# Supporting information to: Long-range corrected hybrid density functionals with improved dispersion corrections

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TABLE S1: -$\epsilon_N(N)$ (in eV) by DFT methods in the IP131 database. [1]

| Molecule | Reference | $\omega$M06-D3 | $\omega$B97X-D3 | M06-2X |
|---|---|---|---|---|
| H (Hydrogen atom) | 13.60 | 11.67 | 11.37 | 10.31 |
| He (Helium atom) | 24.59 | 21.24 | 20.62 | 20.56 |
| Li (Lithium atom) | 5.39 | 5.25 | 5.30 | 4.19 |
| Be (Beryllium atom) | 9.32 | 8.57 | 8.49 | 7.26 |
| B (Boron atom) | 8.30 | 7.70 | 7.51 | 6.17 |
| C (Carbon atom) | 11.26 | 10.23 | 9.87 | 8.84 |
| N (Nitrogen atom) | 14.53 | 12.92 | 12.46 | 11.78 |
| O (Oxygen atom) | 13.62 | 12.29 | 11.83 | 11.21 |
| F (Fluorine atom) | 17.42 | 15.53 | 14.96 | 14.82 |
| Ne (Neon atom) | 21.57 | 19.01 | 18.39 | 18.66 |
| Na (Sodium atom) | 5.14 | 5.09 | 4.92 | 4.19 |
| Mg (Magnesium atom) | 7.65 | 7.32 | 7.21 | 6.17 |
| Al (Aluminum atom) | 5.99 | 5.63 | 5.66 | 4.30 |
| Si (Silicon atom) | 8.15 | 7.64 | 7.56 | 6.26 |
| P (Phosphorus atom) | 10.49 | 9.76 | 9.55 | 8.35 |
| S (Sulfur atom) | 10.36 | 9.79 | 9.60 | 8.51 |
| Cl (Chlorine atom) | 12.97 | 12.21 | 11.89 | 10.96 |
| Ar (Chlorine atom) | 15.76 | 14.66 | 14.28 | 13.57 |
| $CH_3$ (Methyl radical) | 9.84 | 9.14 | 8.89 | 7.83 |
| $CH_4$ (Methane) | 13.60 | 13.65 | 13.33 | 12.43 |
| NH (Imidogen) | 13.49 | 12.35 | 11.97 | 11.26 |
| $NH_2$ (Amino radical) | 12.00 | 11.45 | 11.07 | 10.28 |
| $NH_3$ (Ammonia) | 10.82 | 10.42 | 10.06 | 9.30 |
| OH (Hydroxyl radical) | 13.02 | 12.08 | 11.59 | 11.07 |
| $H_2O$ (Water) | 12.62 | 11.91 | 11.45 | 10.96 |
| HF (Hydrogen fluoride) | 16.12 | 14.77 | 14.23 | 14.06 |
| $SiH_3$ (Silyl) | 8.74 | 8.57 | 8.40 | 7.21 |
| $SiH_4$ (Silane) | 12.30 | 12.38 | 12.13 | 11.07 |

| | | | | |
|---|---|---|---|---|
| $PH_3$ (Phosphine) | 10.59 | 10.23 | 10.04 | 8.95 |
| $H_2S$ (Hydrogen sulfide) | 10.50 | 10.04 | 9.76 | 8.76 |
| HCl (Hydrogen chloride) | 12.77 | 12.13 | 11.78 | 10.91 |
| $C_2H_2$ (Acetylene) | 11.49 | 11.02 | 10.66 | 9.74 |
| $C_2H_4$ (Ethylene) | 10.68 | 10.39 | 10.04 | 9.08 |
| $C_2H_6$ (Ethane) | 11.99 | 12.16 | 11.89 | 10.99 |
| HCN (Hydrogen cyanide) | 13.61 | 13.03 | 12.68 | 11.80 |
| CO (Carbon monoxide) | 14.01 | 13.49 | 13.14 | 12.29 |
| HCO (Formyl radical) | 9.31 | 9.22 | 8.92 | 8.05 |
| $CH_2O$ (Formaldehyde) | 10.89 | 10.50 | 10.12 | 9.52 |
| $CH_3OH$ (Methyl alcohol) | 10.96 | 10.64 | 10.23 | 9.66 |
| $N_2$ (Nitrogen diatomic) | 15.58 | 15.07 | 14.63 | 13.98 |
| $N_2H_4$ (Hydrazine) | 8.98 | 9.44 | 9.11 | 8.38 |
| NO (Nitric oxide) | 9.26 | 9.08 | 8.68 | 8.05 |
| $O_2$ (Oxygen diatomic) | 12.30 | 11.80 | 11.32 | 11.04 |
| $H_2O_2$ (Hydrogen peroxide) | 11.70 | 11.15 | 10.72 | 10.28 |
| $F_2$ (Fluorine diatomic) | 15.70 | 14.77 | 14.23 | 14.23 |
| $CO_2$ (Carbon dioxide) | 13.78 | 13.27 | 12.95 | 12.32 |
| $P_2$ (Phosphorus diatomic) | 10.62 | 10.28 | 10.15 | 9.03 |
| $S_2$ (Sulfur diatomic) | 9.55 | 9.38 | 9.19 | 8.13 |
| $Cl_2$ (Chlorine diatomic) | 11.49 | 11.23 | 10.93 | 10.09 |
| NaCl (Sodium Chloride) | 9.80 | 9.03 | 8.70 | 7.83 |
| SiO (Silicon monoxide) | 11.61 | 11.29 | 11.04 | 10.09 |
| CS (Carbon monosulfide) | 11.34 | 11.51 | 11.23 | 10.20 |
| ClO (Monochlorine monoxide) | 11.01 | 10.58 | 10.23 | 9.49 |
| ClF (Chlorine monofluoride) | 12.77 | 12.13 | 11.78 | 11.04 |
| $Si_2H_6$ (Disilane) | 10.53 | 10.55 | 10.39 | 9.28 |
| $CH_3Cl$ (Methyl chloride) | 11.29 | 11.07 | 10.74 | 9.87 |
| $CH_3SH$ (Methanethiol) | 9.44 | 9.22 | 8.98 | 8.00 |
| $SO_2$ (Sulfur dioxide) | 12.50 | 12.21 | 11.89 | 11.15 |
| $BF_3$ (Borane, trifluoro-) | 15.96 | 15.10 | 14.58 | 14.50 |

| | | | | |
|---|---|---|---|---|
| $BCl_3$ (Borane, trichloro-) | 11.64 | 11.64 | 11.34 | 10.50 |
| $AlCl_3$ (Aluminum trichloride) | 12.01 | 11.91 | 11.61 | 10.77 |
| $CF_4$ (Carbon tetrafluoride) | 16.20 | 15.53 | 15.01 | 14.96 |
| $CCl_4$ Carbon tetrachloride) | 11.69 | 11.64 | 11.32 | 10.50 |
| OCS (Carbonyl sulfide) | 11.19 | 10.99 | 10.80 | 9.85 |
| $CS_2$ (Carbon disulfide) | 10.09 | 9.93 | 9.79 | 8.84 |
| $CF_2O$ (Carbonic difluoride) | 13.60 | 13.14 | 12.70 | 12.32 |
| $SiF_4$ (Silicon tetrafluoride) | 16.40 | 15.67 | 15.15 | 15.01 |
| $N_2O$ (Nitrous oxide) | 12.89 | 12.29 | 12.02 | 11.29 |
| $NF_3$ (Nitrogen trifluoride) | 13.60 | 13.00 | 12.62 | 12.13 |
| $PF_3$ (Phosphorus trifluoride) | 12.20 | 11.18 | 10.99 | 10.04 |
| $O_3$ (Ozone) | 12.73 | 12.76 | 12.29 | 11.67 |
| $F_2O$ (Difluorine monoxide) | 13.26 | 12.89 | 12.35 | 12.21 |
| $ClF_3$ (Chlorine trifluoride) | 13.05 | 12.59 | 12.19 | 11.72 |
| $C_2F_4$ (Tetrafluoroethylene) | 10.69 | 10.28 | 9.98 | 9.25 |
| $CF_3CN$ (Acetonitrile, trifluoro-) | 14.30 | 13.68 | 13.33 | 12.54 |
| $CH_3CCH$ (Propyne) | 10.37 | 10.20 | 9.90 | 8.98 |
| $CH_2CCH_2$ (Allene) | 10.20 | 10.17 | 9.87 | 8.95 |
| $C_3H_4$ (Cyclopropene) | 9.86 | 9.68 | 9.38 | 8.51 |
| $C_3H_6$ (Cyclopropane) | 10.54 | 10.91 | 10.58 | 9.60 |
| $C_3H_8$ (Propane) | 11.51 | 11.67 | 11.40 | 10.53 |
| $CH_3CCCH_3$ (2-Butyne) | 9.79 | 9.55 | 9.28 | 8.38 |
| $C_4H_6$ (Cyclobutene) | 9.43 | 9.55 | 9.28 | 8.35 |
| $CH_3CH(CH_3)CH_3$ (Isobutane) | 11.13 | 11.45 | 11.15 | 10.25 |
| $C_6H_6$ (Benzene) | 9.25 | 9.55 | 9.30 | 8.40 |
| $CH_2F_2$ (Methane, difluoro-) | 13.27 | 12.65 | 12.29 | 11.75 |
| $CHF_3$ (Methane, trifluoro-) | 15.50 | 13.90 | 13.52 | 13.06 |
| $CH_2Cl_2$ (Methylene chloride) | 11.40 | 11.34 | 11.02 | 10.17 |
| $CHCl_3$ (Chloroform) | 11.50 | 11.34 | 11.02 | 10.20 |
| $CH_3NO_2$ (Methane, nitro-) | 11.29 | 11.48 | 11.04 | 10.64 |
| $CH_3SiH_3$ (Methyl silane) | 11.60 | 11.70 | 11.42 | 10.36 |

| | | | | |
|---|---|---|---|---|
| HCOOH (Formic acid) | 11.50 | 11.07 | 10.66 | 10.12 |
| $CH_3CONH_2$ (Acetamide) | 10.00 | 10.06 | 9.66 | 9.08 |
| $C_2H_5N$ (Aziridine) | 9.85 | 9.74 | 9.41 | 8.62 |
| $C_2N_2$ (Cyanogen) | 13.51 | 13.14 | 12.84 | 12.00 |
| $CH_3NHCH_3$ (Dimethylamine) | 8.95 | 8.98 | 8.68 | 7.92 |
| $CH_2CO$ (Ketene) | 9.64 | 9.55 | 9.28 | 8.38 |
| $C_2H_4O$ (Ethylene oxide) | 10.57 | 10.64 | 10.20 | 9.71 |
| $C_2H_2O_2$ (Ethanedial) | 10.60 | 10.53 | 10.17 | 9.49 |
| $CH_3CH_2OH$ (Ethanol) | 10.64 | 10.50 | 10.12 | 9.49 |
| $CH_3OCH_3$ (Dimethyl ether) | 10.10 | 10.04 | 9.66 | 9.03 |
| $C_2H_4S$ (Thiirane) | 9.05 | 9.00 | 8.76 | 7.81 |
| $CH_3SOCH_3$ (Dimethyl sulfoxide) | 9.10 | 9.14 | 8.84 | 8.05 |
| $CH_2CHF$ (Ethene, fluoro-) | 10.63 | 10.25 | 9.96 | 9.06 |
| $CH_3CH_2Cl$ (Ethyl chloride) | 11.06 | 10.91 | 10.61 | 9.74 |
| $CH_2CHCl$ (Ethene, chloro-) | 10.20 | 9.98 | 9.68 | 8.79 |
| $CH_3CClO$ (Acetyl Chloride) | 11.03 | 11.15 | 10.80 | 10.15 |
| $CH_2ClCH_2CH_3$ (Propane, 1-chloro-) | 10.88 | 10.88 | 10.55 | 9.68 |
| $N(CH_3)_3$ (Trimethylamine) | 8.54 | 8.65 | 8.35 | 7.56 |
| $C_4H_4O$ (Furan) | 8.90 | 9.03 | 8.76 | 7.83 |
| $C_4H_5N$ (Pyrrole) | 8.23 | 8.40 | 8.16 | 7.26 |
| $NO_2$ (Nitrogen dioxide) | 11.23 | 11.10 | 10.69 | 10.15 |
| $SF_6$ (Sulfur Hexafluoride) | 15.70 | 15.23 | 14.72 | 14.72 |
| $CFCl_3$ (Trichloromonofluoromethane) | 11.76 | 11.70 | 11.40 | 10.58 |
| $CF_3Cl$ (Methane, chlorotrifluoro-) | 13.08 | 12.73 | 12.40 | 11.61 |
| $CF_3Br$ (Bromotrifluoromethane) | 12.08 | 11.67 | 11.42 | 10.55 |
| HCCF (Fluoroacetylene) | 11.50 | 10.91 | 10.58 | 9.71 |
| HCCCN (Cyanoacetylene) | 11.75 | 11.42 | 11.12 | 10.28 |
| $C_4N_2$ (2-Butynedinitrile) | 11.84 | 11.86 | 11.61 | 10.80 |
| $C_2N_2$ (Cyanogen) | 13.51 | 13.14 | 12.84 | 12.00 |
| $C_3O_2$ (Carbon suboxide) | 10.80 | 10.64 | 10.44 | 9.66 |
| FCN (Cyanogen fluoride) | 13.65 | 12.84 | 12.48 | 11.70 |

| | | | | |
|---|---|---|---|---|
| $C_4N_2$ (Diacetylene) | 10.30 | 10.06 | 9.79 | 8.89 |
| $H_2CS$ (Thioformaldehyde) | 9.38 | 9.17 | 8.92 | 7.97 |
| $CHONH_2$ (Formamide) | 10.40 | 10.28 | 9.90 | 9.36 |
| $CH_2CHCHO$ (Acrolein) | 10.10 | 10.31 | 9.90 | 9.30 |
| $CH_2CCl_2$ (Ethene, 1,1-dichloro-) | 10.00 | 9.96 | 9.71 | 8.79 |
| $C_2HF_3$ (Trifluoroethylene) | 10.62 | 10.06 | 9.79 | 8.98 |
| $CH_2CF_2$ (Ethene, 1,1-difluoro-) | 10.70 | 10.36 | 10.06 | 9.22 |
| $CH_3F$ (Methyl fluoride) | 13.04 | 12.62 | 12.21 | 11.70 |
| $CF_2Cl_2$ (Difluorodichloromethane) | 12.24 | 12.10 | 11.78 | 10.96 |
| $SiF_2$ (Silicon difluoride) | 11.08 | 10.64 | 10.50 | 9.41 |
| MSE | | -0.39 | -0.72 | -1.48 |
| MAE | | 0.45 | 0.72 | 1.48 |
| rms | | 0.66 | 0.93 | 1.57 |

TABLE S2: $-\epsilon_{N+1}(N+1)$ and $-\epsilon_{N+1}(N)$ (in eV) by DFT methods in the EA115 database. [1]

| | Reference | ωM06-D3 | | ωB97X-D3 | | M06-2X | |
|---|---|---|---|---|---|---|---|
| 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 | 1.12 | -0.52 | 1.03 | -0.53 | -0.33 | -0.52 |
| He (Helium atom) | -2.63 | -4.22 | -6.12 | -4.16 | -4.38 | -5.22 | -2.67 |
| Li (Lithium atom) | 0.62 | 0.71 | -0.60 | 0.71 | -0.24 | -0.16 | 0.24 |
| Be (Beryllium atom) | -0.36 | -0.35 | -0.79 | -0.35 | -0.44 | -1.28 | 0.54 |
| B (Boron atom) | 0.25 | 0.54 | 0.08 | 0.30 | 0.33 | -0.76 | 1.39 |
| C (Carbon atom) | 1.25 | 1.36 | 1.36 | 0.98 | 1.66 | -0.11 | 2.72 |
| N (Nitrogen atom) | -0.22 | -0.14 | -0.14 | -0.35 | 0.22 | -1.60 | 1.71 |
| O (Oxygen atom) | 1.45 | 1.28 | 1.71 | 0.87 | 2.15 | -0.03 | 3.05 |
| F (Fluorine atom) | 3.44 | 2.75 | 3.94 | 2.28 | 4.57 | 1.69 | 4.76 |
| Ne (Neon atom) | -5.31 | -7.15 | -7.81 | -7.34 | -6.99 | -7.97 | -5.17 |
| Na (Sodium atom) | 0.54 | 0.71 | -0.73 | 0.68 | -0.27 | -0.14 | 0.16 |
| Mg (Magnesium atom) | -0.23 | -0.41 | -0.92 | -0.30 | -0.46 | -1.03 | 0.33 |
| Al (Aluminum atom) | 0.45 | 0.52 | 0.00 | 0.41 | 0.19 | -0.57 | 1.25 |
| Si (Silicon atom) | 1.42 | 1.44 | 1.17 | 1.25 | 1.31 | 0.11 | 2.39 |
| P (Phosphorus atom) | 0.74 | 0.87 | 0.60 | 0.79 | 0.98 | -0.35 | 2.39 |
| S (Sulfur atom) | 2.10 | 2.18 | 2.20 | 1.96 | 2.50 | 0.84 | 3.51 |
| Cl (Chlorine atom) | 3.69 | 3.51 | 3.94 | 3.21 | 4.27 | 2.20 | 5.09 |
| Ar (Chlorine atom) | -2.81 | -3.24 | -4.24 | -3.43 | -3.51 | -3.92 | -2.09 |
| $CH_3$ (Methyl radical) | -0.07 | 0.19 | -0.49 | 0.03 | -0.19 | -1.06 | 1.20 |
| $CH_4$ (Methane) | -0.62 | -0.95 | -2.31 | -0.95 | -1.20 | -1.50 | -0.08 |
| NH (Imidogen) | 0.33 | 0.44 | 0.16 | 0.14 | 0.54 | -0.95 | 1.80 |
| $NH_2$ (Amino radical) | 0.74 | 0.84 | 0.46 | 0.54 | 0.82 | -0.46 | 1.93 |
| $NH_3$ (Ammonia) | -0.56 | -0.92 | -2.34 | -0.92 | -1.17 | -1.58 | 0.08 |
| OH (Hydroxyl radical) | 1.83 | 1.69 | 1.74 | 1.28 | 2.20 | 0.46 | 2.94 |
| $H_2O$ (Water) | -0.56 | -0.95 | -2.31 | -0.92 | -1.17 | -1.77 | 0.16 |
| HF (Hydrogen fluoride) | -0.63 | -1.01 | -2.37 | -0.98 | -1.17 | -1.93 | 0.16 |
| $SiH_3$ (Silyl) | 0.93 | 1.06 | 0.68 | 0.95 | 1.14 | -0.14 | 2.58 |

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|---|---|---|---|---|---|---|---|
| $SiH_4$ (Silane) | -1.11 | -1.06 | -2.42 | -1.09 | -1.33 | -1.52 | -0.19 |
| $PH_3$ (Phosphine) | -1.21 | -0.84 | -2.18 | -0.92 | -1.14 | -1.36 | -0.03 |
| $H_2S$ (Hydrogen sulfide) | -0.49 | -1.85 | -2.12 | -1.71 | -1.09 | -2.50 | 0.05 |
| HCl (Hydrogen chloride) | -0.52 | -0.79 | -2.04 | -0.84 | -1.06 | -1.55 | 0.11 |
| $C_2H_2$ (Acetylene) | -1.90 | -2.48 | -2.20 | -2.53 | -1.22 | -3.21 | -0.24 |
| $C_2H_4$ (Ethylene) | -1.86 | -1.90 | -2.18 | -2.01 | -1.39 | -2.83 | -0.19 |
| $C_2H_6$ (Ethane) | -0.62 | -0.95 | -2.34 | -0.98 | -1.22 | -1.44 | -0.05 |
| HCN (Hydrogen cyanide) | -0.48 | -2.04 | -2.20 | -1.99 | -1.12 | -2.88 | -0.03 |
| CO (Carbon monoxide) | -1.50 | -1.77 | -1.80 | -1.82 | -1.33 | -2.72 | -0.27 |
| HCO (Formyl radical) | 0.02 | 0.05 | 0.05 | -0.11 | 0.30 | -1.12 | 1.52 |
| $CH_2O$ (Formaldehyde) | -0.55 | -1.12 | -1.06 | -1.25 | -0.73 | -2.09 | 0.35 |
| $CH_3OH$ (Methyl alcohol) | -0.55 | -0.87 | -2.20 | -0.87 | -1.12 | -1.47 | 0.05 |
| $N_2$ (Nitrogen diatomic) | -2.24 | -2.48 | -2.04 | -2.67 | -1.58 | -3.64 | -0.63 |
| $N_2H_4$ (Hydrazine) | -0.45 | -1.50 | -2.23 | -1.41 | -1.06 | -2.01 | 0.27 |
| NO (Nitric oxide) | -0.42 | -0.52 | 0.11 | -0.84 | 0.54 | -1.69 | 1.47 |
| $O_2$ (Oxygen diatomic) | -0.08 | -0.41 | 0.38 | -0.76 | 0.79 | -1.52 | 1.66 |
| $H_2O_2$ (Hydrogen peroxide) | -0.92 | -1.44 | -2.34 | -1.36 | -1.31 | -2.12 | 0.08 |
| $F_2$ (Fluorine diatomic) | 0.42 | -0.03 | 1.20 | -0.44 | 1.82 | -0.84 | 2.26 |
| $CO_2$ (Carbon dioxide) | -0.65 | -4.11 | -2.45 | -4.38 | -1.36 | -1.88 | 0.05 |
| $P_2$ (Phosphorus diatomic) | 0.48 | 0.63 | 0.49 | 0.54 | 0.76 | -0.60 | 1.74 |
| $S_2$ (Sulfur diatomic) | 1.53 | 1.52 | 1.47 | 1.36 | 1.71 | 0.33 | 2.83 |
| $Cl_2$ (Chlorine diatomic) | 0.75 | 0.68 | 0.68 | 0.49 | 1.09 | -0.46 | 2.04 |
| NaCl (Sodium Chloride) | 0.65 | 0.65 | -0.33 | 0.68 | 0.44 | -0.14 | 1.63 |
| SiO (Silicon monoxide) | 0.03 | -0.11 | -0.19 | -0.11 | 0.14 | -1.17 | 1.22 |
| CS (Carbon monosulfide) | -0.09 | 0.05 | 0.00 | -0.08 | 0.30 | -1.22 | 1.36 |
| ClO (Monochlorine monoxide) | 2.19 | 2.01 | 2.28 | 1.71 | 2.50 | 0.95 | 3.54 |
| ClF (Chlorine monofluoride) | 0.44 | 0.22 | 0.52 | 0.03 | 0.98 | -0.95 | 1.88 |
| $Si_2H_6$ (Disilane) | -0.69 | -1.25 | -2.23 | -1.22 | -1.25 | -1.69 | -0.08 |
| $CH_3Cl$ (Methyl chloride) | -0.51 | -0.79 | -2.12 | -0.79 | -1.06 | -1.39 | 0.08 |
| $CH_3SH$ (Methanethiol) | -0.50 | -0.79 | -2.12 | -0.82 | -1.09 | -1.31 | 0.11 |
| $SO_2$ (Sulfur dioxide) | 0.81 | 0.79 | 1.03 | 0.57 | 1.39 | -0.41 | 2.42 |

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|---|---|---|---|---|---|---|---|
| $BF_3$ (Borane, trifluoro-) | -1.04 | -1.09 | -2.61 | -1.20 | -1.39 | -1.69 | 0.11 |
| $BCl_3$ (Borane, trichloro-) | -0.17 | -0.84 | -0.46 | -1.03 | -0.27 | -1.20 | 0.95 |
| $AlCl_3$ (Aluminum trichloride) | 0.06 | 0.05 | -0.65 | -0.08 | -0.33 | -0.71 | 1.01 |
| $CF_4$ (Carbon tetrafluoride) | -1.33 | -1.74 | -3.51 | -1.85 | -2.09 | -2.26 | -0.46 |
| $CCl_4$ Carbon tetrachloride) | -0.46 | -0.22 | -0.76 | -0.24 | -0.38 | -1.06 | 0.68 |
| OCS (Carbonyl sulfide) | -0.74 | -1.28 | -1.36 | -1.41 | -1.03 | -2.31 | 0.03 |
| $CS_2$ (Carbon disulfide) | 0.01 | 0.24 | -0.05 | 0.11 | 0.19 | -0.95 | 1.20 |
| $CF_2O$ (Carbonic difluoride) | -2.37 | -2.39 | -2.01 | -1.41 | -1.60 | -3.13 | -0.08 |
| $SiF_4$ (Silicon tetrafluoride) | -0.81 | -1.03 | -2.37 | -1.25 | -1.33 | -1.60 | 0.16 |
| $N_2O$ (Nitrous oxide) | -2.01 | -2.26 | -2.01 | -2.53 | -1.63 | -3.35 | -0.49 |
| $NF_3$ (Nitrogen trifluoride) | -2.06 | -2.69 | -3.21 | -2.80 | -2.64 | -3.37 | -1.33 |
| $PF_3$ (Phosphorus trifluoride) | -1.23 | -1.52 | -2.45 | -1.50 | -1.66 | -2.12 | -0.38 |
| $O_3$ (Ozone) | 1.93 | 2.31 | 2.80 | 1.88 | 3.18 | 1.33 | 4.16 |
| $F_2O$ (Difluorine monoxide) | -0.31 | -0.63 | -0.03 | -0.87 | 0.49 | -1.66 | 1.14 |
| $ClF_3$ (Chlorine trifluoride) | 1.20 | 1.01 | 1.20 | 0.79 | 1.63 | -0.08 | 2.56 |
| $C_2F_4$ (Tetrafluoroethylene) | -1.65 | -2.31 | -2.91 | -2.37 | -1.74 | -2.80 | -0.16 |
| $CH_3CCH$ (Propyne) | -1.13 | -1.77 | -2.15 | -1.63 | -1.12 | -2.26 | 0.03 |
| $CH_2CCH_2$ (Allene) | -0.56 | -1.55 | -2.37 | -1.47 | -1.25 | -2.07 | -0.08 |
| $C_3H_4$ (Cyclopropene) | -1.82 | -1.85 | -2.26 | -1.96 | -1.33 | -2.72 | -0.19 |
| $C_3H_6$ (Cyclopropane) | -0.65 | -1.09 | -2.58 | -1.12 | -1.36 | -1.55 | -0.14 |
| $CH_2F_2$ (Methane, difluoro-) | -0.58 | -1.01 | -2.37 | -0.92 | -1.22 | -1.71 | -0.03 |
| $CHF_3$ (Methane, trifluoro-) | -0.60 | -1.06 | -2.42 | -0.98 | -1.28 | -1.90 | -0.08 |
| $CH_2Cl_2$ (Methylene chloride) | -0.49 | -0.76 | -1.90 | -0.73 | -1.06 | -1.41 | 0.14 |
| $CHCl_3$ (Chloroform) | -0.83 | -0.73 | -1.41 | -0.73 | -0.95 | -1.47 | 0.22 |
| $CH_3NO_2$ (Methane, nitro-) | -0.37 | -0.16 | -0.38 | -0.44 | 0.00 | -1.22 | 0.98 |
| $CH_3SiH_3$ (Methyl silane) | -0.53 | -0.87 | -2.18 | -0.87 | -1.14 | -1.36 | 0.03 |
| HCOOH (Formic acid) | -0.57 | -2.01 | -2.18 | -2.09 | -1.31 | -2.88 | -0.03 |
| $CH_3CONH_2$ (Acetamide) | -0.31 | -1.60 | -2.01 | -1.50 | -0.90 | -2.12 | 0.33 |
| $C_2N_2$ (Cyanogen) | -0.19 | -0.05 | 0.14 | -0.16 | 0.44 | -1.20 | 1.44 |
| $CH_2CO$ (Ketene) | -0.51 | -1.39 | -1.47 | -1.31 | -1.14 | -2.01 | 0.00 |
| $C_2H_4O$ (Ethylene oxide) | -0.86 | -1.01 | -2.42 | -0.98 | -1.28 | -1.58 | -0.08 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| $C_2H_2O_2$ (Ethanedial) | 0.69 | 0.84 | 0.84 | 0.71 | 1.14 | -0.27 | 2.18 |
| $CH_3CH_2OH$ (Ethanol) | -0.53 | -0.87 | -2.23 | -0.84 | -1.12 | -1.39 | 0.08 |
| $CH_3OCH_3$ (Dimethyl ether) | -0.58 | -0.92 | -2.28 | -0.92 | -1.17 | -1.41 | -0.03 |
| $C_2H_4S$ (Thiirane) | -0.78 | -1.20 | -2.20 | -1.20 | -1.25 | -1.69 | -0.05 |
| $CH_2CHF$ (Ethene, fluoro-) | -0.88 | -2.01 | -2.28 | -2.12 | -1.31 | -2.94 | -0.14 |
| $CH_3CH_2Cl$ (Ethyl chloride) | -0.51 | -0.82 | -2.23 | -0.82 | -1.12 | -1.31 | 0.08 |
| $CH_2CHCl$ (Ethene, chloro-) | -1.11 | -1.39 | -1.80 | -1.52 | -1.22 | -2.39 | -0.08 |
| $CH_3CClO$ (Acetyl Chloride) | -0.85 | -0.84 | -1.20 | -0.98 | -0.90 | -1.82 | 0.19 |
| $NO_2$ (Nitrogen dioxide) | 1.44 | 1.36 | 1.60 | 1.06 | 1.90 | 0.24 | 3.05 |
| $CFCl_3$ (Trichloromonofluoromethane) | -0.68 | -0.57 | -1.03 | -0.63 | -0.65 | -1.44 | 0.46 |
| $CF_3Cl$ (Methane, chlorotrifluoro-) | -1.06 | -1.55 | -2.31 | -1.52 | -1.71 | -2.04 | -0.38 |
| HCCF (Fluoroacetylene) | -0.55 | -0.90 | -2.07 | -0.82 | -1.12 | -1.47 | -0.05 |
| HCCCN (Cyanoacetylene) | -0.36 | -0.57 | -0.57 | -0.63 | -0.30 | -1.63 | 0.76 |
| $C_4N_2$ (2-Butynedinitrile) | 0.68 | 0.95 | 0.87 | 0.90 | 1.14 | -0.11 | 2.18 |
| $C_2N_2$ (Cyanogen) | -0.19 | -0.05 | 0.14 | -0.16 | 0.44 | -1.20 | 1.44 |
| $C_3O_2$ (Carbon suboxide) | -0.74 | -0.73 | -0.52 | -0.87 | -0.27 | -1.82 | 0.79 |
| FCN (Cyanogen fluoride) | -0.66 | -3.84 | -1.96 | -4.03 | -1.06 | -1.63 | 0.33 |
| $C_4N_2$ (Diacetylene) | -0.64 | -1.09 | -1.31 | -1.14 | -1.03 | -2.07 | 0.08 |
| $H_2CS$ (Thioformaldehyde) | 0.28 | 0.41 | 0.35 | 0.27 | 0.57 | -0.82 | 1.66 |
| $CHONH_2$ (Formamide) | -0.35 | -2.45 | -2.18 | -2.42 | -1.01 | -1.41 | 0.24 |
| $CH_2CCl_2$ (Ethene, 1,1-dichloro-) | -1.07 | -0.92 | -1.47 | -0.90 | -1.20 | -1.47 | 0.00 |
| $C_2HF_3$ (Trifluoroethylene) | -0.54 | -1.03 | -2.45 | -0.98 | -1.28 | -1.69 | -0.03 |
| $CH_2CF_2$ (Ethene, 1,1-difluoro-) | -1.03 | -2.18 | -2.50 | -2.23 | -1.31 | -3.02 | -0.05 |
| $CH_3F$ (Methyl fluoride) | -0.58 | -0.95 | -2.28 | -0.90 | -1.17 | -1.60 | -0.03 |
| $CF_2Cl_2$ (Difluorodichloromethane) | -0.90 | -1.20 | -1.60 | -1.25 | -1.17 | -1.90 | -0.03 |
| $SiF_2$ (Silicon difluoride) | 0.10 | 0.00 | -0.11 | -0.03 | 0.22 | -1.12 | 1.31 |
| MSE | | -0.34 | -0.78 | -0.42 | -0.11 | -1.15 | 1.01 |
| MAE | | 0.42 | 0.90 | 0.48 | 0.49 | 1.15 | 1.05 |
| rms | | 0.69 | 1.15 | 0.75 | 0.58 | 1.22 | 1.14 |

TABLE S3: HOMO-LUMO gap results by DFT methods in the FG115 database. [1]

| Molecule | Reference | ωM06-D3 | ωB97X-D3 | M06-2X |
|---|---|---|---|---|
| H (Hydrogen atom) | 12.86 | 12.19 | 11.90 | 10.83 |
| He (Helium atom) | 27.23 | 27.36 | 25.00 | 23.28 |
| Li (Lithium atom) | 4.22 | 5.85 | 5.55 | 3.94 |
| Be (Beryllium atom) | 9.66 | 9.36 | 8.92 | 6.72 |
| B (Boron atom) | 7.99 | 7.62 | 7.18 | 4.79 |
| C (Carbon atom) | 9.97 | 8.87 | 8.21 | 6.12 |
| N (Nitrogen atom) | 14.74 | 13.06 | 12.24 | 10.06 |
| O (Oxygen atom) | 12.14 | 10.58 | 9.68 | 8.16 |
| F (Fluorine atom) | 13.98 | 11.59 | 10.39 | 10.06 |
| Ne (Neon atom) | 26.91 | 26.82 | 25.38 | 23.83 |
| Na (Sodium atom) | 4.14 | 5.82 | 5.20 | 4.03 |
| Mg (Magnesium atom) | 7.76 | 8.24 | 7.67 | 5.85 |
| Al (Aluminum atom) | 5.53 | 5.63 | 5.47 | 3.05 |
| Si (Silicon atom) | 6.73 | 6.47 | 6.26 | 3.86 |
| P (Phosphorus atom) | 9.78 | 9.17 | 8.60 | 5.96 |
| S (Sulfur atom) | 8.23 | 7.59 | 7.10 | 5.00 |
| Cl (Chlorine atom) | 9.30 | 8.27 | 7.62 | 5.88 |
| Ar (Chlorine atom) | 18.65 | 18.90 | 17.79 | 15.67 |
| $CH_3$ (Methyl radical) | 9.86 | 9.63 | 9.08 | 6.64 |
| $CH_4$ (Methane) | 15.06 | 15.97 | 14.52 | 12.51 |
| NH (Imidogen) | 13.17 | 12.19 | 11.42 | 9.47 |
| $NH_2$ (Amino radical) | 11.34 | 10.99 | 10.25 | 8.35 |
| $NH_3$ (Ammonia) | 11.54 | 12.76 | 11.23 | 9.22 |
| OH (Hydroxyl radical) | 11.27 | 10.34 | 9.38 | 8.13 |
| $H_2O$ (Water) | 13.35 | 14.23 | 12.62 | 10.80 |
| HF (Hydrogen fluoride) | 16.91 | 17.14 | 15.40 | 13.90 |
| $SiH_3$ (Silyl) | 7.95 | 7.89 | 7.26 | 4.62 |
| $SiH_4$ (Silane) | 14.03 | 14.80 | 13.46 | 11.26 |

| | | | | |
|---|---|---|---|---|
| $PH_3$ (Phosphine) | 11.83 | 12.40 | 11.18 | 8.98 |
| $H_2S$ (Hydrogen sulfide) | 11.00 | 12.16 | 10.85 | 8.70 |
| HCl (Hydrogen chloride) | 13.36 | 14.17 | 12.84 | 10.80 |
| $C_2H_2$ (Acetylene) | 13.43 | 13.22 | 11.89 | 9.98 |
| $C_2H_4$ (Ethylene) | 12.57 | 12.57 | 11.42 | 9.28 |
| $C_2H_6$ (Ethane) | 13.41 | 14.50 | 13.11 | 11.04 |
| HCN (Hydrogen cyanide) | 14.31 | 15.23 | 13.79 | 11.83 |
| CO (Carbon monoxide) | 15.57 | 15.29 | 14.47 | 12.57 |
| HCO (Formyl radical) | 9.56 | 9.17 | 8.62 | 6.53 |
| $CH_2O$ (Formaldehyde) | 11.56 | 11.56 | 10.85 | 9.17 |
| $CH_3OH$ (Methyl alcohol) | 11.67 | 12.84 | 11.34 | 9.60 |
| $N_2$ (Nitrogen diatomic) | 17.88 | 17.11 | 16.21 | 14.61 |
| $N_2H_4$ (Hydrazine) | 10.30 | 11.67 | 10.17 | 8.11 |
| NO (Nitric oxide) | 10.11 | 8.98 | 8.13 | 6.58 |
| $O_2$ (Oxygen diatomic) | 12.52 | 11.42 | 10.53 | 9.38 |
| $H_2O_2$ (Hydrogen peroxide) | 12.65 | 13.49 | 12.02 | 10.20 |
| $F_2$ (Fluorine diatomic) | 15.53 | 13.57 | 12.40 | 11.97 |
| $CO_2$ (Carbon dioxide) | 14.58 | 15.72 | 14.31 | 12.27 |
| $P_2$ (Phosphorus diatomic) | 10.19 | 9.79 | 9.38 | 7.29 |
| $S_2$ (Sulfur diatomic) | 7.96 | 7.92 | 7.48 | 5.30 |
| $Cl_2$ (Chlorine diatomic) | 10.93 | 10.55 | 9.85 | 8.05 |
| NaCl (Sodium Chloride) | 8.64 | 9.36 | 8.27 | 6.20 |
| SiO (Silicon monoxide) | 11.60 | 11.48 | 10.91 | 8.87 |
| CS (Carbon monosulfide) | 11.58 | 11.51 | 10.93 | 8.84 |
| ClO (Monochlorine monoxide) | 8.86 | 8.30 | 7.72 | 5.96 |
| ClF (Chlorine monofluoride) | 12.43 | 11.61 | 10.80 | 9.17 |
| $Si_2H_6$ (Disilane) | 11.33 | 12.78 | 11.64 | 9.36 |
| $CH_3Cl$ (Methyl chloride) | 12.01 | 13.19 | 11.80 | 9.79 |
| $CH_3SH$ (Methanethiol) | 10.01 | 11.34 | 10.06 | 7.89 |
| $SO_2$ (Sulfur dioxide) | 11.74 | 11.18 | 10.50 | 8.73 |
| $BF_3$ (Borane, trifluoro-) | 17.22 | 17.71 | 15.97 | 14.39 |

| | | | | |
|---|---|---|---|---|
| $BCl_3$ (Borane, trichloro-) | 12.07 | 12.10 | 11.61 | 9.55 |
| $AlCl_3$ (Aluminum trichloride) | 12.14 | 12.57 | 11.94 | 9.76 |
| $CF_4$ (Carbon tetrafluoride) | 17.85 | 19.04 | 17.11 | 15.42 |
| $CCl_4$ Carbon tetrachloride) | 11.97 | 12.40 | 11.70 | 9.82 |
| OCS (Carbonyl sulfide) | 12.13 | 12.35 | 11.83 | 9.82 |
| $CS_2$ (Carbon disulfide) | 10.19 | 9.98 | 9.60 | 7.64 |
| $CF_2O$ (Carbonic difluoride) | 16.08 | 15.15 | 14.31 | 12.40 |
| $SiF_4$ (Silicon tetrafluoride) | 16.95 | 18.03 | 16.48 | 14.85 |
| $N_2O$ (Nitrous oxide) | 15.01 | 14.31 | 13.65 | 11.78 |
| $NF_3$ (Nitrogen trifluoride) | 15.76 | 16.21 | 15.26 | 13.46 |
| $PF_3$ (Phosphorus trifluoride) | 13.00 | 13.63 | 12.65 | 10.42 |
| $O_3$ (Ozone) | 11.06 | 9.96 | 9.11 | 7.51 |
| $F_2O$ (Difluorine monoxide) | 13.82 | 12.92 | 11.86 | 11.07 |
| $ClF_3$ (Chlorine trifluoride) | 11.79 | 11.40 | 10.55 | 9.17 |
| $C_2F_4$ (Tetrafluoroethylene) | 12.45 | 13.19 | 11.72 | 9.41 |
| $CH_3CCH$ (Propyne) | 11.70 | 12.35 | 11.02 | 8.95 |
| $CH_2CCH_2$ (Allene) | 10.83 | 12.54 | 11.12 | 9.03 |
| $C_3H_4$ (Cyclopropene) | 11.87 | 11.94 | 10.72 | 8.70 |
| $C_3H_6$ (Cyclopropane) | 11.64 | 13.49 | 11.94 | 9.74 |
| $CH_2F_2$ (Methane, difluoro-) | 14.15 | 15.01 | 13.52 | 11.78 |
| $CHF_3$ (Methane, trifluoro-) | 15.44 | 16.32 | 14.80 | 13.14 |
| $CH_2Cl_2$ (Methylene chloride) | 12.18 | 13.25 | 12.08 | 10.04 |
| $CHCl_3$ (Chloroform) | 12.38 | 12.76 | 11.97 | 9.98 |
| $CH_3NO_2$ (Methane, nitro-) | 11.95 | 11.86 | 11.04 | 9.66 |
| $CH_3SiH_3$ (Methyl silane) | 12.35 | 13.87 | 12.57 | 10.34 |
| HCOOH (Formic acid) | 11.98 | 13.25 | 11.97 | 10.15 |
| $CH_3CONH_2$ (Acetamide) | 10.05 | 12.08 | 10.55 | 8.76 |
| $C_2N_2$ (Cyanogen) | 13.90 | 13.00 | 12.40 | 10.55 |
| $CH_2CO$ (Ketene) | 10.32 | 11.02 | 10.42 | 8.38 |
| $C_2H_4O$ (Ethylene oxide) | 11.68 | 13.06 | 11.48 | 9.79 |
| $C_2H_2O_2$ (Ethanedial) | 10.04 | 9.68 | 9.03 | 7.32 |

| | | | | |
|---|---|---|---|---|
| $CH_3CH_2OH$ (Ethanol) | 11.38 | 12.73 | 11.23 | 9.41 |
| $CH_3OCH_3$ (Dimethyl ether) | 10.79 | 12.32 | 10.83 | 9.06 |
| $C_2H_4S$ (Thiirane) | 9.93 | 11.21 | 10.01 | 7.86 |
| $CH_2CHF$ (Ethene, fluoro-) | 11.55 | 12.54 | 11.26 | 9.19 |
| $CH_3CH_2Cl$ (Ethyl chloride) | 11.74 | 13.14 | 11.72 | 9.66 |
| $CH_2CHCl$ (Ethene, chloro-) | 11.35 | 11.78 | 10.91 | 8.87 |
| $CH_3CClO$ (Acetyl Chloride) | 11.97 | 12.35 | 11.70 | 9.96 |
| $NO_2$ (Nitrogen dioxide) | 9.79 | 9.49 | 8.79 | 7.10 |
| $CFCl_3$ (Trichloromonofluoromethane) | 12.61 | 12.73 | 12.05 | 10.12 |
| $CF_3Cl$ (Methane, chlorotrifluoro-) | 14.27 | 15.04 | 14.12 | 12.00 |
| HCCF (Fluoroacetylene) | 12.04 | 12.97 | 11.70 | 9.76 |
| HCCCN (Cyanoacetylene) | 12.20 | 12.00 | 11.42 | 9.52 |
| $C_4N_2$ (2-Butynedinitrile) | 11.52 | 10.99 | 10.47 | 8.62 |
| $C_2N_2$ (Cyanogen) | 13.90 | 13.00 | 12.40 | 10.55 |
| $C_3O_2$ (Carbon suboxide) | 11.64 | 11.15 | 10.72 | 8.87 |
| FCN (Cyanogen fluoride) | 14.33 | 14.80 | 13.55 | 11.37 |
| $C_4N_2$ (Diacetylene) | 11.00 | 11.37 | 10.83 | 8.81 |
| $H_2CS$ (Thioformaldehyde) | 9.18 | 8.81 | 8.35 | 6.31 |
| $CHONH_2$ (Formamide) | 10.81 | 12.46 | 10.91 | 9.11 |
| $CH_2CCl_2$ (Ethene, 1,1-dichloro-) | 11.17 | 11.42 | 10.91 | 8.79 |
| $C_2HF_3$ (Trifluoroethylene) | 11.11 | 12.51 | 11.07 | 9.00 |
| $CH_2CF_2$ (Ethene, 1,1-difluoro-) | 11.81 | 12.87 | 11.37 | 9.28 |
| $CH_3F$ (Methyl fluoride) | 14.09 | 14.91 | 13.38 | 11.72 |
| $CF_2Cl_2$ (Difluorodichloromethane) | 13.33 | 13.71 | 12.95 | 10.99 |
| $SiF_2$ (Silicon difluoride) | 11.04 | 10.74 | 10.28 | 8.11 |
| MSE | | 0.23 | -0.75 | -2.64 |
| MAE | | 0.77 | 0.83 | 2.64 |
| rms | | 0.93 | 1.07 | 2.73 |

TABLE S4. Atomic energies (in kcal/mol) from the H atom to the Ar atom [2].

| Atom | Reference | ωM06-D3 | ωB97X-D3 | M06-2X |
|---|---|---|---|---|
| H | -313.76 | -312.64 | -315.17 | -312.62 |
| He | -1822.12 | -1820.15 | -1823.18 | -1820.89 |
| Li | -4692.56 | -4691.39 | -4697.55 | -4693.69 |
| Be | -9203.92 | -9197.60 | -9202.20 | -9201.54 |
| B | -15470.58 | -15467.52 | -15469.02 | -15467.26 |
| C | -23748.12 | -23749.38 | -23746.81 | -23745.48 |
| N | -34255.28 | -34257.81 | -34253.17 | -34252.40 |
| O | -47105.50 | -47109.47 | -47105.58 | -47102.06 |
| F | -62584.04 | -62588.74 | -62584.45 | -62579.51 |
| Ne | -80909.66 | -80910.05 | -80907.17 | -80899.63 |
| Na | -101816.42 | -101813.89 | -101817.11 | -101806.82 |
| Mg | -125535.30 | -125537.51 | -125537.98 | -125533.86 |
| Al | -152074.59 | -152075.96 | -152077.91 | -152071.75 |
| Si | -181575.73 | -181576.46 | -181577.36 | -181570.29 |
| P | -214143.51 | -214140.10 | -214140.40 | -214131.83 |
| S | -249818.09 | -249816.58 | -249817.64 | -249809.65 |
| Cl | -288747.57 | -288747.09 | -288747.12 | -288738.36 |
| Ar | -331036.74 | -331037.14 | -331036.75 | -331026.76 |
| MSE | | 0.22 | -0.17 | 4.95 |
| MAE | | 2.17 | 1.64 | 5.07 |
| rms | | 2.69 | 2.07 | 6.20 |

TABLE S5. Non-hydrogen transfer barrier heights (in kcal/mol) of the NHTBH38/04 set [3].

| Reactions | | $\Delta E_{ref}$ | $\omega$M06-D3 | $\omega$B97X-D3 | M06-2X |
|---|---|---|---|---|---|
| **Heavy-atom transfer reactions** | | | | | |
| $H + N_2O \rightarrow OH + N_2$ | $V^f$ | 18.14 | 17.99 | 18.16 | 16.90 |
| | $V^r$ | 83.22 | 82.68 | 78.82 | 81.59 |
| $H + FH \rightarrow HF + H$ | $V^f$ | 42.18 | 40.24 | 41.46 | 38.38 |
| | $V^r$ | 42.18 | 40.24 | 41.46 | 38.38 |
| $H + ClH \rightarrow HCl + H$ | $V^f$ | 18 | 20.49 | 19.33 | 18.07 |
| | $V^r$ | 18 | 20.49 | 19.33 | 18.07 |
| $H + FCH_3 \rightarrow HF + CH_3$ | $V^f$ | 30.38 | 30.37 | 30.98 | 30.67 |
| | $V^r$ | 57.02 | 54.06 | 54.75 | 53.97 |
| $H + F_2 \rightarrow HF + F$ | $V^f$ | 2.27 | 1.56 | 0.10 | 1.97 |
| | $V^r$ | 106.18 | 103.77 | 104.08 | 108.93 |
| $CH_3 + FCl \rightarrow CH_3F + Cl$ | $V^f$ | 7.43 | 5.19 | 3.61 | 4.84 |
| | $V^r$ | 60.17 | 58.37 | 57.85 | 59.44 |
| **Nucleophilic substitution reactions** | | | | | |
| $F^- + CH_3F \rightarrow FCH_3 + F^-$ | $V^f$ | -0.34 | -1.79 | -1.55 | -0.48 |
| | $V^r$ | -0.34 | -1.79 | -1.55 | -0.48 |
| $F^- \cdots CH_3F \rightarrow FCH_3 \cdots F^-$ | $V^f$ | 13.38 | 13.59 | 13.06 | 15.39 |
| | $V^r$ | 13.38 | 13.59 | 13.06 | 15.39 |
| $Cl^- + CH_3Cl \rightarrow ClCH_3 + Cl^-$ | $V^f$ | 3.1 | 4.26 | 4.38 | 2.17 |
| | $V^r$ | 3.1 | 4.26 | 4.38 | 2.17 |
| $Cl^- \cdots CH_3Cl \rightarrow ClCH_3 \cdots Cl^-$ | $V^f$ | 13.61 | 15.13 | 15.20 | 13.77 |
| | $V^r$ | 13.61 | 15.13 | 15.20 | 13.77 |
| $F^- + CH_3Cl \rightarrow FCH_3 + Cl^-$ | $V^f$ | -12.54 | -13.21 | -13.14 | -14.94 |
| | $V^r$ | 20.11 | 22.24 | 21.33 | 23.86 |
| $F^- \cdots CH_3Cl \rightarrow FCH_3 \cdots Cl^-$ | $V^f$ | 2.89 | 3.79 | 3.60 | 3.37 |
| | $V^r$ | 29.62 | 32.20 | 30.91 | 34.06 |
| $OH^- + CH_3F \rightarrow HOCH_3 + F^-$ | $V^f$ | -2.78 | -3.34 | -3.19 | -2.70 |
| | $V^r$ | 17.33 | 16.77 | 17.89 | 16.93 |
| $OH^- \cdots CH_3F \rightarrow HOCH_3 \cdots F^-$ | $V^f$ | 10.96 | 11.59 | 11.06 | 12.71 |
| | $V^r$ | 47.2 | 49.10 | 49.43 | 50.85 |
| **Unimolecular and association reactions** | | | | | |
| $H + N_2 \rightarrow HN_2$ | $V^f$ | 14.69 | 14.18 | 12.96 | 13.61 |
| | $V^r$ | 10.72 | 12.56 | 13.74 | 11.27 |
| $H + CO \rightarrow HCO$ | $V^f$ | 3.17 | 3.97 | 3.71 | 3.52 |
| | $V^r$ | 22.68 | 24.75 | 26.24 | 22.75 |
| $H + C_2H_4 \rightarrow CH_3CH_2$ | $V^f$ | 1.72 | 3.71 | 3.42 | 2.72 |
| | $V^r$ | 41.75 | 44.44 | 46.01 | 43.67 |
| $CH_3 + C_2H_4 \rightarrow CH_3CH_2CH_2$ | $V^f$ | 6.85 | 6.14 | 4.93 | 5.77 |
| | $V^r$ | 32.97 | 34.67 | 34.64 | 34.21 |
| $HCN \rightarrow HNC$ | $V^f$ | 48.16 | 46.27 | 46.19 | 45.78 |
| | $V^r$ | 33.11 | 32.44 | 33.07 | 32.80 |
| MSE | | | 0.18 | 0.04 | 0.00 |
| MAE | | | 1.40 | 1.53 | 1.41 |
| rms | | | 1.62 | 1.89 | 1.91 |

TABLE S6. Hydrogen transfer barrier heights (in kcal/mol) of the HTBH38/04 set [3, 4].

| Reactions | | $\Delta E_{ref}$ | $\omega$M06-D3 | $\omega$B97X-D3 | M06-2X |
|---|---|---|---|---|---|
| $H + HCl \rightarrow H_2 + Cl$ | $V^f$ | 5.7 | 5.75 | 4.71 | 4.36 |
| | $V^r$ | 8.7 | 4.86 | 4.98 | 6.25 |
| $OH + H_2 \rightarrow H + H_2O$ | $V^f$ | 5.1 | 2.15 | 2.48 | 4.74 |
| | $V^r$ | 21.2 | 19.76 | 19.13 | 21.00 |
| $CH_3 + H_2 \rightarrow H + CH_4$ | $V^f$ | 12.1 | 9.40 | 9.36 | 11.89 |
| | $V^r$ | 15.3 | 15.83 | 14.22 | 15.52 |
| $OH + CH_4 \rightarrow CH_3 + H_2O$ | $V^f$ | 6.7 | 3.79 | 3.43 | 5.02 |
| | $V^r$ | 19.6 | 14.97 | 15.22 | 17.65 |
| $H + H_2 \rightarrow H_2 + H$ | $V^f$ | 9.6 | 9.87 | 9.77 | 11.57 |
| | $V^r$ | 9.6 | 9.87 | 9.77 | 11.57 |
| $OH + NH_3 \rightarrow H_2O + NH_2$ | $V^f$ | 3.2 | 1.70 | 0.85 | 2.31 |
| | $V^r$ | 12.7 | 10.75 | 10.38 | 12.02 |
| $HCl + CH_3 \rightarrow Cl + CH_4$ | $V^f$ | 1.7 | -0.32 | -1.45 | -0.17 |
| | $V^r$ | 7.9 | 5.22 | 3.69 | 5.35 |
| $OH + C_2H_6 \rightarrow H_2O + C_2H_5$ | $V^f$ | 3.4 | 0.87 | 0.56 | 2.41 |
| | $V^r$ | 19.9 | 16.75 | 16.82 | 19.04 |
| $F + H_2 \rightarrow HF + H$ | $V^f$ | 1.8 | -2.55 | -3.55 | 0.52 |
| | $V^r$ | 33.4 | 30.79 | 29.20 | 32.13 |
| $O + CH_4 \rightarrow OH + CH_3$ | $V^f$ | 13.7 | 10.81 | 9.55 | 11.46 |
| | $V^r$ | 8.1 | 4.78 | 4.71 | 6.38 |
| $H + PH_3 \rightarrow PH_2 + H_2$ | $V^f$ | 3.1 | 3.81 | 3.79 | 3.45 |
| | $V^r$ | 23.2 | 22.57 | 23.78 | 25.32 |
| $H + HO \rightarrow H_2 + O$ | $V^f$ | 10.7 | 9.29 | 9.17 | 9.81 |
| | $V^r$ | 13.1 | 8.88 | 9.15 | 11.25 |
| $H + H_2S \rightarrow H_2 + HS$ | $V^f$ | 3.5 | 4.96 | 4.62 | 4.37 |
| | $V^r$ | 17.3 | 15.58 | 16.64 | 17.95 |
| $O + HCl \rightarrow OH + Cl$ | $V^f$ | 9.8 | 7.67 | 6.42 | 6.80 |
| | $V^r$ | 10.4 | 7.18 | 6.71 | 7.24 |
| $NH_2 + CH_3 \rightarrow CH_4 + NH$ | $V^f$ | 8 | 6.59 | 6.13 | 6.50 |
| | $V^r$ | 22.4 | 20.55 | 18.99 | 20.59 |
| $NH_2 + C_2H_5 \rightarrow C_2H_6 + NH$ | $V^f$ | 7.5 | 8.38 | 7.83 | 7.85 |
| | $V^r$ | 18.3 | 17.64 | 16.23 | 17.93 |
| $C_2H_6 + NH_2 \rightarrow NH_3 + C_2H_5$ | $V^f$ | 10.4 | 9.85 | 9.26 | 9.95 |
| | $V^r$ | 17.4 | 16.67 | 16.00 | 16.88 |
| $NH_2 + CH_4 \rightarrow CH_3 + NH_3$ | $V^f$ | 14.5 | 12.67 | 11.95 | 12.50 |
| | $V^r$ | 17.8 | 14.80 | 14.21 | 15.42 |
| *s-trans cis*-$C_5H_8 \rightarrow$ *s-trans cis*-$C_5H_8$ | $V^f$ | 38.4 | 41.39 | 39.92 | 39.08 |
| | $V^r$ | 38.4 | 41.39 | 39.92 | 39.08 |
| MSE | | | -1.54 | -2.08 | -0.81 |
| MAE | | | 2.08 | 2.40 | 1.32 |
| rms | | | 2.41 | 2.75 | 1.56 |

TABLE S7. Interaction energies (in kcal/mol) for the S22 set with new reference values. [5] The counterpoise corrections are used to reduce the basis set superposition errors. Monomer deformation energies are not included.

| Complex [Symmetry] | $\Delta E_{ref}$ | $\omega$M06-D3 | $\omega$B97X-D3 | M06-2X |
|---|---|---|---|---|
| **Hydrogen bonded complexes** | | | | |
| $(NH_3)_2$ [$C_{2h}$] | -3.133 | -3.21 | -3.09 | -3.18 |
| $(H_2O)_2$ [$C_s$] | -4.989 | -5.17 | -5.04 | -5.02 |
| Formic acid dimer [$C_{2h}$] | -18.753 | -19.44 | -19.52 | -19.09 |
| Formamide dimer [$C_{2h}$] | -16.062 | -16.21 | -16.26 | -15.61 |
| Uracil dimer [$C_{2h}$] | -20.641 | -20.31 | -20.51 | -19.47 |
| 2-pyridoxine·2-aminopyridine [$C_1$] | -16.934 | -16.53 | -16.98 | -15.56 |
| Adenine·thymine WC [$C_1$] | -16.66 | -16.12 | -16.43 | -15.03 |
| MSE | | 0.03 | -0.09 | 0.60 |
| MAE | | 0.34 | 0.21 | 0.72 |
| **Dispersion complexes** | | | | |
| $(CH_4)_2$ [$D_{3d}$] | -0.527 | -0.40 | -0.61 | -0.48 |
| $(C_2H_4)_2$ [$D_{2d}$] | -1.472 | -1.77 | -1.54 | -1.62 |
| Benzene·$CH_4$[$C_3$] | -1.448 | -1.59 | -1.64 | -1.35 |
| Benzene dimer [$C_{2h}$] | -2.654 | -2.82 | -3.00 | -2.68 |
| Pyrazine dimer [$C_s$] | -4.255 | -4.03 | -4.15 | -4.17 |
| Uracil dimer [$C_2$] | -9.805 | -9.80 | -9.83 | -9.80 |
| Indole·benzene [$C_1$] | -4.524 | -4.56 | -4.61 | -4.64 |
| Adenine·thymine stack [$C_1$] | -11.73 | -11.78 | -11.26 | -12.26 |
| MSE | | -0.04 | -0.03 | -0.07 |
| MAE | | 0.13 | 0.17 | 0.13 |
| **Mixed complexes** | | | | |
| Ethene·ethine [$C_{2v}$] | -1.496 | -1.32 | -1.65 | -1.35 |
| Benzene·$H_2O$ [$C_s$] | -3.275 | -3.50 | -3.58 | -3.57 |
| Benzene·$NH_3$ [$C_s$] | -2.312 | -2.45 | -2.56 | -2.34 |
| Benzene·HCN [$C_s$] | -4.541 | -4.71 | -4.65 | -4.85 |
| Benzene dimer [$C_{2v}$] | -2.717 | -2.65 | -2.82 | -2.33 |
| Indole·benzene T-shape [$C_1$] | -5.627 | -5.38 | -5.52 | -5.04 |
| Phenol dimer [$C_1$] | -7.097 | -7.08 | -7.00 | -6.56 |
| MSE | | 0.00 | -0.10 | 0.15 |
| MAE | | 0.15 | 0.16 | 0.33 |
| MSE | | -0.01 | -0.07 | 0.21 |
| MAE | | 0.20 | 0.18 | 0.38 |
| rms | | 0.26 | 0.24 | 0.59 |

TABLE S8. 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 [3, 4].

| Reactions | $\Delta E_{ref}$ | $\omega$M06-D3 | $\omega$B97X-D3 | M06-2X |
|---|---|---|---|---|
| $H + N_2O \rightarrow OH + N_2$ | -65.08 | -64.69 | -60.66 | -64.69 |
| $H + FCH_3 \rightarrow HF + CH_3$ | -26.64 | -23.69 | -23.76 | -23.30 |
| $H + F_2 \rightarrow HF + F$ | -103.91 | -102.21 | -103.99 | -106.96 |
| $CH_3 + FCl \rightarrow CH_3F + Cl$ | -52.74 | -53.18 | -54.25 | -54.60 |
| $F^- + CH_3Cl \rightarrow FCH_3 + Cl^-$ | -32.65 | -35.45 | -34.48 | -38.80 |
| $F^- \cdots CH_3Cl \rightarrow FCH_3 \cdots Cl^-$ | -26.73 | -28.41 | -27.32 | -30.68 |
| $OH^- + CH_3F \rightarrow HOCH_3 + F^-$ | -20.11 | -20.11 | -21.09 | -19.63 |
| $OH^- \cdots CH_3F \rightarrow HOCH_3 \cdots F^-$ | -36.24 | -37.51 | -38.37 | -38.14 |
| $H + N_2 \rightarrow HN_2$ | 3.97 | 1.63 | -0.78 | 2.34 |
| $H + CO \rightarrow HCO$ | -19.51 | -20.78 | -22.52 | -19.23 |
| $H + C_2H_4 \rightarrow CH_3CH_2$ | -40.03 | -40.74 | -42.59 | -40.95 |
| $CH_3 + C_2H_4 \rightarrow CH_3CH_2CH_2$ | -26.12 | -28.53 | -29.71 | -28.45 |
| $HCN \rightarrow HNC$ | 15.05 | 13.83 | 13.12 | 12.98 |
| $H + HCl \rightarrow H_2 + Cl$ | -3.0 | 0.89 | -0.28 | -1.89 |
| $OH + H_2 \rightarrow H + H_2O$ | -16.1 | -17.62 | -16.66 | -16.26 |
| $CH_3 + H_2 \rightarrow H + CH_4$ | -3.2 | -6.43 | -4.86 | -3.64 |
| $OH + CH_4 \rightarrow CH_3 + H_2O$ | -12.9 | -11.19 | -11.80 | -12.63 |
| $OH + NH_3 \rightarrow H_2O + NH_2$ | -9.5 | -9.05 | -9.53 | -9.70 |
| $HCl + CH_3 \rightarrow Cl + CH_4$ | -6.2 | -5.54 | -5.14 | -5.52 |
| $OH + C_2H_6 \rightarrow H_2O + C_2H_5$ | -16.5 | -15.87 | -16.26 | -16.63 |
| $F + H_2 \rightarrow HF + H$ | -31.6 | -33.34 | -32.74 | -31.61 |
| $O + CH_4 \rightarrow OH + CH_3$ | 5.6 | 6.02 | 4.84 | 5.08 |
| $H + PH_3 \rightarrow PH_2 + H_2$ | -20.1 | -18.76 | -19.99 | -21.87 |
| $H + HO \rightarrow H_2 + O$ | -2.4 | 0.41 | 0.02 | -1.45 |
| $H + H_2S \rightarrow H_2 + HS$ | -13.8 | -10.63 | -12.01 | -13.58 |
| $O + HCl \rightarrow OH + Cl$ | -0.6 | 0.49 | -0.30 | -0.44 |
| $NH_2 + CH_3 \rightarrow CH_4 + NH$ | -14.4 | -13.96 | -12.86 | -14.09 |
| $NH_2 + C_2H_5 \rightarrow C_2H_6 + NH$ | -10.8 | -9.27 | -8.39 | -10.08 |
| $C_2H_6 + NH_2 \rightarrow NH_3 + C_2H_5$ | -7.0 | -6.82 | -6.74 | -6.93 |
| $NH_2 + CH_4 \rightarrow CH_3 + NH_3$ | -3.3 | -2.13 | -2.27 | -2.92 |
| MSE | | 0.13 | -0.16 | -0.59 |
| MAE | | 1.51 | 1.65 | 1.21 |
| rms | | 1.82 | 2.06 | 1.84 |

TABLE S9. Binding energies (in kcal/mol) of several sets of noncovalent interactions. The first three sets are taken from Ref. [6] with monomer deformation energies taken into considerations. The last three sets are taken from Ref. [7] without considering monomer deformation energies. The counter-point corrections are applied for all the cases.

| Complex | $\Delta E_{ref}$ | $\omega$M06-D3 | $\omega$B97X-D3 | M06-2X |
|---|---|---|---|---|
| **Charge-transfer complexes** | | | | |
| $C_2H_4\cdots F_2$ | 1.06 | 0.85 | 0.80 | 1.06 |
| $NH_3\cdots F_2$ | 1.81 | 1.58 | 1.50 | 1.56 |
| $C_2H_2\cdots ClF$ | 3.81 | 4.00 | 3.76 | 4.40 |
| $HCN\cdots ClF$ | 4.86 | 4.71 | 4.43 | 4.68 |
| $NH_3\cdots Cl_2$ | 4.88 | 4.76 | 4.82 | 4.98 |
| $H_2O\cdots ClF$ | 5.36 | 5.65 | 5.38 | 5.70 |
| $NH_3\cdots ClF$ | 10.62 | 10.26 | 10.92 | 10.02 |
| MSE | | -0.08 | -0.11 | 0.00 |
| MAE | | 0.22 | 0.20 | 0.29 |
| **Dipole-dipole interaction complexes** | | | | |
| $H_2S\cdots H_2S$ | 1.66 | 1.58 | 1.71 | 1.38 |
| $HCl\cdots HCl$ | 2.01 | 1.87 | 1.83 | 1.70 |
| $H_2S\cdots HCl$ | 3.35 | 3.46 | 3.52 | 3.22 |
| $CH_3Cl\cdots HCl$ | 3.55 | 3.50 | 3.29 | 3.37 |
| $HCN\cdots CH_3SH$ | 3.59 | 3.69 | 3.81 | 3.60 |
| $CH_3SH\cdots HCl$ | 4.16 | 5.00 | 4.97 | 4.85 |
| MSE | | 0.13 | 0.14 | -0.03 |
| MAE | | 0.22 | 0.28 | 0.27 |
| **Weak interaction complexes** | | | | |
| $He\cdots Ne$ | 0.04 | -0.20 | 0.02 | 0.13 |
| $He\cdots Ar$ | 0.06 | -0.21 | 0.04 | 0.14 |
| $Ne\cdots Ne$ | 0.08 | -0.23 | -0.02 | 0.16 |
| $Ne\cdots Ar$ | 0.13 | -0.22 | 0.01 | 0.19 |
| $CH_4\cdots Ne$ | 0.22 | -0.12 | 0.15 | 0.27 |
| $C_6H_6\cdots Ne$ | 0.47 | 0.23 | 0.30 | 0.68 |
| $CH_4\cdots CH_4$ | 0.51 | 0.47 | 0.60 | 0.52 |
| MSE | | -0.26 | -0.06 | 0.08 |
| MAE | | 0.26 | 0.09 | 0.08 |
| **Hydrogen-bonded DNA base pairs** | | | | |
| G$\cdots$A HB | -11.30 | -12.61 | -13.30 | -11.42 |
| C$\cdots$G WC | -30.70 | -32.05 | -32.49 | -30.77 |
| G$\cdots$C WC | -31.40 | -31.99 | -32.38 | -30.77 |
| MSE | | -1.09 | -1.59 | 0.15 |
| MAE | | 1.09 | 1.59 | 0.27 |
| **Interstrand base pairs** | | | | |
| G$\cdots$G IS | -5.20 | -5.08 | -5.62 | -4.64 |
| G$\cdots$G IS | 0.80 | 1.19 | 0.92 | 1.97 |
| C$\cdots$C IS | 3.10 | 3.54 | 3.29 | 3.43 |
| MSE | | 0.32 | -0.04 | 0.69 |
| MAE | | 0.32 | 0.25 | 0.69 |
| **Stacked base pairs** | | | | |
| A$\cdots$G S | -6.50 | -6.21 | -6.17 | -5.61 |
| C$\cdots$G S | -12.40 | -11.08 | -10.76 | -10.03 |
| G$\cdots$C S | -11.60 | -11.00 | -11.04 | -10.03 |
| MSE | | 0.74 | 0.84 | 1.61 |
| MAE | | 0.74 | 0.84 | 1.61 |
| MSE | | -0.06 | -0.09 | 0.27 |
| MAE | | 0.38 | 0.41 | 0.41 |

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