon dioxide)	14.58	14.66	13.27	13.95
P_2 (Phosphorus diatomic)	10.19	9.19	7.43	8.95
S_2 (Sulfur diatomic) ($^3\Sigma_g$)	7.96	7.26	5.58	6.94
Cl_2 (Chlorine diatomic)	10.93	9.71	8.19	9.30
NaCl (Sodium Chloride)	8.64	8.43	7.15	7.94
SiO (Silicon monoxide)	11.60	10.77	9.11	10.44
CS (Carbon monosulfide)	11.58	10.66	9.17	10.36
ClO (Monochlorine monoxide)	8.85	7.53	6.34	7.13
ClF (Chlorine monofluoride)	12.43	10.74	9.33	10.17
Si_2H_6 (Disilane)	11.33	11.72	10.17	11.32
CH_3Cl (Methyl chloride)	12.01	12.00	10.66	11.42
CH_3SH (Methanethiol)	10.01	10.20	8.68	9.71
SO_2 (Sulfur dioxide)	11.74	10.36	8.87	9.93
BF_3 (Borane, trifluoro-)	17.22	16.54	15.53	15.59
BCl_3 (Borane, trichloro-)	12.07	11.34	9.82	11.04
$AlCl_3$ (Aluminum trichloride)	12.13	11.83	10.12	11.48
CF_4 (Carbon tetrafluoride)	17.85	17.71	16.67	16.73
CCl_4 (Carbon tetrachloride)	11.97	11.56	10.01	11.12
OCS (Carbonyl sulfide)	12.13	11.67	10.04	11.34
CS_2 (Carbon disulfide)	10.19	9.41	7.78	9.22
CF_2O (Carbonic difluoride)	16.08	14.33	13.08	13.74
SiF_4 (Silicon tetrafluoride)	16.95	17.03	15.88	16.08
N_2O (Nitrous oxide)	15.01	13.57	12.16	13.11
NF_3 (Nitrogen trifluoride)	15.76	15.29	14.17	14.69
PF_3 (Phosphorus trifluoride)	13.00	12.62	11.15	12.24
O_3 (Ozone)	11.06	9.11	7.70	8.49
F_2O (Difluorine monoxide)	13.82	12.08	11.18	11.21
ClF_3 (Chlorine trifluoride)	11.79	10.58	9.30	9.96

C_2F_4 (Tetrafluoroethylene)	12.45	12.00	10.44	11.37
CH_3CCH (Propyne)	11.69	11.23	9.90	10.66
CH_2CCH_2 (Allene)	10.83	11.40	9.98	10.83
C_3H_4 (Cyclopropene)	11.87	10.99	9.52	10.42
C_3H_6 (Cyclopropane)	11.64	12.19	10.77	11.61
CH_2F_2 (Methane, difluoro-)	14.15	13.79	12.92	13.16
CF_3H (Methane, trifluoro-)	15.44	15.10	14.28	14.47
CH_2Cl_2 (Methylene chloride)	12.18	12.16	10.77	11.70
$CHCl_3$ (Chloroform)	12.38	11.86	10.34	11.48
CH_3NO_2 (Methane, nitro-)	11.94	11.07	9.79	10.44
CH_3SiH_3 (Methyl silane)	12.35	12.70	11.23	12.21
HCOOH (Formic acid)	11.98	12.32	11.10	11.61
CH_3CONH_2 (Acetamide)	10.05	10.88	9.66	10.20
C_2N_2 (Cyanogen)	13.90	12.27	10.72	11.86
CH_2CO (Ketene)	10.32	10.23	8.65	9.87
C_2H_4O (Ethylene oxide)	11.68	11.86	10.74	11.12
$C_2H_2O_2$ (Ethanedial)	10.04	8.84	7.45	8.46
CH_3CH_2OH (Ethanol)	11.38	11.53	10.39	10.88
CH_3OCH_3 (Dimethyl ether)	10.79	11.18	9.98	10.50
C_2H_4S (Thiirane)	9.93	10.17	8.73	9.66
CH_2CHF (Ethene, fluoro-)	11.55	11.56	10.17	10.93
CH_3CH_2Cl (Ethyl chloride)	11.74	11.91	10.58	11.37
CH_2CHCl (Ethene, chloro-)	11.35	11.02	9.38	10.61
CH_3COCl (Acetyl Chloride)	11.97	11.56	10.12	11.18
NO_2 (Nitrogen dioxide)	9.79	8.73	7.40	8.19
$CFCl_3$ (Trichloromonofluoromethane)	12.61	11.89	10.34	11.48
CF_3Cl (Methane, chlorotrifluoro-)	14.27	14.09	12.59	13.57
HCCF (Fluoroacetylene)	12.04	11.91	10.66	11.37
HCCCN (Cyanoacetylene)	12.20	11.26	9.71	10.93
C_4N_2 (2-Butynedinitrile)	11.52	10.31	8.76	9.98
C_2N_2 (Cyanogen)	13.90	12.27	10.72	11.86

C_3O_2 (Carbon suboxide)	11.64	10.58	9.06	10.28
FCN (Cyanogen fluoride)	14.33	13.76	12.21	13.11
C_4H_2 (Diacetylene)	11.00	10.64	9.03	10.34
H_2CS (Thioformaldehyde)	9.18	8.05	6.47	7.81
$CHONH_2$ (Formamide)	10.81	11.23	10.06	10.53
CH_2CCl_2 (Ethene, 1,1-dichloro-)	11.17	10.69	9.06	10.39
C_2HF_3 (Trifluoroethylene)	11.11	11.34	10.06	10.77
CH_2CF_2 (Ethene, 1,1-difluoro-)	11.81	11.67	10.28	11.04
CH_3F (Methyl fluoride)	14.09	13.71	12.76	13.06
CF_2Cl_2 (Difluorodichloromethane)	13.33	12.81	11.29	12.38
SiF_2 (Silicon difluoride)	11.04	10.04	8.32	9.79
MSE		-0.70	-2.08	-1.21
MAE		0.84	2.08	1.25
rms		1.07	2.24	1.48

TABLE S4: Experimental molecular geometries (in angstrom) for IP131, EA115 and FG115 databases collected from the NIST database [1]. The integers following the molecule are in order the spin multiplicities of neutral species, cation and anion. The molecules with only the spin multiplicity of the neutral species shown are in neither EA115 nor FG115 database. The spin multiplicities of neutral species are experimental values specified in the NIST database [1]. Each spin multiplicity of cations and anions is decided by CCSD(T)/aug-cc-pVTZ calculations, and corresponds to the lowest energy in between various spin multiplicities.

H (Hydrogen atom) 2 Null 1

H

He (Helium atom) 1 2 2

He

Li (Lithium atom) 2 1 1

Li

Be (Beryllium atom) 1 2 2

Be

B (Boron atom) 2 1 3

B

C (Carbon atom) 3 2 4

C

N (Nitrogen atom) 4 3 3

N

O (Oxygen atom) 3 4 2

O

F (Fluorine atom) 2 3 1

F

Ne (Neon atom) 1 2 2

Ne

Na (Sodium atom) 2 1 1			
Na			
Mg (Magnesium atom) 1 2 2			
Mg			
Al (Aluminum atom) 2 1 3			
Al			
Si (Silicon atom) 3 2 4			
Si			
P (Phosphorus atom) 4 3 3			
P			
S (Sulfur atom) 3 4 2			
S			
Cl (Chlorine atom) 2 3 1			
Cl			
Ar (Argon atom) 1 2 2			
Ar			
CH_3 (Methyl radical) 2 1 1			
C1	0.0000	0.0000	0.0000
H2	1.0790	0.0000	0.0000
H3	-0.5395	-0.9344	0.0000
H4	-0.5395	0.9344	0.0000
CH_4 (Methane) 1 2 2			
C1	0.0000	0.0000	0.0000
H2	0.6276	0.6276	0.6276
H3	0.6276	-0.6276	-0.6276
H4	-0.6276	0.6276	-0.6276
H5	-0.6276	-0.6276	0.6276
NH (Imidogen) ($^3\Sigma^-$) 3 2 2			
N1	0.0000	0.0000	0.0000
H2	0.0000	0.0000	1.0362

NH_2 (Amino radical) 2 3 1			
N1	0.0000	0.0000	0.0000
H2	0.0000	0.8036	0.6347
H3	0.0000	-0.8036	0.6347
NH_3 (Ammonia) 1 2 2			
N1	0.0000	0.0000	0.0000
H2	0.0000	-0.9377	-0.3816
H3	0.8121	0.4689	-0.3816
H4	-0.8121	0.4689	-0.3816
OH (Hydroxyl radical) 2 3 1			
O1	0.0000	0.0000	0.0000
H2	0.0000	0.0000	0.9697
H_2O (Water) 1 2 2			
O1	0.0000	0.0000	0.1173
H2	0.0000	0.7572	-0.4692
H3	0.0000	-0.7572	-0.4692
HF (Hydrogen fluoride) 1 2 2			
F1	0.0000	0.0000	0.0000
H2	0.0000	0.0000	0.9168
SiH_3 (Silyl) 2 1 1			
Si1	0.0000	0.0000	0.0819
H2	0.0000	1.3928	-0.3820
H3	1.2062	-0.6964	-0.3820
H4	-1.2062	-0.6964	-0.3820
SiH_4 (Silane) 1 2 2			
Si1	0.0000	0.0000	0.0000
H2	0.8544	0.8544	0.8544
H3	-0.8544	-0.8544	0.8544
H4	-0.8544	0.8544	-0.8544

H5	0.8544	-0.8544	-0.8544
PH_3 (Phosphine) 1 2 2			
P1	0.0000	0.0000	0.0000
H2	0.0000	-1.1932	-0.7717
H3	1.0333	0.5966	-0.7717
H4	-1.0333	0.5966	-0.7717
H_2S (Hydrogen sulfide) 1 2 2			
S1	0.0000	0.0000	0.0000
H2	0.0000	0.9569	0.9208
H3	0.0000	-0.9569	0.9208
HCl (Hydrogen chloride) 1 2 2			
Cl1	0.0000	0.0000	0.0000
H2	0.0000	0.0000	1.2746
C_2H_2 (Acetylene) 1 2 2			
C1	0.0000	0.0000	0.6013
C2	0.0000	0.0000	-0.6013
H3	0.0000	0.0000	1.6644
H4	0.0000	0.0000	-1.6644
C_2H_4 (Ethylene) 1 2 2			
C1	0.0000	0.0000	0.6695
C2	0.0000	0.0000	-0.6695
H3	0.0000	0.9289	1.2321
H4	0.0000	-0.9289	1.2321
H5	0.0000	0.9289	-1.2321
H6	0.0000	-0.9289	-1.2321
C_2H_6 (Ethane) 1 2 2			
C1	0.0000	0.0000	0.7680
C2	0.0000	0.0000	-0.7680
H3	-1.0192	0.0000	1.1573

H4	0.5096	0.8826	1.1573
H5	0.5096	-0.8826	1.1573
H6	1.0192	0.0000	-1.1573
H7	-0.5096	-0.8826	-1.1573
H8	-0.5096	0.8826	-1.1573
HCN (Hydrogen cyanide) 1 2 2			
C1	0.0000	0.0000	0.0000
H2	0.0000	0.0000	1.0640
N3	0.0000	0.0000	-1.1560
CO (Carbon monoxide) 1 2 2			
C1	0.0000	0.0000	0.0000
O2	0.0000	0.0000	1.1283
HCO (Formyl radical) 2 1 1			
C1	0.0000	0.0000	0.0000
H2	1.0800	0.0000	0.0000
O3	-0.5899	1.0427	0.0000
H_2CO (Formaldehyde) 1 2 2			
O1	0.0000	0.0000	1.2050
C2	0.0000	0.0000	0.0000
H3	0.0000	0.9429	-0.5876
H4	0.0000	-0.9429	-0.5876
CH_3OH (Methyl alcohol) 1 2 2			
C1	-0.0503	0.6685	0.0000
O2	-0.0503	-0.7585	0.0000
H3	-1.0807	1.0417	0.0000
H4	0.4650	1.0417	0.8924
H5	0.4650	1.0417	-0.8924
H6	0.8544	-1.0677	0.0000
N_2 (Nitrogen diatomic) 1 2 2			

N1	0.0000	0.0000	0.5488
N2	0.0000	0.0000	-0.5488
N_2H_4 (Hydrazine) 1 2 2			
N1	0.0000	0.7230	-0.1123
N2	0.0000	-0.7230	-0.1123
H3	-0.4470	1.0031	0.7562
H4	0.4470	-1.0031	0.7562
H5	0.9663	1.0031	0.0301
H6	-0.9663	-1.0031	0.0301
NO (Nitric oxide) 2 1 3			
O1	0.0000	0.0000	0.0000
N2	0.0000	0.0000	1.1508
O_2 (Oxygen diatomic) ($^3\Sigma_g$) 3 2 2			
O1	0.0000	0.0000	0.0000
O2	0.0000	0.0000	1.2075
H_2O_2 (Hydrogen peroxide) 1 2 2			
O1	0.0000	0.7375	-0.0528
O2	0.0000	-0.7375	-0.0528
H3	0.8190	0.8170	0.4220
H4	-0.8190	-0.8170	0.4220
F_2 (Fluorine diatomic) 1 2 2			
F1	0.0000	0.0000	0.0000
F2	0.0000	0.0000	1.4119
CO_2 (Carbon dioxide) 1 2 2			
C1	0.0000	0.0000	0.0000
O2	0.0000	0.0000	1.1621
O3	0.0000	0.0000	-1.1621
P_2 (Phosphorus diatomic) 1 2 2			
P1	0.0000	0.0000	0.0000

P2	0.0000	0.0000	1.8934
S_2 (Sulfur diatomic) ($^3\Sigma_g$) 3 2 2			
S1	0.0000	0.0000	0.0000
S2	0.0000	0.0000	1.8892
Cl_2 (Chlorine diatomic) 1 2 2			
Cl1	0.0000	0.0000	0.0000
Cl2	0.0000	0.0000	1.9879
NaCl (Sodium Chloride) 1 2 2			
Na1	0.0000	0.0000	0.0000
Cl2	0.0000	0.0000	2.3608
SiO (Silicon monoxide) 1 2 2			
Si1	0.0000	0.0000	0.0000
O2	0.0000	0.0000	1.5097
CS (Carbon monosulfide) 1 2 2			
C1	0.0000	0.0000	0.0000
S2	0.0000	0.0000	1.5349
ClO (Monochlorine monoxide) 2 3 1			
O1	0.0000	0.0000	0.0000
Cl2	0.0000	0.0000	1.5696
ClF (Chlorine monofluoride) 1 2 2			
F1	0.0000	0.0000	0.0000
Cl2	0.0000	0.0000	1.6283
Si_2H_6 (Disilane) 1 2 2			
Si1	0.0000	0.0000	1.1600
Si2	0.0000	0.0000	-1.1600
H3	0.0000	1.3865	1.6483
H4	-1.2008	-0.6933	1.6483
H5	1.2008	-0.6933	1.6483
H6	0.0000	-1.3865	-1.6483

H7	-1.2008	0.6933	-1.6483
H8	1.2008	0.6933	-1.6483
CH_3Cl (Methyl chloride) 1 2 2			
C1	0.0000	0.0000	0.0000
Cl2	0.0000	0.0000	1.7810
H3	1.0424	0.0000	-0.3901
H4	-0.5212	0.9027	-0.3901
H5	-0.5212	-0.9027	-0.3901
CH_3SH (Methanethiol) 1 2 2			
C1	-0.8500	-0.0344	-0.2000
S2	0.9000	-0.5125	-0.1219
H3	1.4219	0.5781	0.4250
H4	-0.9406	0.8688	-0.8219
H5	-1.4219	-0.8688	-0.6469
H6	-1.2031	0.1656	0.8219
SO_2 (Sulfur dioxide) 1 2 2			
S1	0.0000	0.0000	0.0000
O2	0.0000	1.2371	0.7215
O3	0.0000	-1.2371	0.7215
BF_3 (Borane, trifluoro-) 1 2 2			
B1	0.0000	0.0000	0.0000
F2	0.0000	1.3070	0.0000
F3	1.1319	-0.6535	0.0000
F4	-1.1319	-0.6535	0.0000
BCl_3 (Borane, trichloro-) 1 2 2			
B1	0.0000	0.0000	0.0000
Cl2	0.0000	1.7421	0.0000
Cl3	1.5087	-0.8711	0.0000
Cl4	-1.5087	-0.8711	0.0000

$AlCl_3$ (Aluminum trichloride) 1 2 2			
Al1	0.0000	0.0000	0.0000
Cl2	0.0000	2.0600	0.0000
Cl3	1.7840	-1.0300	0.0000
Cl4	-1.7840	-1.0300	0.0000
CF_4 (Carbon tetrafluoride) 1 2 2			
C1	0.0000	0.0000	0.0000
F2	0.7593	0.7593	0.7593
F3	-0.7593	-0.7593	0.7593
F4	-0.7593	0.7593	-0.7593
F5	0.7593	-0.7593	-0.7593
CCl_4 (Carbon tetrachloride) 1 2 2			
C1	0.0000	0.0000	0.0000
Cl2	1.0202	1.0202	1.0202
Cl3	-1.0202	-1.0202	1.0202
Cl4	-1.0202	1.0202	-1.0202
Cl5	1.0202	-1.0202	-1.0202
OCS (Carbonyl sulfide) 1 2 2			
C1	0.0000	0.0000	0.0000
O2	0.0000	0.0000	1.1600
S3	0.0000	0.0000	-1.5600
CS_2 (Carbon disulfide) 1 2 2			
C1	0.0000	0.0000	0.0000
S2	0.0000	0.0000	1.5540
S3	0.0000	0.0000	-1.5540
CF_2O (Carbonic difluoride) 1 2 2			
O1	0.0000	0.0000	1.3143
C2	0.0000	0.0000	0.1403
F3	0.0000	1.0614	-0.6309

F4	0.0000	-1.0614	-0.6309
SiF_4 (Silicon tetrafluoride) 1 2 2			
Si1	0.0000	0.0000	0.0000
F2	0.8972	0.8972	0.8972
F3	-0.8972	-0.8972	0.8972
F4	-0.8972	0.8972	-0.8972
F5	0.8972	-0.8972	-0.8972
N_2O (Nitrous oxide) 1 2 2			
N1	0.0000	0.0000	-1.1998
N2	0.0000	0.0000	-0.0716
O3	0.0000	0.0000	1.1126
NF_3 (Nitrogen trifluoride) 1 2 2			
N1	0.0000	0.0000	0.4731
F2	0.0000	1.2279	-0.1226
F3	1.0634	-0.6140	-0.1226
F4	-1.0634	-0.6140	-0.1226
PF_3 (Phosphorus trifluoride) 1 2 2			
P1	0.0000	0.0000	0.4602
F2	0.0000	1.3578	-0.2557
F3	1.1759	-0.6789	-0.2557
F4	-1.1759	-0.6789	-0.2557
O_3 (Ozone) 1 2 2			
O1	0.0000	0.0000	0.0000
O2	0.0000	1.0885	0.6697
O3	0.0000	-1.0885	0.6697
F_2O (Difluorine monoxide) 1 2 2			
O1	0.0000	0.0000	0.6074
F2	0.0000	1.1063	-0.2700
F3	0.0000	-1.1063	-0.2700

ClF_3 (Chlorine trifluoride) 1 2 2			
Cl1	0.0000	0.0000	0.3572
F2	0.0000	0.0000	-1.2408
F3	0.0000	1.6964	0.2831
F4	0.0000	-1.6964	0.2831
C_2F_4 (Tetrafluoroethylene) 1 2 2			
C1	0.0000	0.0000	0.6555
C2	0.0000	0.0000	-0.6555
F3	0.0000	1.0961	1.3893
F4	0.0000	-1.0961	1.3893
F5	0.0000	-1.0961	-1.3893
F6	0.0000	1.0961	-1.3893
CF_3CN (Acetonitrile, trifluoro-) 1			
C1	0.0000	0.0000	-0.3406
C2	0.0000	0.0000	1.1518
N3	0.0000	0.0000	2.3054
F4	0.0000	1.2540	-0.7780
F5	1.0860	-0.6270	-0.7780
F6	-1.0860	-0.6270	-0.7780
CH_3CCH (Propyne) 1 2 2			
C1	0.0000	0.0000	-1.2455
C2	0.0000	0.0000	0.2135
C3	0.0000	0.0000	1.4195
H4	0.0000	0.0000	2.4755
H5	0.0000	1.0465	-1.6003
H6	0.9063	-0.5232	-1.6003
H7	-0.9063	-0.5232	-1.6003
CH_2CCH_2 (Allene) 1 2 2			
C1	0.0000	0.0000	0.0000

C2	0.0000	0.0000	1.3080
C3	0.0000	0.0000	-1.3080
H4	0.0000	0.9327	1.8662
H5	0.0000	-0.9327	1.8662
H6	0.9327	0.0000	-1.8662
H7	-0.9327	0.0000	-1.8662
C_3H_4 (Cyclopropene) 1 2 2			
C1	0.0000	0.0000	0.8628
C2	0.0000	0.6476	-0.5001
C3	0.0000	-0.6476	-0.5001
H4	0.0000	1.5745	-1.0386
H5	0.0000	-1.5745	-1.0386
H6	0.9154	0.0000	1.4509
H7	-0.9154	0.0000	1.4509
C_3H_6 (Cyclopropane) 1 2 2			
C1	0.0000	0.8666	0.0000
C2	0.7505	-0.4333	0.0000
C3	-0.7505	-0.4333	0.0000
H4	0.0000	1.4525	0.9108
H5	1.2579	-0.7262	0.9108
H6	-1.2579	-0.7262	0.9108
H7	0.0000	1.4525	-0.9108
H8	1.2579	-0.7262	-0.9108
H9	-1.2579	-0.7262	-0.9108
C_3H_8 (Propane) 1			
C1	0.0000	0.5863	-0.0000
C2	-1.2681	-0.2626	0.0000
C3	1.2681	-0.2626	-0.0000
H4	0.0000	1.2449	0.8760

H5	-0.0003	1.2453	-0.8758
H6	-2.1576	0.3742	0.0000
H7	2.1576	0.3743	-0.0000
H8	-1.3271	-0.9014	0.8800
H9	-1.3271	-0.9014	-0.8800
H10	1.3271	-0.9014	-0.8800
H11	1.3272	-0.9014	0.8800
CH_3CCCH_3 (2-Butyne) 1			
C1	0.0000	0.0000	0.6070
C2	0.0000	0.0000	-0.6070
C3	0.0000	0.0000	2.0750
C4	0.0000	0.0000	-2.0750
H5	0.0000	1.0440	2.4695
H6	-0.9041	-0.5220	2.4695
H7	0.9041	-0.5220	2.4695
H8	0.0000	1.0440	-2.4695
H9	0.9041	-0.5220	-2.4695
H10	-0.9041	-0.5220	-2.4695
C_4H_6 (Cyclobutene) 1			
C1	0.0000	0.6710	0.8107
C2	0.0000	-0.6710	0.8107
C3	0.0000	0.7821	-0.7023
C4	0.0000	-0.7821	-0.7023
H5	0.0000	1.4165	1.5962
H6	0.0000	-1.4165	1.5962
H7	0.8986	1.2425	-1.1233
H8	-0.8986	-1.2425	-1.1233
H9	-0.8986	1.2425	-1.1233
H10	0.8986	-1.2425	-1.1233

$CH_3CH(CH_3)CH_3$ (Isobutane) 1			
C1	0.0000	0.0000	0.3650
H2	0.0000	0.0000	1.4730
C3	0.0000	1.4528	-0.0987
C4	1.2582	-0.7264	-0.0987
C5	-1.2582	-0.7264	-0.0987
H6	0.0000	1.4867	-1.1931
H7	1.2875	-0.7433	-1.1931
H8	-1.2875	-0.7433	-1.1931
H9	0.8941	1.9575	0.2821
H10	-0.8941	1.9575	0.2821
H11	1.2482	-1.7530	0.2821
H12	2.1422	-0.2045	0.2821
H13	-2.1422	-0.2045	0.2821
H14	-1.2482	-1.7530	0.2821
C_6H_6 (Benzene) 1			
C1	0.0000	1.3970	0.0000
C2	1.2098	0.6985	0.0000
C3	1.2098	-0.6985	0.0000
C4	0.0000	-1.3970	0.0000
C5	-1.2098	-0.6985	0.0000
C6	-1.2098	0.6985	0.0000
H7	0.0000	2.4810	0.0000
H8	2.1486	1.2405	0.0000
H9	2.1486	-1.2405	0.0000
H10	0.0000	-2.4810	0.0000
H11	-2.1486	-1.2405	0.0000
H12	-2.1486	1.2405	0.0000
CH_2F_2 (Methane, difluoro-) 1 2 2			

C1	0.0000	0.0000	0.5003
H2	-0.9029	0.0000	1.1002
H3	0.9029	0.0000	1.1002
F4	0.0000	1.0962	-0.2890
F5	0.0000	-1.0962	-0.2890
CHF_3 (Methane, trifluoro-) 1 2 2			
C1	0.0000	0.0000	0.3086
H2	0.0000	0.0000	1.4066
F3	0.0000	1.2609	-0.1207
F4	1.0920	-0.6305	-0.1207
F5	-1.0920	-0.6305	-0.1207
CH_2Cl_2 (Methylene chloride) 1 2 2			
C1	0.0000	0.0000	0.7761
H2	-0.8854	0.0000	1.3734
H3	0.8854	0.0000	1.3734
Cl4	0.0000	1.4675	-0.2178
Cl5	0.0000	-1.4675	-0.2178
$CHCl_3$ (Chloroform) 1 2 2			
C1	0.0000	0.0000	0.5231
H2	0.0000	0.0000	1.5961
Cl3	0.0000	1.6562	-0.0928
Cl4	1.4343	-0.8281	-0.0928
Cl5	-1.4343	-0.8281	-0.0928
CH_3NO_2 (Methane, nitro-) 1 2 2			
C1	1.4008	0.0000	0.0000
N2	-0.0878	0.0000	0.0000
H3	1.7215	-1.0392	0.0000
H4	1.7215	0.5196	0.9000
H5	1.7215	0.5196	-0.9000

O6	-0.6498	1.0874	0.0000
O7	-0.6498	-1.0874	0.0000
CH_3SiH_3 (Methyl silane) 1 2 2			
C1	0.0000	0.0000	-1.2367
Si2	0.0000	0.0000	0.6319
H3	0.0000	-1.0237	-1.6272
H4	-0.8866	0.5119	-1.6272
H5	0.8866	0.5119	-1.6272
H6	0.0000	1.3893	1.1514
H7	-1.2031	-0.6946	1.1514
H8	1.2031	-0.6946	1.1514
HCOOH (Formic acid) 1 2 2			
C1	0.0000	0.4199	0.0000
O2	-1.0543	-0.4121	0.0000
O3	1.1506	0.0721	0.0000
H4	-0.0799	1.5140	0.0000
H5	-0.6905	-1.3134	0.0000
CH_3CONH_2 (Acetamide) 1 2 2			
C1	-1.3674	-0.3302	0.0013
C2	0.0720	0.1552	-0.0019
N3	1.0259	-0.8416	-0.0326
O4	0.3726	1.3376	0.0057
H5	-2.0656	0.5484	-0.0612
H6	-1.5426	-1.0080	-0.8780
H7	-1.5719	-0.9088	0.9430
H8	2.0050	-0.5675	0.0710
H9	0.7853	-1.8244	0.1113
C_2H_5N (Aziridine) 1			
N1	-0.0037	0.8559	-0.1934

H2	-0.0140	1.4040	0.6620
C3	-0.7380	-0.4043	0.0261
C4	0.7425	-0.3952	0.0380
H5	-1.2757	-0.4486	0.9652
H6	-1.2332	-0.8641	-0.8216
H7	1.2820	-0.7584	-0.8280
H8	1.2404	-0.5270	0.9918
C_2N_2 (Cyanogen) 1 2 2			
C1	0.0000	0.0000	0.6950
C2	0.0000	0.0000	-0.6950
N3	0.0000	0.0000	1.8450
N4	0.0000	0.0000	-1.8450
CH_3NHCH_3 (Dimethylamine) 1			
N1	0.0934	-0.5520	0.0000
H2	-0.6454	-1.2544	0.0000
C3	-0.0220	0.2554	1.2139
C4	-0.0220	0.2554	-1.2139
H5	-0.9221	0.8833	1.2437
H6	-0.9221	0.8833	-1.2437
H7	0.8440	0.9287	1.2609
H8	0.8440	0.9287	-1.2609
H9	-0.0138	-0.3909	2.0843
H10	-0.0138	-0.3909	-2.0843
CH_2CO (Ketene) 1 2 2			
C1	0.0000	0.0000	0.0000
C2	0.0000	0.0000	1.3150
O3	0.0000	0.0000	2.4750
H4	0.0000	0.9451	-0.5206
H5	0.0000	-0.9451	-0.5206

C_2H_4O (Ethylene oxide) 1 2 2			
O1	0.0000	0.0000	0.8517
C2	0.0000	0.7297	-0.3725
C3	0.0000	-0.7297	-0.3725
H4	-0.9230	1.2565	-0.5859
H5	0.9230	1.2565	-0.5859
H6	0.9230	-1.2565	-0.5859
H7	-0.9230	-1.2565	-0.5859
$C_2H_2O_2$ (Ethanedial) 1 2 2			
C1	0.0000	0.7630	0.0000
C2	0.0000	-0.7630	0.0000
H3	1.0481	1.1907	0.0000
H4	-1.0481	-1.1907	0.0000
O5	-1.0367	1.3908	0.0000
O6	1.0367	-1.3908	0.0000
CH_3CH_2OH (Ethanol) 1 2 2			
C1	1.1879	-0.3829	0.0000
C2	0.0000	0.5526	0.0000
O3	-1.1867	-0.2472	0.0000
H4	-1.9237	0.3850	0.0000
H5	2.0985	0.2306	0.0000
H6	1.1184	-1.0093	0.8869
H7	1.1184	-1.0093	-0.8869
H8	-0.0227	1.1812	0.8852
H9	-0.0227	1.1812	-0.8852
CH_3OCH_3 (Dimethyl ether) 1 2 2			
O1	0.0000	0.0000	0.5952
C2	0.0000	1.1669	-0.1963
C3	0.0000	-1.1669	-0.1963

H4	0.0000	2.0489	0.4542
H5	0.0000	-2.0489	0.4542
H6	0.8950	1.1787	-0.8287
H7	-0.8950	1.1787	-0.8287
H8	-0.8950	-1.1787	-0.8287
H9	0.8950	-1.1787	-0.8287
C_2H_4S (Thiirane) 1 2 2			
S1	0.0000	0.0000	0.8622
C2	0.0000	0.7421	-0.7942
C3	0.0000	-0.7421	-0.7942
H4	-0.9174	1.2493	-1.0661
H5	0.9174	1.2493	-1.0661
H6	0.9174	-1.2493	-1.0661
H7	-0.9174	-1.2493	-1.0661
CH_3SOCH_3 (Dimethyl sulfoxide) 1			
S1	0.0000	0.1432	0.4202
O2	0.0000	1.4024	-0.3667
C3	1.3425	-0.8664	-0.2227
C4	-1.3425	-0.8664	-0.2227
H5	2.2553	-0.4311	0.0751
H6	-2.2553	-0.4311	0.0751
H7	1.3057	-1.8579	0.2349
H8	1.2255	-0.9383	-1.3113
H9	-1.3057	-1.8579	0.2349
H10	-1.2255	-0.9383	-1.3113
CH_2CHF (Ethene, fluoro-) 1 2 2			
C1	0.0000	0.4476	0.0000
C2	1.1877	-0.1487	0.0000
F3	-1.1356	-0.2769	0.0000

H4	-0.2349	1.5038	0.0000
H5	1.2321	-1.2348	0.0000
H6	2.0966	0.4290	0.0000
CH_3CH_2Cl (Ethyl chloride) 1 2 2			
C1	1.5949	-0.3563	-0.0000
C2	0.4757	0.6568	-0.0004
H3	2.5527	0.1648	0.0000
H4	1.5351	-0.9919	-0.8828
H5	1.5347	-0.9917	0.8828
Cl6	-1.1206	-0.1505	-0.0005
H7	0.5089	1.2945	-0.8790
H8	0.4949	1.2796	0.8893
CH_2CHCl (Ethene, chloro-) 1 2 2			
C1	0.0000	0.0000	1.3320
C2	0.0000	0.0000	0.0000
Cl3	0.0000	1.4589	2.2543
H4	0.0000	-0.9058	1.9384
H5	0.0000	0.9249	-0.5557
H6	0.0000	-0.9391	-0.5313
CH_3COCl (Acetyl Chloride) 1 2 2			
C1	0.0000	0.5272	0.0000
C2	1.4961	0.6994	0.0000
O3	-0.8349	1.3710	0.0000
Cl4	-0.4665	-1.2092	0.0000
H5	1.7591	1.7726	0.0000
H6	1.9367	0.2285	0.8973
H7	1.9367	0.2285	-0.8973
$CH_2ClCH_2CH_3$ (Propane, 1-chloro-) 1			
Cl1	1.7375	0.1388	0.0000

C2	0.0000	0.5937	0.0000
H3	-0.1639	1.2199	0.9054
H4	-0.1639	1.2199	-0.9054
C5	-0.8957	-0.6405	0.0000
H6	-0.6638	-1.2607	0.8947
H7	-0.6638	-1.2607	-0.8947
C8	-2.3710	-0.2543	0.0000
H9	-2.6338	0.3458	0.8998
H10	-2.6338	0.3458	-0.8998
H11	-3.0133	-1.1633	0.0000
$N(CH_3)_3$ (Trimethylamine) 1			
N1	0.0000	-0.0000	-0.3852
C2	-0.9758	-0.9757	0.0634
C3	1.3330	-0.3571	0.0634
C4	-0.3572	1.3328	0.0634
H5	-1.0253	-1.0252	1.1492
H6	1.4006	-0.3752	1.1492
H7	-0.3753	1.4004	1.1492
H8	-1.9833	-0.7091	-0.3156
H9	-0.7093	-1.9833	-0.3156
H10	1.6060	-1.3629	-0.3156
H11	2.0722	0.3776	-0.3156
H12	0.3774	2.0722	-0.3156
H13	-1.3631	1.6057	-0.3156
C_4H_4O (Furan) 1			
O1	0.0000	0.0000	1.1626
C2	0.0000	1.0920	0.3487
C3	0.0000	-1.0920	0.3487
C4	0.0000	0.7169	-0.9596

C5	0.0000	-0.7169	-0.9596
H6	0.0000	2.0473	0.8439
H7	0.0000	-2.0473	0.8439
H8	0.0000	1.3509	-1.8290
H9	0.0000	-1.3509	-1.8290
C_4H_5N (Pyrrole) 1			
N1	0.0000	0.0000	1.1218
H2	0.0000	0.0000	2.1178
C3	0.0000	1.1209	0.3341
C4	0.0000	-1.1209	0.3341
C5	0.0000	0.7076	-0.9847
C6	0.0000	-0.7076	-0.9847
H7	0.0000	2.1084	0.7614
H8	0.0000	-2.1084	0.7614
H9	0.0000	1.3566	-1.8429
H10	0.0000	-1.3566	-1.8429
NO_2 (Nitrogen dioxide) 2 1 1			
N1	0.0000	0.0000	0.0000
O2	0.0000	1.0989	0.4653
O3	0.0000	-1.0989	0.4653
SF_6 (Sulfur Hexafluoride) 1			
S1	0.0000	0.0000	0.0000
F2	0.0000	0.0000	1.5607
F3	0.0000	1.5607	0.0000
F4	1.5607	0.0000	0.0000
F5	0.0000	-1.5607	0.0000
F6	-1.5607	0.0000	0.0000
F7	0.0000	0.0000	-1.5607
$CFCl_3$ (Trichloromonofluoromethane) 1 2 2			

C1	0.0000	0.0000	0.2472
F2	0.0000	0.0000	1.5922
Cl3	0.0000	1.6732	-0.3101
Cl4	1.4491	-0.8366	-0.3101
Cl5	-1.4491	-0.8366	-0.3101
CF_3Cl (Methane, chlorotrifluoro-) 1 2 2			
C1	0.0000	0.0000	-0.3471
Cl2	0.0000	0.0000	1.4049
F3	0.0000	1.2425	-0.8074
F4	1.0760	-0.6212	-0.8074
F5	-1.0760	-0.6212	-0.8074
CF_3Br (Bromotrifluoromethane) 1			
C1	0.0000	0.0000	-0.8088
Br2	0.0000	0.0000	1.1146
F3	0.0000	1.2455	-1.2651
F4	1.0787	-0.6228	-1.2651
F5	-1.0787	-0.6228	-1.2651
HCCF (Fluoroacetylene) 1 2 2			
C1	0.0000	0.0000	-0.0942
C2	0.0000	0.0000	-1.2922
F3	0.0000	0.0000	1.1848
H4	0.0000	0.0000	-2.3452
HCCCN (Cyanoacetylene) 1 2 2			
N1	0.0000	0.0000	1.9018
C2	0.0000	0.0000	0.7413
C3	0.0000	0.0000	-0.6351
C4	0.0000	0.0000	-1.8409
H5	0.0000	0.0000	-2.9033
C_4N_2 (2-Butynedinitrile) 1 2 2			

C1	0.0000	0.0000	2.5100
C2	0.0000	0.0000	3.7000
C3	0.0000	0.0000	1.1400
C4	0.0000	0.0000	5.0700
N5	0.0000	0.0000	0.0000
N6	0.0000	0.0000	6.2100
C_2N_2 (Cyanogen) 1 2 2			
C1	0.0000	0.0000	0.6950
C2	0.0000	0.0000	-0.6950
N3	0.0000	0.0000	1.8450
N4	0.0000	0.0000	-1.8450
C_3O_2 (Carbon suboxide) 1 2 2			
C1	0.0000	0.0000	0.0308
C2	0.0000	1.2509	0.0123
C3	0.0000	-1.2509	0.0123
O4	0.0000	2.3964	-0.0207
O5	0.0000	-2.3964	-0.0207
FCN (Cyanogen fluoride) 1 2 2			
C1	0.0000	0.0000	0.0000
F2	0.0000	0.0000	-1.2620
N3	0.0000	0.0000	1.1590
C_4H_2 (Diacetylene) 1 2 2			
C1	0.0000	0.0000	0.6890
C2	0.0000	0.0000	-0.6890
C3	0.0000	0.0000	1.8940
C4	0.0000	0.0000	-1.8940
H5	0.0000	0.0000	2.9520
H6	0.0000	0.0000	-2.9520
H_2CS (Thioformaldehyde) 1 2 2			

S1	0.0000	0.0000	0.5846
C2	0.0000	0.0000	-1.0262
H3	0.0000	0.9244	-1.5980
H4	0.0000	-0.9244	-1.5980
$CHONH_2$ (Formamide) 1 2 2			
C1	0.0000	0.4165	0.0000
O2	1.1942	0.2217	0.0000
N3	-0.9373	-0.5551	0.0000
H4	-0.4299	1.4182	0.0000
H5	-0.6608	-1.5171	0.0000
H6	-1.9020	-0.2881	0.0000
CH_2CHCHO (Acrolein) 1			
C1	-0.1496	-0.7423	0.0000
C2	0.0000	0.7200	0.0000
C3	1.2291	1.2662	0.0000
O4	-1.2313	-1.3044	0.0000
H5	0.8007	-1.3120	0.0000
H6	-0.9066	1.3142	0.0000
H7	1.3716	2.3428	0.0000
H8	2.1072	0.6273	0.0000
CH_2CCl_2 (Ethene, 1,1-dichloro-) 1 2 2			
C1	0.0000	0.0000	1.7363
C2	0.0000	0.0000	0.4123
H3	0.0000	0.9266	2.2713
H4	0.0000	-0.9266	2.2713
Cl5	0.0000	1.4382	-0.5128
Cl6	0.0000	-1.4382	-0.5128
C_2HF_3 (Trifluoroethylene) 1 2 2			
C1	0.0000	0.4436	0.0000

C2	-0.7139	-0.6916	0.0000
F3	1.3153	0.4857	0.0000
F4	-0.5506	1.6388	0.0000
F5	-0.0873	-1.8784	0.0000
H6	-1.8133	-0.7269	0.0000
CH_2CF_2 (Ethene, 1,1-difluoro-) 1 2 2			
C1	0.0000	0.0000	1.3851
C2	0.0000	0.0000	0.0701
H3	0.0000	0.9419	1.9094
H4	0.0000	-0.9419	1.9094
F5	0.0000	1.0777	-0.6972
F6	0.0000	-1.0777	-0.6972
CH_3F (Methyl fluoride) 1 2 2			
C1	0.0000	0.0000	-0.6289
F2	0.0000	0.0000	0.7541
H3	0.0000	1.0201	-1.0043
H4	0.8835	-0.5101	-1.0043
H5	-0.8835	-0.5101	-1.0043
CF_2Cl_2 (Difluorodichloromethane) 1 2 2			
C1	0.0000	0.0000	0.3171
F2	0.0000	1.0758	1.1243
F3	0.0000	-1.0758	1.1243
Cl4	1.4505	0.0000	-0.6512
Cl5	-1.4505	0.0000	-0.6512
SiF_2 (Silicon difluoride) 1 2 2			
Si1	0.0000	0.0000	0.5703
F2	0.0000	1.2249	-0.4436
F3	0.0000	-1.2249	-0.4436

TABLE S5. Atomic energies (in kcal/mol) from the H atom to the Ar atom [15].

Atom	Reference	ωM05-D	M05-2X	ωB97X-D
H	-313.76	-311.52	-313.31	-315.51
He	-1822.12	-1822.11	-1823.25	-1824.57
Li	-4692.56	-4693.72	-4694.37	-4699.80
Be	-9203.92	-9198.97	-9204.50	-9202.60
B	-15470.58	-15466.17	-15471.98	-15468.00
C	-23748.12	-23746.17	-23752.06	-23745.12
N	-34255.28	-34254.32	-34260.32	-34251.37
O	-47105.50	-47107.44	-47113.72	-47103.64
F	-62584.04	-62587.59	-62593.80	-62583.06
Ne	-80909.66	-80910.31	-80917.57	-80906.81
Na	-101816.42	-101814.09	-101820.46	-101818.06
Mg	-125535.30	-125538.45	-125549.12	-125538.97
Al	-152074.59	-152077.17	-152084.44	-152078.77
Si	-181575.73	-181577.53	-181581.20	-181577.86
P	-214143.51	-214141.04	-214140.76	-214140.27
S	-249818.09	-249817.74	-249815.58	-249817.21
Cl	-288747.57	-288747.04	-288743.15	-288746.55
Ar	-331036.74	-331035.35	-331028.07	-331036.25
MSE		0.37	-3.01	-0.05
MAE		2.02	5.10	2.51
rms		2.42	6.31	2.96

TABLE S6. Non-hydrogen transfer barrier heights (in kcal/mol) of the NHTBH38/04 set [16].

Reactions		ΔE_{ref}	ωM05-D	M05-2X	ωB97X-D
Heavy-atom transfer reactions					
$H + N_2O \rightarrow OH + N_2$	V^f	18.14	16.52	18.82	17.47
	V^r	83.22	80.54	85.45	77.75
$H + FH \rightarrow HF + H$	V^f	42.18	38.34	41.16	40.56
	V^r	42.18	38.34	41.16	40.56
$H + ClH \rightarrow HCl + H$	V^f	18.00	17.83	19.64	18.19
	V^r	18.00	17.83	19.64	18.19
$H + FCH_3 \rightarrow HF + CH_3$	V^f	30.38	28.76	31.70	30.02
	V^r	57.02	54.26	55.28	54.47
$H + F_2 \rightarrow HF + F$	V^f	2.27	-0.07	2.90	-0.60
	V^r	106.18	106.50	114.64	103.96
$CH_3 + FCl \rightarrow CH_3F + Cl$	V^f	7.43	4.22	4.04	2.76
	V^r	60.17	57.63	59.94	56.55
Nucleophilic substitution reactions					
$F^- + CH_3F \rightarrow FCH_3 + F^-$	V^f	-0.34	-1.79	-1.93	-1.37
	V^r	-0.34	-1.79	-1.93	-1.37
$F^- \cdots CH_3F \rightarrow FCH_3 \cdots F^-$	V^f	13.38	12.98	14.01	12.85
	V^r	13.38	12.98	14.01	12.85
$Cl^- + CH_3Cl \rightarrow ClCH_3 + Cl^-$	V^f	3.10	2.29	0.75	3.70
	V^r	3.10	2.29	0.75	3.70
$Cl^- \cdots CH_3Cl \rightarrow ClCH_3 \cdots Cl^-$	V^f	13.61	12.85	12.01	14.30
	V^r	13.61	12.85	12.01	14.30
$F^- + CH_3Cl \rightarrow FCH_3 + Cl^-$	V^f	-12.54	-14.38	-15.89	-13.58
	V^r	20.11	21.65	21.86	21.26
$F^- \cdots CH_3Cl \rightarrow FCH_3 \cdots Cl^-$	V^f	2.89	2.41	2.13	3.07
	V^r	29.62	31.11	31.97	30.50
$OH^- + CH_3F \rightarrow HOCH_3 + F^-$	V^f	-2.78	-3.96	-4.22	-3.31
	V^r	17.33	16.05	15.54	17.90
$OH^- \cdots CH_3F \rightarrow HOCH_3 \cdots F^-$	V^f	10.96	10.32	11.14	10.57
	V^r	47.20	49.33	48.84	49.20
Unimolecular and association reactions					
$H + N_2 \rightarrow HN_2$	V^f	14.69	11.94	14.65	12.32
	V^r	10.72	12.01	13.07	13.40
$H + CO \rightarrow HCO$	V^f	3.17	2.91	4.96	3.37
	V^r	22.68	24.38	25.23	26.20
$H + C_2H_4 \rightarrow CH_3CH_2$	V^f	1.72	2.46	3.68	3.03
	V^r	41.75	44.44	44.88	45.37
$CH_3 + C_2H_4 \rightarrow CH_3CH_2CH_2$	V^f	6.85	4.13	4.09	4.57
	V^r	32.97	33.17	32.57	33.85
$HCN \rightarrow HNC$	V^f	48.16	44.78	46.45	46.42
	V^r	33.11	31.56	33.10	33.27
MSE			-0.94	0.13	-0.45
MAE			1.57	1.75	1.51
rms			1.89	2.24	2.00

TABLE S7. Hydrogen transfer barrier heights (in kcal/mol) of the HTBH38/04 set [16, 17].

Reactions		ΔE_{ref}	ωM05-D	M05-2X	ωB97X-D
$H + HCl \rightarrow H_2 + Cl$	V^f	5.7	3.61	4.82	4.08
	V^r	8.7	4.68	5.94	4.58
$OH + H_2 \rightarrow H + H_2O$	V^f	5.1	1.94	4.61	2.22
	V^r	21.2	18.69	21.90	18.77
$CH_3 + H_2 \rightarrow H + CH_4$	V^f	12.1	9.14	11.72	9.06
	V^r	15.3	13.35	16.07	13.54
$OH + CH_4 \rightarrow CH_3 + H_2O$	V^f	6.7	2.53	4.69	3.04
	V^r	19.6	15.06	17.64	15.11
$H + H_2 \rightarrow H_2 + H$	V^f	9.6	8.83	12.66	9.21
	V^r	9.6	8.83	12.66	9.21
$OH + NH_3 \rightarrow H_2O + NH_2$	V^f	3.2	-0.14	2.67	-0.02
	V^r	12.7	9.73	12.41	9.69
$HCl + CH_3 \rightarrow Cl + CH_4$	V^f	1.7	-1.60	-1.30	-1.86
	V^r	7.9	3.69	4.17	3.11
$OH + C_2H_6 \rightarrow H_2O + C_2H_5$	V^f	3.4	-0.28	2.19	0.17
	V^r	19.9	16.88	19.24	16.57
$F + H_2 \rightarrow HF + H$	V^f	1.8	-2.22	0.10	-3.70
	V^r	33.4	30.78	33.40	29.01
$O + CH_4 \rightarrow OH + CH_3$	V^f	13.7	8.85	10.62	9.20
	V^r	8.1	4.39	5.50	4.67
$H + PH_3 \rightarrow PH_2 + H_2$	V^f	3.1	2.21	4.25	3.28
	V^r	23.2	23.45	25.62	23.46
$H + HO \rightarrow H_2 + O$	V^f	10.7	7.90	10.38	8.84
	V^r	13.1	8.15	11.16	8.89
$H + H_2S \rightarrow H_2 + HS$	V^f	3.5	3.24	5.42	4.05
	V^r	17.3	16.10	18.21	16.31
$O + HCl \rightarrow OH + Cl$	V^f	9.8	4.95	7.01	5.47
	V^r	10.4	5.78	7.35	5.91
$NH_2 + CH_3 \rightarrow CH_4 + NH$	V^f	8.0	5.41	7.10	5.65
	V^r	22.4	18.17	20.33	18.41
$NH_2 + C_2H_5 \rightarrow C_2H_6 + NH$	V^f	7.5	7.09	8.56	7.26
	V^r	18.3	15.22	17.68	15.69
$C_2H_6 + NH_2 \rightarrow NH_3 + C_2H_5$	V^f	10.4	7.97	10.11	8.60
	V^r	17.4	15.26	17.42	15.29
$NH_2 + CH_4 \rightarrow CH_3 + NH_3$	V^f	14.5	10.81	12.71	11.28
	V^r	17.8	13.47	15.91	13.65
s−trans cis−$C_5H_8 \rightarrow$ s−trans cis−C_5H_8	V^f	38.4	37.23	39.06	39.07
	V^r	38.4	37.23	39.06	39.07
MSE			-2.82	-0.65	-2.57
MAE			2.83	1.51	2.70
rms			3.16	1.83	3.10

TABLE S8. Interaction energies (in kcal/mol) for the S22 set with new reference values. [18] The counterpoise corrections are used to reduce the basis set superposition errors. Monomer deformation energies are not included.

Complex [Symmetry]	ΔE_{ref}	ωM05-D	M05-2X	ωB97X-D
Hydrogen bonded complexes				
$(NH_3)_2[C_{2h}]$	-3.133	-3.00	-3.12	-3.08
$(H_2O)_2[C_s]$	-4.989	-4.89	-5.08	-4.97
Formic acid dimer $[C_{2h}]$	-18.753	-18.98	-19.41	-19.28
Formamide dimer $[C_{2h}]$	-16.062	-15.65	-15.81	-16.17
Uracil dimer $[C_{2h}]$	-20.641	-19.90	-19.64	-20.43
2-pyridoxine·2-aminopyridine $[C_1]$	-16.934	-16.40	-15.36	-17.06
Adenine·thymine WC $[C_1]$	-16.660	-15.87	-14.84	-16.46
MSE		0.35	0.56	-0.04
MAE		0.42	0.77	0.18
Dispersion complexes				
$(CH_4)_2[D_{3d}]$	-0.527	-0.65	-0.51	-0.57
$(C_2H_4)_2[D_{2d}]$	-1.472	-1.70	-1.42	-1.79
Benzene·$CH_4[C_3]$	-1.448	-1.68	-1.13	-1.70
Benzene dimer $[C_{2h}]$	-2.654	-3.55	-1.38	-3.16
Pyrazine dimer $[C_s]$	-4.255	-4.40	-2.95	-4.27
Uracil dimer $[C_2]$	-9.805	-9.83	-8.32	-9.79
Indole·benzene $[C_1]$	-4.524	-5.47	-2.57	-5.10
Adenine·thymine stack $[C_1]$	-11.730	-12.00	-9.40	-11.86
MSE		-0.36	1.09	-0.23
MAE		0.36	1.09	0.23
Mixed complexes				
Ethene·ethine $[C_{2v}]$	-1.496	-1.52	-1.44	-1.63
Benzene·H2O $[C_s]$	-3.275	-3.60	-3.57	-3.50
Benzene·NH3 $[C_s]$	-2.312	-2.54	-2.23	-2.53
Benzene·HCN $[C_s]$	-4.541	-4.76	-4.90	-4.79
Benzene dimer $[C_{2v}]$	-2.717	-2.88	-1.97	-2.89
Indole·benzene T-shape $[C_1]$	-5.627	-5.85	-4.76	-5.64
Phenol dimer $[C_1]$	-7.097	-6.89	-6.03	-6.99
MSE		-0.14	0.31	-0.13
MAE		0.20	0.50	0.16
MSE		-0.06	0.67	-0.14
MAE		0.33	0.80	0.19
rms		0.42	1.06	0.25

TABLE S9. Comparison of errors of different functionals for the reaction energies (in kcal/mol) of the 30 chemical reactions in the NHTBH38/04 and HTBH38/04 database [16, 17].

Reactions	ΔE_{ref}	ωM05-D	M05-2X	ωB97X-D
$H + N_2O \rightarrow OH + N_2$	-65.08	-64.03	-66.63	-60.28
$H + FCH_3 \rightarrow HF + CH_3$	-26.64	-25.50	-23.58	-24.44
$H + F_2 \rightarrow HF + F$	-103.91	-106.58	-111.74	-104.56
$CH_3 + FCl \rightarrow CH_3F + Cl$	-52.74	-53.41	-55.90	-53.79
$F^- + CH_3Cl \rightarrow FCH_3 + Cl^-$	-32.65	-36.03	-37.75	-34.84
$F^- \cdots CH_3Cl \rightarrow FCH_3 \cdots Cl^-$	-26.73	-28.71	-29.84	-27.43
$OH^- + CH_3F \rightarrow HOCH_3 + F^-$	-20.11	-20.02	-19.76	-21.21
$OH^- \cdots CH_3F \rightarrow HOCH_3 \cdots F^-$	-36.24	-39.01	-37.70	-38.63
$H + N_2 \rightarrow HN_2$	3.97	-0.07	1.58	-1.09
$H + CO \rightarrow HCO$	-19.51	-21.47	-20.27	-22.83
$H + C_2H_4 \rightarrow CH_3CH_2$	-40.03	-41.98	-41.20	-42.35
$CH_3 + C_2H_4 \rightarrow CH_3CH_2CH_2$	-26.12	-29.04	-28.48	-29.28
$HCN \rightarrow HNC$	15.05	13.22	13.35	13.16
$H + HCl \rightarrow H_2 + Cl$	-3.0	-1.08	-1.12	-0.49
$OH + H_2 \rightarrow H + H_2O$	-16.1	-16.75	-17.29	-16.55
$CH_3 + H_2 \rightarrow H + CH_4$	-3.2	-4.22	-4.35	-4.48
$OH + CH_4 \rightarrow CH_3 + H_2O$	-12.9	-12.53	-12.94	-12.07
$OH + NH_3 \rightarrow H_2O + NH_2$	-9.5	-9.87	-9.75	-9.71
$HCl + CH_3 \rightarrow Cl + CH_4$	-6.2	-5.29	-5.47	-4.98
$OH + C_2H_6 \rightarrow H_2O + C_2H_5$	-16.5	-17.16	-17.06	-16.40
$F + H_2 \rightarrow HF + H$	-31.6	-33.00	-33.29	-32.71
$O + CH_4 \rightarrow OH + CH_3$	5.6	4.46	5.13	4.53
$H + PH_3 \rightarrow PH_2 + H_2$	-20.1	-21.25	-21.37	-20.18
$H + HO \rightarrow H_2 + O$	-2.4	-0.25	-0.78	-0.05
$H + H_2S \rightarrow H_2 + HS$	-13.8	-12.87	-12.79	-12.25
$O + HCl \rightarrow OH + Cl$	-0.6	-0.83	-0.34	-0.45
$NH_2 + CH_3 \rightarrow CH_4 + NH$	-14.4	-12.76	-13.23	-12.76
$NH_2 + C_2H_5 \rightarrow C_2H_6 + NH$	-10.8	-8.13	-9.11	-8.43
$C_2H_6 + NH_2 \rightarrow NH_3 + C_2H_5$	-7.0	-7.29	-7.31	-6.69
$NH_2 + CH_4 \rightarrow CH_3 + NH_3$	-3.3	-2.66	-3.20	-2.37
MSE		-0.58	-0.86	-0.24
MAE		1.49	1.65	1.63
rms		1.79	2.29	2.06

TABLE S10. Binding energies (in kcal/mol) of several sets of noncovalent interactions. The first three sets are taken from Ref. [19] with monomer deformation energies taken into considerations. The last three sets are taken from Ref. [20] without considering monomer deformation energies. The counter-point corrections are applied for all the cases.

Complex	ΔE_{ref}	ωM05-D	M05-2X	ωB97X-D
Charge-transfer complexes				
$C_2H_4\cdots F_2$	1.06	0.79	1.00	0.78
$NH_3\cdots F_2$	1.81	1.41	1.44	1.50
$C_2H_2\cdots ClF$	3.81	3.82	4.51	3.66
$HCN\cdots ClF$	4.86	4.21	4.72	4.21
$NH_3\cdots Cl_2$	4.88	4.61	5.02	4.81
$H_2O\cdots ClF$	5.36	5.21	5.83	5.18
$NH_3\cdots ClF$	10.62	10.64	11.07	11.12
MSE		-0.24	0.17	-0.16
MAE		0.25	0.33	0.31
Dipole-dipole interaction complexes				
$H_2S\cdots H_2S$	1.66	1.44	1.42	1.54
$HCl\cdots HCl$	2.01	1.62	1.71	1.69
$H_2S\cdots HCl$	3.35	3.26	3.23	3.38
$CH_3Cl\cdots HCl$	3.55	3.08	3.24	3.17
$HCN\cdots CH_3SH$	3.59	3.68	3.65	3.72
$CH_3SH\cdots HCl$	4.16	4.82	4.84	4.87
MSE		-0.07	-0.04	0.01
MAE		0.32	0.28	0.28
Weak interaction complexes				
$He\cdots Ne$	0.04	-0.02	0.04	0.00
$He\cdots Ar$	0.06	-0.03	0.07	0.00
$Ne\cdots Ne$	0.08	-0.03	0.07	-0.02
$Ne\cdots Ar$	0.13	-0.02	0.13	-0.01
$CH_4\cdots Ne$	0.22	0.13	0.20	0.13
$C_6H_6\cdots Ne$	0.47	0.44	0.62	0.24
$CH_4\cdots CH_4$	0.51	0.68	0.51	0.60
MSE		-0.05	0.02	-0.08
MAE		0.10	0.03	0.11
Hydrogen-bonded DNA base pairs				
G$\cdots$A HB	-11.30	-12.63	-10.82	-13.48
C$\cdots$G WC	-30.70	-31.42	- -30.66	-32.45
G$\cdots$C WC	-31.40	-31.34	-30.67	-32.28
MSE		-0.67	0.42	-1.60
MAE		0.70	0.42	1.60
Interstrand base pairs				
G$\cdots$G IS	-5.20	-5.38	-4.80	-5.43
G$\cdots$G IS	0.80	0.88	2.38	1.15
C$\cdots$C IS	3.10	3.34	3.75	3.29
MSE		0.04	0.88	0.10
MAE		0.17	0.88	0.25
Stacked base pairs				
A$\cdots$G S	-6.50	-6.84	-3.61	-6.66
C$\cdots$G S	-12.40	-11.09	-8.57	-10.83
G$\cdots$C S	-11.60	-11.26	-8.78	-11.06
MSE		0.44	3.18	0.65
MAE		0.66	3.18	0.76
MSE		-0.11	0.50	-0.15
MAE		0.31	0.61	0.43

[1] NIST Computational Chemistry Comparison and Benchmark Database, NIST Standard Reference Database Number 101, Release 15b, August 2011, Editor: Russell D. Johnson III, http://cccbdb.nist.gov/.

[2] P. M. W. Gill, B. G. Johnson, J. A. Pople, and M. J. Frisch, Int. J. Quantum Chem. Symp. **26**, 319 (1992).

[3] C. R. Brundle, M. B. Robin, N. A. Kuebler, and H. J. Basch, J. Am. Chem. Soc. **94**, 1451 (1972).

[4] W. von Niessen, L. Åsbrink, and G. Bieri, J. Electron Spectrosc. Relat. Phenom. **26**, 173 (1982).

[5] E. A. Colbourne, J. M. Dyke, E. P. F. Lee, A. Morris, and I. R. Trickle, Mol. Phys. **35**, 873 (1978).

[6] D. C. Frost, S. T. Lee, and C. A. McDowell, Chem. Phys. Lett. **17**, 153 (1972).

[7] G. Bieri, L. Åsbrink, and W. von Niessen, J. Electron Spectrosc. Relat. Phenom. **27**, 129 (1982).

[8] T. Cvitas, H. Güsten, L. Klasinc, I. Novak, and H. Vansik, Z. Naturforsch. A **32A**, 1528 (1977).

[9] G. Bieri, L. Åsbrink, and W. von Niessen, J. Electron Spectrosc. Relat. Phenom. **23**, 281 (1981).

[10] L. Åsbrink, W. von Niessen, and G. Bieri, J. Electron Spectrosc. Relat. Phenom. **21**, 93 (1980).

[11] U. Gelius, C. J. Allan, D. A. Allison, H. Siegbahn, and K. Siegbahn, Chem. Phys. Lett. **11**, 224 (1971).

[12] L. Åsbrink, A. Svensson, W. von Niessen, and G. Bieri, J. Electron Spectrosc. Relat. Phenom. **24**, 293 (1981).

[13] G. Bieri and L. Åsbrink, J. Electron Spectrosc. Relat. Phenom. **20**, 149 (1980).

[14] W. von Niessen, G. Bieri, and L. Åsbrink, J. Electron Spectrosc. Relat. Phenom. **21**, 175 (1980).

[15] S. J. Chakravorty, S. R. Gwaltney, E. R. Davidson, F. A. Parpia, and C. F. Fischer, Phys. Rev. A **47**, 3649 (1993).

[16] Y. Zhao, N. González-García, and D. G. Truhlar, J. Phys. Chem. A **109**, 2012 (2005); **110**, 4942(E) (2006).

[17] Y. Zhao, B. J. Lynch, and D. G. Truhlar, J. Phys. Chem. A **108**, 2715 (2004).

[18] M. S. Marshall, L. A. Burns, and C. D. Sherrill, J. Chem. Phys. **135**, 194102 (2011).

[19] Y. Zhao and D. G. Truhlar, J. Phys. Chem. A **109**, 5656 (2005).

[20] P. Jurečka, J. Šponer, J. Černý, and P. Hobza, Phys. Chem. Chem. Phys. **8**, 1985 (2006).