## Supporting Information for:

# Hybrid Meta Density Functional Theory Methods for Thermochemistry, Thermochemical Kinetics, and Noncovalent Interaction: The MPW1B95 and MPWB1K Models and Comparative Assessments for Hydrogen Bonding and van der Waals Interaction

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Table S1: AE109/3 Database Zero-Point-Exclusive Atomization Energies (kcal/mol)

| Molecule | $D_e$ | Molecule | $D_e$ | Molecule | $D_e$ |
|---|---|---|---|---|---|
| CH ($^2$ ) | 84.00 | $S_2$ | 101.67 | $H_2CCH$ | 445.79 |
| $CH_2$ ($^3B_1$) | 190.97 | $Cl_2$ | 57.97 | $HCOOCH_3$ | 785.26 |
| $CH_2$ ($^1A_1$) | 181.50 | SiO | 192.08 | HCOOH | 500.98 |
| $CH_3$ ($^2A''_2$) | 307.46 | SC | 171.31 | $NF_3$ | 204.53 |
| $CH_4$ | 420.11 | SO | 125.00 | $PF_3$ | 363.87 |
| NH | 83.67 | ClO | 64.49 | SH | 86.98 |
| $NH_2$ | 181.90 | ClF | 61.36 | $SiCl_4$ | 384.94 |
| $NH_3$ | 297.90 | $Si_2H_6$ | 530.81 | $SiF_4$ | 574.35 |
| OH | 107.06 | $CH_3Cl$ | 394.64 | $C_2H_5$ | 603.75 |
| $OH_2$ | 232.60 | $CH_3SH$ | 473.84 | $C_4H_6$ [d] | 987.2 |
| FH | 141.05 | HOCl | 164.36 | $C_4H_6$ [e] | 1001.61 |
| $SiH_2$ ($^1A_1$) | 151.79 | $SO_2$ | 257.86 | HCOCOH | 633.35 |
| $SiH_2$ ($^3B_1$) | 131.05 | $AlCl_3$ | 306.26 | $CH_3CHO$ | 677.03 |
| $SiH_3$ | 227.37 | $AlF_3$ | 426.50 | $C_2H_4O$ | 650.70 |
| $SiH_4$ | 322.40 | $BCl_3$ | 322.90 | $C_2H_5O$ | 698.64 |
| $PH_2$ | 153.20 | $BF_3$ | 470.04 | $H_3COCH_3$ | 798.05 |
| $PH_3$ | 242.55 | $C_2Cl_4$ | 466.28 | $H_3CCH_2OH$ | 810.36 |
| $SH_2$ | 182.74 | $C_2F_4$ | 583.96 | $C_3H_4$ [f] | 703.20 |
| ClH | 106.50 | $C_3H_4$ [a] | 704.79 | $C_3H_4$ [g] | 682.74 |
| HCCH | 405.39 | $C_4H_4O$ | 993.74 | $H_3CCOOH$ | 803.04 |
| $H_2CCH_2$ | 563.47 | $C_4H_4S$ | 962.73 | $H_3CCOCH_3$ | 977.96 |
| $H_3CCH_3$ | 712.80 | $C_4H_5N$ | 1071.57 | $C_3H_6$ | 853.41 |
| CN | 180.58 | $C_4H_6$ [b] | 1012.37 | $H_3CCHCH_2$ | 860.61 |
| HCN | 313.20 | $C_4H_6$ [c] | 1004.13 | $C_3H_8$ | 1006.87 |
| CO | 259.31 | $C_5H_5N$ | 1237.69 | $C_2H_5OCH_3$ | 1095.12 |
| HCO | 278.39 | CCH | 267.83 | $C_4H_{10}$ [h] | 1303.04 |
| $H_2CO$ | 373.73 | $CCl_4$ | 312.74 | $C_4H_{10}$ [i] | 1301.32 |
| $H_3COH$ | 512.78 | $CF_3CN$ | 639.85 | $C_4H_8$ [j] | 1149.01 |

| | | | | | |
|---|---|---|---|---|---|
| $N_2$ | 228.46 | $CF_4$ | 476.32 | $C_4H_8$ [k] | 1158.61 |
| $H_2NNH_2$ | 438.60 | $CH_2OH$ | 409.76 | $C_5H_8$ [l] | 1284.28 |
| NO | 155.22 | $CH_3CN$ | 615.84 | $C_6H_6$ | 1367.56 |
| $O_2$ | 119.99 | $CH_3NH_2$ | 582.56 | $CH_3CO$ | 581.58 |
| HOOH | 268.57 | $CH_3NO_2$ | 601.27 | $(CH_3)_2CH$ | 900.75 |
| $F_2$ | 38.20 | $CHCl_3$ | 343.18 | $(CH_3)_3C$ | 1199.34 |
| $CO_2$ | 389.14 | $CHF_3$ | 457.50 | $H_2CCO$ | 532.73 |
| $Si_2$ | 74.97 | $ClF_3$ | 125.33 | | |
| $P_2$ | 117.09 | $H_2$ | 109.48 | | |

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[a] propyne

[b] *trans*-1,3-butadiene

[c] 2-butyne

[d] bicylobutane

[e] cyclobutene

[f] allene

[g] cyclopropene

[h] cyclobutane

[i] isobutane

[j] *trans*-2-butene

[k] isobutene

[l] spiropentane

Table S2: BH42/03 Database

| Reaction | best estimate | |
|---|---|---|
| A + BC → AB + C | $V_f^{\neq}$ | $V_r^{\neq}$ |
| 1. H + HCl → $H_2$ + Cl | 5.7 | 8.7 |
| 2. OH + $H_2$ → H + $H_2O$ | 5.1 | 21.2 |
| 3. $CH_3$ + $H_2$ → H + $CH_4$ | 12.1 | 15.3 |
| 4. OH + $CH_4$ → $CH_3$ + $H_2O$ | 6.7 | 19.6 |
| 5. H + $H_2$ → $H_2$ + H | 9.6 | 9.6 |
| 6. OH + $NH_3$ → $H_2O$ + $NH_2$ | 3.2 | 12.7 |
| 7. HCl + $CH_3$ → Cl + $CH_4$ | 1.7 | 7.9 |
| 8. OH + $C_2H_6$ →$H_2O$ + $C_2H_5$ | 3.4 | 19.9 |
| 9. F + $H_2$ → HF + H | 1.8 | 33.4 |
| 10. O + $CH_4$ →OH + $CH_3$ | 13.7 | 8.1 |
| 11. H + $PH_3$→ $PH_2$ + $H_2$ | 3.1 | 23.2 |
| 12. H + ClH′ → HCl + H′ | 18.0 | 18.0 |
| 13. H + HO → $H_2$ +O | 10.7 | 13.1 |
| 14. H + *trans*-$N_2H_2$→ $H_2$ + $N_2H$ | 5.9 | 40.9 |
| 15. H + $H_2S$ → $H_2$ + HS | 3.5 | 17.3 |
| 16. O + HCl → OH + Cl | 9.8 | 10.4 |
| 17. $NH_2$ + $CH_3$→ $CH_4$ + NH | 8.0 | 22.4 |
| 18. $NH_2$ + $C_2H_5$ → $C_2H_6$ + NH | 7.5 | 18.3 |
| 19. $C_2H_6$ + $NH_2$ → $NH_3$ + $C_2H_5$ | 10.4 | 17.4 |
| 20. $NH_2$ + $CH_4$ → $CH_3$ + $NH_3$ | 14.5 | 17.8 |
| 21. *s-trans cis*-$C_5H_8$ → *s-trans cis*-$C_5H_8$ | 38.4 | 38.4 |

Table S3: SPG15/01 Database

| Reaction | Best Estimate | | | | |
|---|---|---|---|---|---|
| A + BC → AB + C | $R^{\neq}_{AB}$ | $R^{\neq}_{BC}$ | $R^{\neq}_{sum}$ | $\theta^{\neq}_{ABC}$ | Ref. |
| H + HCl → $H_2$ + Cl | 0.981 | 1.431 | 2.412 | 180 | [1] |
| H + $H_2$ → $H_2$ + H | 0.930 | 0.930 | 1.860 | 180 | [2] |
| H + ClH' → HCl + H' | 1.480 | 1.480 | 2.960 | 180 | [1] |
| H + HO → $H_2$ +O | 0.894 | 1.215 | 2.109 | 180 | [3] |
| F + $H_2$ → HF + H | 1.546 | 0.771 | 2.317 | 119 | [4] |


(1) Bian, W.; Werner, H.-J. *J. Chem. Phys.* **2000**, *112*, 220.
(2) Diedrich, D. L.; Anderson, J. B. *J. Chem. Phys.* **1994**, *100*, 8089.
(3) Peterson, K. A.; Dunning, T. H. *J. Phys. Chem. A* **1997**, *101*, 6280.
(4) Stark, R.; Werner, H.-J. *J. Chem. Phys.* **1996**, *104*, 6515.

Table S4: Zero-point-exclusive Ionization Potentials (IP13/3) and Electron Affinities (EA13/3) Database (kcal/mol)

| | IP | EA |
|---|---|---|
| C | 259.7 | 29.1 |
| S | 238.9 | 47.9 |
| SH | 238.9 | 53.3 |
| Cl | 299.1 | 83.4 |
| $Cl_2$ | 265.3 | 55.6 |
| OH | 299.1 | 42.1 |
| O | 313.9 | 33.7 |
| $O_2$ | 278.9 | 10.8 |
| P | 241.9 | 17.2 |
| PH | 234.1 | 23.2 |
| $PH_2$ | 226.3 | 29.4 |
| $S_2$ | 216.0 | 38.5 |
| Si | 187.9 | 31.9 |

Table S5: AE6 Database

| Molecule | $D_e$ (kcal/mol) |
|---|---|
| propyne (C3H4) | 704.79 |
| glyoxal (C2H2O2) | 633.35 |
| cyclobutane (C4H8) | 1149.01 |
| SiH4 | 322.40 |
| SiO | 192.08 |
| S2 | 101.67 |

Table S6: Barrier Heights and Energies of Reaction (kcal/mol) for the Kinetics9 database[a]

| Reaction | Best Estimates | | |
|---|---|---|---|
| | $V_f^{\neq}$ | $V_r^{\neq}$ | ΔE |
| $OH + CH_4 \rightarrow CH_3 + H2O$ | 6.7 | 19.6 | -12.9 |
| $H + OH \rightarrow O + H_2$ | 10.7 | 13.1 | -2.4 |
| $H + H_2S \rightarrow H_2 + HS$ | 3.5 | 17.3 | -13.7 |

[a] From Lynch, B. J.; Truhlar, D. G. *J. Phys. Chem. A* **2003**, *107*, 8996; **2004**; *108*; 1460 (E).

Table S7: ZPE13/99 Database

| Molecule | Anharmonic ZPE (kcal/mol) |
|---|---|
| $H_2$ | 6.21 |
| $CH_4$ | 27.71 |
| $NH_3$ | 21.20 |
| $H_2O$ | 13.25 |
| HF | 5.85 |
| CO | 3.11 |
| $N_2$ | 3.36 |
| $F_2$ | 1.30 |
| $C_2H_2$ | 16.46 |
| HCN | 9.95 |
| $H_2CO$ | 16.53 |
| $CO_2$ | 7.24 |
| $N_2O$ | 6.77 |

Table S8: Root-mean-square Errors and Root-mean-square Errors per Bond for Table 5.

| | AE109/3 | IP13/3 | AE13/3 |
|---|---|---|---|
| | RMSEPB | RMSE | RMSE |
| X1B95/DIDZ | 1.59 | 3.47 | 4.13 |
| X1B95/MG3S | 0.74 | 3.98 | 3.70 |
| B1B95/DIDZ | 1.65 | 3.36 | 4.13 |
| B1B95/MG3S | 0.74 | 2.82 | 3.73 |
| B97-2/DIDZ | 1.67 | 3.65 | 4.15 |
| B97-2/MG3S | 0.86 | 2.90 | 3.45 |
| MPW1B95/DIDZ | 1.59 | 3.61 | 4.03 |
| MPW1B95/MG3S | 0.91 | 2.83 | 3.50 |
| B97-1/DIDZ | 1.81 | 4.21 | 3.86 |
| B97-1/MG3S | 0.98 | 3.57 | 2.48 |
| B98/DIDZ | 2.03 | 4.84 | 4.07 |
| B98/MG3S | 0.86 | 4.01 | 2.39 |
| MPW3LYPX/DIDZ | 2.17 | 5.99 | 4.75 |
| MPW3LYPX/MG3S | 0.99 | 5.47 | 2.93 |
| PBE1PBE/DIDZ | 2.03 | 4.82 | 4.30 |
| PBE1PBE/MG3S | 1.29 | 4.03 | 3.31 |
| mPW1PW91/DIDZ | 2.30 | 5.43 | 4.35 |
| mPW1PW91/MG3S | 1.16 | 4.57 | 3.13 |
| MPWB1K/DIDZ | 2.43 | 4.33 | 5.23 |
| MPWB1K/MG3S | 1.29 | 2.99 | 4.96 |
| B3LYP/DIDZ | 2.55 | 6.50 | 5.06 |
| B3LYP/MG3S | 1.32 | 5.97 | 3.23 |
| XB1K/DIDZ | 2.55 | 3.89 | 5.32 |
| XB1K/MG3S | 1.42 | 3.04 | 5.10 |
| BB1K/DIDZ | 2.72 | 4.10 | 5.37 |
| BB1K/MG3S | 1.61 | 2.88 | 5.18 |
| X3LYP/DIDZ | 3.10 | 6.19 | 5.17 |
| X3LYP/MG3S | 1.98 | 5.74 | 3.60 |
| MPW1K/DIDZ | 3.94 | 6.35 | 5.57 |
| MPW1K/MG3S | 2.75 | 4.95 | 4.82 |

Table S9: Root-mean-square Errors and Root-mean-square Errors per Bond for Table 6.

| | BH6 | AE6 |
|---|---|---|
| Method | RMSE | RMSEPB |
| XB1K/DIDZ | 2.04 | 2.23 |
| XB1K/MG3S | 1.61 | 1.41 |
| MPWB1K/DIDZ | 2.24 | 2.08 |
| MPWB1K/MG3S | 1.91 | 1.26 |
| BB1K/DIDZ | 1.99 | 2.35 |
| BB1K/MG3S | 1.48 | 1.58 |
| B1B95/DIDZ | 3.66 | 1.19 |
| B1B95/MG3S | 3.37 | 0.71 |
| B97-2/DIDZ | 3.84 | 1.11 |
| B97-2/MG3S | 3.70 | 0.81 |
| X1B95/DIDZ | 3.67 | 1.22 |
| X1B95/MG3S | 3.41 | 0.71 |
| MPW1K/DIDZ | 1.71 | 3.62 |
| MPW1K/MG3S | 1.49 | 2.69 |
| MPW1B95/DIDZ | 4.00 | 1.27 |
| MPW1B95/MG3S | 3.79 | 0.93 |
| B98/DIDZ | 4.79 | 1.48 |
| B98/MG3S | 4.49 | 0.74 |
| B97-1/DIDZ | 5.02 | 1.32 |
| B97-1/MG3S | 4.86 | 0.95 |
| mPW1PW91/DIDZ | 4.16 | 1.96 |
| mPW1PW91/MG3S | 4.11 | 1.17 |
| PBE1PBE/DIDZ | 4.81 | 1.81 |
| PBE1PBE/MG3S | 4.85 | 1.26 |
| B3LYP/DIDZ | 5.63 | 1.67 |
| B3LYP/MGS3S | 5.07 | 0.85 |
| X3LYP/DIDZ | 5.73 | 1.60 |
| X3LYP/MG3S | 5.20 | 0.72 |
| MPW3LYP/DIDZ | 6.84 | 1.33 |
| MPW3LYP/MG3S | 5.55 | 0.43 |

Table S10: Root-mean-square errors and Root-mean-square errors per bond for Table 7.

| Methods | AE109/3 | BH42/04 |
|---|---|---|
| | RMSEPB | RMSE |
| MPWB1K/MG3S | 1.29 | 1.65 |
| XB1K/MG3S | 1.42 | 1.57 |
| BB1K/MG3S | 1.61 | 1.52 |
| X1B95 | 0.74 | 3.12 |
| B1B95/MG3S | 0.74 | 3.12 |
| MPW1B95/MG3S | 0.91 | 3.30 |
| MPW1K/MG3S | 2.75 | 1.66 |
| B97-2/MG3S | 0.86 | 3.65 |
| B98/MG3S | 0.86 | 4.55 |
| B97-1/MG3S | 0.98 | 4.85 |
| mPW1PW91/MG3S | 1.16 | 3.87 |
| B3LYP/MG3S | 1.32 | 4.89 |
| PBE1PBE/MG3S | 1.29 | 4.51 |
| MPW3LYP/MG3S | 0.99 | 5.31 |
| X3LYP/MG3S | 1.98 | 5.17 |

Table S11: Root-mean-square errors for Table 8 [a]

| | bond distance | perpendicular looseness | 15 distances |
|---|---|---|---|
| Method | RMSE | RMSE | RMSE |
| BB1K/MG3S | 0.02 | 0.01 | 0.02 |
| XB1K/MG3S | 0.02 | 0.01 | 0.02 |
| MPW1K/MG3S | 0.02 | 0.02 | 0.02 |
| MPWB1K/MG3S | 0.02 | 0.01 | 0.02 |
| QCISD/MG3 | 0.03 | 0.03 | 0.03 |
| MPW1B95/MG3S | *0.06* | *0.08* | *0.07* |
| X1B95/MG3S | *0.06* | *0.09* | *0.07* |
| B1B95/MG3S | *0.06* | *0.09* | *0.07* |
| mPW1PW91/MG3S | *0.06* | *0.09* | *0.07* |
| B97-2/MG3S | *0.08* | *0.09* | *0.09* |
| X3LYP/MG3S | *0.09* | *0.10* | *0.10* |
| MPW3LYP/MG3S | *0.09* | *0.10* | *0.10* |
| B3LYP/MG3S | *0.10* | *0.11* | *0.10* |

[a] MPW3LYP, MPW1B95, B97-2, B1B95, B3LYP and mPW1PW91 do not yield a finite-distance saddle point for $F + H_2 \rightarrow HF + H$. Therefore, in computing errors for these methods, the error in the forming bond length and perpendicular looseness were arbitrarily set equal to 0.15 Å and 0.18 Å, respectively, which are respectively 1.5 times the largest errors that any other method makes in these quantities. Since this an underestimate (the true error is infinite), these values are in italics.

Table S12: Root-Mean-Square Error for Calculating Zero Point Energies

| | RMS error in ZPE [a] | |
|---|---|---|
| Method | unscaled | scaled |
| B3LYP/MG3S | 0.23 | 0.11 |
| MPW3LYP/DIDZ | 0.25 | 0.10 |
| MPW1B95/DIDZ | 0.39 | 0.12 |
| X1B95/DIDZ | 0.41 | 0.12 |
| MPW3LYP/MG3S | 0.25 | 0.11 |
| B1B95/MG3S | 0.35 | 0.14 |
| MPW1B95/MG3S | 0.37 | 0.15 |
| XB1K/DIDZ | 0.64 | 0.15 |
| MPWB1K/DIDZ | 0.65 | 0.15 |
| X1B95/MG3S | 0.39 | 0.15 |
| BB1K/MG3S | 0.59 | 0.18 |
| MPW1K/MG3S | 0.60 | 0.18 |
| XB1K/MG3S | 0.60 | 0.19 |
| MPWB1K/MG3S | 0.62 | 0.19 |
| HF/MG3S | 1.16 | 0.27 |

[a] kcal/mol