

Correction to ‘‘Evaluating Transition Metal Barrier Heights with the Latest Density Functional Theory Exchange–Correlation Functionals: The MOBH35 Benchmark Database’’ [*J. Phys. Chem. A*, **2019**, *123*, 3761. DOI: 10.1021/acs.jpca.9b01546]

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Supporting Information

Table S1. Evaluation of the MOBH35 database for a wide variety of exchange–correlation functionals (ordered by class alphabetically), low-cost methods and wavefunction methods using the new CCSD(T)/CBSw1+Δ(T)/TZVP benchmark reference values.

Functional	No Dispersion		With Dispersion		
	MAD	RMSD	Type	MAD	RMSD
LSDA					
SVWN5 ^{S1,S2,S3,S4}	6.9	9.5	N/A ^b		
GGA					
B97-D3BJ ^{S5,S6}	— ^a	— ^a	D3(BJ)	5.4	7.6
BLYP ^{S7,S8}	6.8	9.8	D3(BJ)	5.9	8.3
			D4	5.4	7.6
			NL	5.1	6.9
BP86 ^{S7,S9}	4.8	6.6	D3(BJ)	5.6	8.2
			D4	5.1	7.2
			NL	5.5	7.7
GLYP ^{S10,S11}	7.2	11.2	D4	6.0	8.3
HCTH ^{S12}	6.1	90	D3(BJ)	4.8	6.9
mPWLYP ^{S8,S13}	6.3	8.9	D3(BJ)	5.4	7.5
			D4	5.6	7.8

mPW PW91 ^{S13,S14,S15,S16,S17,S18}	4.7	6.4	D3(BJ)	5.2	7.5
			D4	4.9	6.7
N12 ^{S19}	4.5	6.1	D3(0)	5.0	7.5
OLYP ^{S8,S20}	7.0	11.4	D3(BJ)	5.1	7.3
			D4	4.9	6.5
PBE ^{S21,S22}	4.2	5.6	D3(BJ)	4.7	6.5
			D4	4.6	6.3
			NL	4.8	6.6
revPBE ^{S23}	5.4	8.0	D3(BJ)	5.0	7.2
			D4	4.9	6.6
			NL	5.1	7.0
rPW86PBE ^{S21,S22}	5.7	7.2	D3(BJ)	5.3	7.3
			D4	5.1	7.0
			NL	5.0	6.9
			SCNL(<i>i.e.</i> , VV10)	5.0	6.9
SOGGA11 ^{S24}	5.6	7.1	N/A ^b		
XLYP ^{S8,S25}	6.6	9.3	D3(BJ)	6.1	8.5
			D4	5.5	7.5

ω B97 ^{S26}	3.1	4.0	D4	2.9	3.9
meta-GGA					
B97M-D3BJ ^{S27,S28}	— ^a	— ^a	D3(BJ)	3.4	4.9
B97M-V ^{S27}	— ^a	— ^a	NL	2.9	4.2
M06-L ^{S29}	3.8	5.2	D3(0)	4.0	5.7
			D4	4.1	5.8
			NL	4.1	5.9
M11-L ^{S30}	4.2	5.8	D3(0)	4.1	6.1
MN12-L ^{S31}	4.1	6.1	D3(BJ)	4.8	7.5
MN15-L ^{S32}	3.5	5.5	D3(0)	3.5	5.5
PKZB ^{S33,S34}	4.0	5.6	D3(0)	5.6	7.9
revTPSS ^{S35,S36}	3.8	5.0	D3(BJ)	4.4	6.1
			D4	4.2	5.7
SCAN ^{c,S37}	3.3	4.4	D3(BJ)	3.8	5.2
			D4	3.7	5.0
			NL	3.8	5.2
			SCNL	3.8	5.2
TPSS ^{S38}	4.3	6.1	D3(BJ)	4.4	6.2

			D4	4.3	5.9
			NL	4.6	6.4
VSXC ^{S39}	12.8	24.0	N/A ^b		
τ HCTH ^{S40}	5.6	8.3	D3(BJ)	5.0	6.9
hybrid-GGA					
APFD ^{S41}	— ^a	— ^a	PFD	3.8	5.6
B1LYP ^{S42}	5.5	8.6	D3(BJ)	3.8	5.3
			D4	3.3	4.4
B3LYP ^{S43}	5.2	8.1	D3(BJ)	3.8	5.2
			D4	3.3	4.5
			NL	2.8	3.9
B3PW91 ^{S44}	4.0	6.3	D3(BJ)	3.4	5.2
			D4	2.9	4.1
			NL	3.3	4.7
B97-1 ^{S45}	3.7	5.5	D3(BJ)	2.8	3.9
B97-2 ^{S46}	4.4	7.0	D3(BJ)	3.4	5.0
B98 ^{S47}	4.1	6.2	D3(BJ)	2.9	4.1
BH&HLYP ^{S48}	6.1	9.1	D3(BJ)	3.8	4.9

			D4	3.7	4.7
CAM-B3LYP ^{S49}	4.0	6.3	D3(0)	2.4	3.1
			D4	2.2	2.8
CAM-QTP00 ^{S50}	5.9	8.3	D3(BJ) ^d	4.5	5.9
CAM-QTP01 ^{S51}	3.5	4.8	D3(BJ) ^d	2.6	3.5
CAM-QTP02 ^{S52}	3.9	5.2	D3(BJ) ^d	3.1	
HISS ^{S53,S54}	3.8	5.4	D3(BJ)	3.2	4.4
HSE03 ^{S55,S56,S57,S58,S59,S60,S61}	3.1	4.5	D3(BJ)	2.9	4.2
HSE06 ^{S55,S56,S57,S58,S59,S60,S61}	3.1	4.5	D3(BJ)	2.7	4.0
LC- ω HPBE ^{S61}	4.1	5.9	D3(BJ)	3.2	4.5
LC- ω PBE ^{S62,S63,S64}	4.1	5.9	D3(0)	3.3	4.5
LRC- ω PBEh ^{e,S65}	3.2	4.7	D3(BJ) ^d	2.6	3.4
mPW1K ^{S66}	4.2	6.5	N/A ^b		
mPW1PW91 ^{S13}	3.5	5.5	D3(BJ)	2.9	4.3
			D4	2.5	3.4
N12-SX ^{S67}	3.3	4.8	D3(BJ)	3.0	4.5
O3LYP ^{S8,S20,S68}	6.2	10.4	D3(BJ)	3.4	4.7
			D4	3.8	5.2

PBE0 ^{S69}	3.0	4.5	D3(BJ)	2.6	3.8
			D4	2.5	3.4
			NL	3.2	4.5
revPBE0 ^{S23,S69}	4.2	7.1	D3(BJ)	2.8	4.0
			D4	3.2	4.3
			NL	2.9	4.1
			SCNL	2.9	4.2
revPBE38 ^{S70}	4.6	7.4	D4	2.4	3.2
			NL	2.9	3.9
SOGGA11-X ^{S71}	4.0	6.0	D3(BJ)	2.9	3.9
X3LYP ^{S25}	4.9	7.4	D4	3.3	4.4
ω B97X ^{S26}	3.0	4.0	D3(0) ^{S72,S73}	2.2	3.0
			D3(BJ) ^{S28,S74}	2.3	3.3
			D4	2.5	3.4
			NL(<i>i.e.</i> ,	2.0	2.7
			ω B97X-V) ^{S74}		

hybrid-meta-GGA

B1B95 ^{S75}	2.9	4.2	D3(BJ)	3.3	5.0
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			D4	2.9	4.1
BB1K ^{S76}	3.5	4.9	N/A ^b		
BMK ^{S77}	3.6	5.8	D3(BJ)	3.1	4.3
M06 ^{S78}	3.2	4.3	D3(0)	3.7	5.4
			D4	3.6	5.2
			NL	3.6	5.3
M06-2X ^{S78}	3.2	4.4	D3(0)	3.1	4.2
M06-HF ^{S79}	5.1	7.1	D3(0)	4.7	6.5
M08-HX ^{S80}	3.5	5.0	D3(0)	3.4	4.8
M11 ^{S81}	3.0	6.7	D3(BJ)	2.7	3.8
MN12-SX ^{S67}	2.8	4.1	D3(BJ)	2.8	4.2
MN15 ^{S82}	2.5	3.6	D3(BJ)	2.5	3.6
mPW1B95 ^{S83}	2.7	3.6	D3(BJ)	2.8	3.9
			D4	2.6	3.4
mPW1KCIS ^{S84}	4.2	6.3	D3(BJ)	3.9	5.3
mPWB1K ^{S83}	3.3	4.6	D3(BJ)	3.2	4.3
			D4	2.8	3.9
mPWKCIS1K ^{S84}	4.6	7.0	D3(BJ)	3.1	4.1

PBE1KCIS ^{S85}	3.7	5.3	D3(BJ)	3.0	4.1
PW6B95 ^{S86}	2.6	3.6	D3(BJ)	2.4	3.5
			D4	2.1	2.9
			NL	2.4	3.3
PWB6K ^{S86}	3.0	4.1	D3(BJ)	2.8	3.9
revTPSS0 ^{S35,S36,S87}	2.9	4.6	D3(BJ)	2.5	3.8
			D4	2.1	3.0
revTPSSh ^{S35,S36,S38}	3.0	4.5	D3(BJ)	3.4	5.0
			D4	3.0	4.3
SCAN0 ^{S88}	2.3	3.3	D3(BJ) ^d	2.3	3.3
TPSS0 ^{S87}	3.6	5.5	D3(BJ)	3.2	4.7
			D4	3.0	4.2
			NL	2.7	3.7
TPSS1KCIS ^{S89}	3.8	6.0	D3(BJ)	3.4	4.9
TPSSh ^{S38}	3.5	5.5	D3(BJ)	3.6	5.0
			D4	3.1	4.4
τ HCTHhyb ^{S40}	3.9	5.7	D3(BJ)	3.5	4.9
ω B97M-D3BJ ^{S28,S90}	— ^a	— ^a	D3(BJ)	1.9	2.5

ω B97M-V ^{S90}	— ^a	— ^a	NL	1.7	2.3
double hybrid					
B2GP-PLYP ^{S91}	1.7	2.6	D3(BJ)	2.3	3.7
			D4	2.2	3.4
			NL	2.2	3.7
B2K-PLYP ^{S92}	1.4	2.0	D3(BJ)	2.0	3.3
B2NC-PLYP ^{e,S93}	1.7	2.2	D3(BJ) ^f	1.8	2.4
B2PLYP ^{S94}	6.8	9.8	D3(BJ)	5.5	7.7
			D4	5.6	7.8
			NL	2.8	4.5
B2T-PLYP ^{S91}	2.2	3.1	N/A ^b		
DOD-PBEB95 ^{S95}	— ^a	— ^a	D3(BJ)	2.1	3.7
			D4	2.9	5.6
DOD-PBEP86 ^{S95}	— ^a	— ^a	D3(BJ)	2.1	3.9
			D4	1.6	2.7
			NL	1.7	2.9
DOD-SCAN ^{S96}	— ^a	— ^a	D3(BJ)	1.8	3.0
			D4	1.6	2.5

DOD-SVWN5 ^{S95}	---^a	---^a	D3(BJ)	1.8	3.3
			D4	1.4	2.4
DSD-BLYP ^{S95,S97}	---^a	---^a	D3(BJ)	2.6	4.6
			D4	3.3	3.8
			NL	2.4	3.9
DSD-PBEB95 ^{S95}	---^a	---^a	D3(BJ)	2.2	3.8
			D4	2.8	5.2
			NL	2.1	3.4
DSD-PBEP86 ^{S95,S98}	---^a	---^a	D3(BJ)	2.2	3.8
			D4	1.9	3.1
			NL	2.1	3.6
DSD-PBEPBE ^{S95}	---^a	---^a	D3(BJ)	2.4	4.4
			NL	2.4	4.1
DSD-SCAN ^{S96}	---^a	---^a	D4	1.6	2.5
LS1-DH ^{e,g,S99}	2.4	3.3	D3(BJ) ^f	2.9	4.4
mPW2K-PLYP ^{S92}	3.4	9.0	N/A ^b		
mPW2NC-PLYP ^{e,S93}	3.3	4.8	D3(BJ) ^f	3.7	5.7
mPW2PLYP ^{S100}	2.4	3.4	D3(BJ)	2.5	3.6

			D4	2.3	3.3
noDispSD-SCAN ^{S96}	2.6	3.9	N/A ^b		
PBE0-2 ^{S101}	2.8	4.0	D3(BJ)	3.5	5.5
			D4	3.1	4.7
PBE0-DH ^{S102}	2.3	3.1	D3(BJ)	2.5	3.5
			D4	2.3	3.0
PBE-QIDH ^{S103}	2.1	2.7	D3(BJ)	2.6	3.8
PWPB95 ^{S104}	1.5	2.2	D3(BJ)	2.1	3.4
			D4	1.8	2.8
			NL	2.0	3.2
revDOD-BLYP ^{S96}	— ^a	— ^a	D4	1.6	2.3
revDOD-PBEB95 ^{S96}	— ^a	— ^a	D3(BJ)	1.8	3.0
			D4	1.6	2.4
revDOD-PBEP86 ^{S96}	— ^a	— ^a	D3(BJ)	1.6	2.7
			D4	1.4	2.2
revDOD-PBEPBE ^{S96}	— ^a	— ^a	D4	1.6	2.6
revDSD-BLYP ^{S96}	— ^a	— ^a	D3(BJ)	2.0	3.2
			D4	1.8	2.6

revDSD-PBEB95 ^{S96}	— ^a	— ^a	D3(BJ)	1.9	3.2
			D4	1.6	2.5
revDSD-PBEP86 ^{S96}	— ^a	— ^a	D3(BJ)	1.7	2.9
			D4	1.5	2.4
revDSD-PBEPBE ^{S96}	— ^a	— ^a	D4	1.7	2.7
SCAN0-2 ^{S88}	2.9	4.4	N/A ^b		
SCAN0-DH ^{S88}	1.8	2.5	N/A ^b		
SCAN-QIDH ^{S88}	2.2	2.9	N/A ^b		
SOS0-PBE0-2 ^{e,S105}	1.5	2.0	D3(BJ) ^f	1.7	2.7
SOS0-PBE0-DH ^{e,S105}	2.6	3.8	D3(BJ) ^f	2.4	3.4
SOS0-PBE-CIDH ^{e,S105}	2.5	3.6	D3(BJ) ^f	2.4	3.4
SOS0-PBE-QIDH ^{e,S105}	2.0	2.7	D3(BJ) ^f	1.9	2.5
ωB97M(2) ^{h,S106}	— ^a	— ^a	NL	1.9	3.2

wave function methods

HF/QZVPP	13.5	19.3	N/A ^b
DLPNO-MP2/TZVP	5.8	9.4	N/A ^b
DLPNO-MP2/QZVPP	6.0	9.2	N/A ^b
DLPNO-CCSD(T)/SVP	1.8	2.4	N/A ^b

DLPNO-CCSD(T)/TZVP	1.2	1.6	N/A ^b
DLPNO-CCSD/QZVPP	2.6	3.6	N/A ^b
DLPNO-CCSD(T)/CBS(SVP/TZVP)	1.7	2.2	N/A ^b
DLPNO-CCSD(T)/CBS(SVP/TZVP)	6.4	10.5	N/A ^b
MP2/CBS(SVP/TZVP)	5.9	9.1	N/A ^b
RI-SCS-MP2/TZVPP	3.2	5.4	N/A ^b
RI-SCS-MP2/QZVPP	2.9	4.6	N/A ^b
RI-SCS-MP2/CBS(TZVPP/QZVPP)	2.8	4.5	N/A ^b
CCSD(T)/CBS _{W1}	0.5	0.7	

low cost/semi-empirical methods

B97-3c ^{S107}	— ^a	— ^a	D3(0)	4.5	6.6
HF-3c ^{S108}	— ^a	— ^a	D3(0)	13.7	17.7
PBEh-3c ^{S109}	— ^a	— ^a	D3(0)	5.0	9.6
PM6 ^{S110}	21.8	29.1	D3(0) ^{S111}	20.5	27.9
			DH+ ^{S112}	21.1	28.5

	DH2S ^{S113,S114}	21.2	28.6
	DH2X ^{S115}	21.2	28.6
	D3H4 ^{S116,S117}	19.2	26.0
	D3H4X	19.2	26.0
PM7 ^{S118}	106.4	146.3	N/A ^b
PM7-TS	68.0	141.4	N/A ^b

^a By definition, a dispersion correction is part of the functional form. ^b Not available or not applicable. ^c SCAN has been reported to have significant grid dependence,^{S119} so the calculations were repeated with other integration grids, yielding (MAD, RMSD – both in kcal/mol) of GRID4 (3.1, 4.3), GRID5 (3.1, 4.3), GRID6 (3.3, 4.4), GRID7 (3.3, 4.5); clearly, this is not an issue here. ^d Dispersion parameters from Santra *et al.*^{S120} ^e New results. ^f D3(BJ) parameters from Mehta *et al.*^{S121} ^g Toulouse *et al.* suggest three values for the parameter λ that defines the functional form – 0.75, 0.70 and 0.50;^{S99} the first was used as this was used to fit the D3(BJ) parameters.^{S122} ^h ω B97M(2) results taken from Santra *et al.*^{S106}

References

- S1. Hohenberg, P.; Kohn, W. Inhomogeneous Electron Gas. *Phys. Rev.* **1964**, *136*, B864-B871.
- S2. Kohn, W.; Sham, L. J. Self-Consistent Equations Including Exchange and Correlation Effects. *Phys. Rev.* **1965**, *140*, A1133-A1138.
- S3. Slater, J. C., *Quantum Theory of Molecular and Solids Vol. 4: The Self-Consistent Field for Molecular and Solids*. McGraw-Hill: New York, 1974.

- S4. Vosko, S. H.; Wilk, L.; Nusair, M. Accurate spin-dependent electron liquid correlation energies for local spin density calculations: a critical analysis. *Can. J. Phys.* **1980**, *58*, 1200-1211.
- S5. Grimme, S. Semiempirical GGA-type density functional constructed with a long-range dispersion correction. *J. Comput. Chem.* **2006**, *27*, 1787-1799.
- S6. Grimme, S.; Ehrlich, S.; Goerigk, L. Effect of the damping function in dispersion corrected density functional theory. *J. Comput. Chem.* **2011**, *32*, 1456-1465.
- S7. Becke, A. D. Density-functional exchange-energy approximation with correct asymptotic behavior. *Phys. Rev. A* **1988**, *38*, 3098-3100.
- S8. Lee, C.; Yang, W.; Parr, R. G. Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1988**, *37*, 785-789.
- S9. Perdew, J. P. Density-functional approximation for the correlation energy of the inhomogeneous electron gas. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1986**, *33*, 8822-8824.
- S10. Adamo, C.; Barone, V. Implementation and validation of the Lacke-Gordon exchange functional in conventional density functional and adiabatic connection methods. *J. Comput. Chem.* **1998**, *19*, 418-429.
- S11. Gill, P. M. W. A new gradient-corrected exchange functional. *Mol. Phys.* **1996**, *89*, 433-445.
- S12. Boese, A. D.; Handy, N. C. A new parametrization of exchange-correlation generalized gradient approximation functionals. *J. Chem. Phys.* **2001**, *114*, 5497-5503.

- S13. Adamo, C.; Barone, V. Exchange functionals with improved improved long-range behavior and adiabatic connection methods without adjustable parameters: The mPW and mP1PW models. *J. Chem. Phys.* **1998**, *108*, 664-675.
- S14. Perdew, J. P. In *Electronic Structures of Solids*, Ziesche, P.; Eschrig, H., Eds.; Akademie Verlag: Berlin, 1991; p 11.
- S15. Perdew, J. P.; Chevary, J. A.; Vosko, S. H.; Jackson, K. A.; Pederson, M. A.; Singh, D. J.; Fiolhais, C. Atoms, molecules, solids, and surfaces: Applications of the generalized gradient approximation for exchange and correlation. *Phys. Rev. B* **1992**, *46*, 6671-6687.
- S16. Perdew, J. P.; Chevary, J. A.; Vosko, S. H.; Jackson, K. A.; Pederson, M. A.; Singh, D. J.; Fiolhais, C. Erratum: Atoms, molecules, solids, and surfaces: Applications of the generalized gradient approximation for exchange and correlation. *Phys. Rev. B* **1993**, *48*, 4978.
- S17. Perdew, J. P.; Burke, K.; Wang, Y. Generalized gradient approximation for the exchange-correlation hole of a many-electron system. *Phys. Rev. B* **1996**, *54*, 16533-16539.
- S18. Burke, K.; Perdew, J. P.; Wang, Y. In *Electronic Density Functional Theory: Recent Progress and New Directions*, Dobson, J. F.; Vignale, G.; Das, M. P., Eds.; Plenum Publishing: New York, NY, 1998.
- S19. Peverati, R.; Truhlar, D. G. Exchange–Correlation Functional with Good Accuracy for Both Structural and Energetic Properties while Depending Only on the Density and Its Gradient. *J. Chem. Theory Comput.* **2012**, *8*, 2310-2319.
- S20. Handy, N. C.; Cohen, A. J. Left-right correlation energy. *Mol. Phys.* **2001**, *99*, 403-412.
- S21. Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.* **1996**, *77*, 3865-3868.

- S22. Perdew, J. P.; Burke, K.; Ernzerhof, M. Gerneralized Gradient Approximation Made Simple [Phys. Rev. Lett. 77, 3865 (1996)]. *Phys. Rev. Lett.* **1997**, *78*, 1396.
- S23. Zhang, Y.; Yang, W. Comment on “Generalized Gradient Approximation Made Simple”. *Phys. Rev. Lett.* **1998**, *80*, 890.
- S24. Peverati, R.; Zhao, Y.; Truhlar, D. G. Generalized Gradient Approximation That Recovers the Second-Order Density-Gradient Expansion with Optimized Across-the-Board Performance. *J. Phys. Chem. Lett.* **2011**, *2*, 1991-1997.
- S25. Xu, X.; Goddard III, W. A. The X3LYP extended density functional for accurate descriptions of nonbond interactions, spin states, and thermochemical properties. *Proc. Natl. Acad. Sci. U. S. A.* **2004**, *101*, 2673-2677.
- S26. Chai, J.-D.; Head-Gordon, M. Systematic optimization of long-range corrected hybrid density functionals. *J. Chem. Phys.* **2008**, *128*, 084106.
- S27. Mardirossian, N.; Head-Gordon, M. Mapping the genome of meta-generalized gradient approximation density functionals: The search for B97M-V. *J. Chem. Phys.* **2015**, *142*, 074111.
- S28. Najibi, A.; Goerigk, L. The Nonlocal Kernel in van der Waals Density Functionals as an Additive Correction: An Extensive Analysis with Special Emphasis on the B97M-V and ω B97M-V Approaches. *J. Chem. Theory Comput.* **2018**, *14*, 5725-5738.
- S29. Zhao, Y.; Truhlar, D. G. A new local density functional for main-group thermochemistry, transition metal bonding, thermochemical kinetics, and non-covalent interactions. *J. Chem. Phys.* **2006**, *125*, 194101.

S30. Peverati, R.; Truhlar, D. G. M11-L: A Local Density Functional That Provides Improved Accuracy for Electronic Structure Calculations in Chemistry and Physics. *J. Phys. Chem. Lett.* **2012**, *3*, 117-124.

S31. Peverati, R.; Truhlar, D. G. An improved and broadly accurate local approximation to the exchange–correlation density functional: The MN12-L functional for electronic structure calculations in chemistry and physics. *Phys. Chem. Chem. Phys.* **2012**, *14*, 13171-13174.

S32. Yu, H. S.; He, X.; Truhlar, D. G. MN15-L: A New Local Exchange-Correlation Functional for Kohn–Sham Density Functional Theory with Broad Accuracy for Atoms, Molecules, and Solids. *J. Chem. Theory Comput.* **2016**, *12*, 1280-1293.

S33. Perdew, J. P.; Kurth, S.; Zupan, A.; Blaha, P. Accurate Density Functional with Correct Formal Properties: A Step Beyond the Generalized Gradient Approximation. *Phys. Rev. Lett.* **1999**, *82*, 2544-2547.

S34. Perdew, J. P.; Kurth, S.; Zupan, A.; Blaha, P. Erratum: Accurate Density Functional with Correct Formal Properties: A Step Beyond the Generalized Gradient Approximation [Phys. Rev. Lett. 82, 2544 (1999)]. *Phys. Rev. Lett.* **1999**, *82*, 5179.

S35. Perdew, J. P.; Ruzsinszky, A.; Csonka, G. I.; Constantin, L. A.; Sun, J. Workhorse Semilocal Density Functional for Condensed Matter Physics and Quantum Chemistry. *Phys. Rev. Lett.* **2009**, *103*, 026403.

S36. Perdew, J. P.; Ruzsinszky, A.; Csonka, G. I.; Constantin, L. A.; Sun, J. Erratum: Workhorse Semilocal Density Functional for Condensed Matter Physics and Quantum Chemistry [Phys. Rev. Lett. 103, 026403 (2009)]. *Phys. Rev. Lett.* **2011**, *106*, 179902.

S37. Sun, J.; Ruzsinszky, A.; Perdew, J. P. Strongly Constrained and Appropriately Normed Semilocal Density Functional. *Phys. Rev. Lett.* **2015**, *115*, 036402.

- S38. Tao, J.; Perdew, J. P.; Staroverov, V. N.; Scuseria, G. E. Climbing the Density Functional Ladder: Nonempirical Meta-Generalized Gradient Approximation Designed for Molecules and Solids. *Phys. Rev. Lett.* **2003**, *91*, 146401.
- S39. Van Voorhis, T.; Scuseria, G. E. A novel form for the exchange-correlation energy functional. *J. Chem. Phys.* **1998**, *109*, 400-410.
- S40. Boese, A. D.; Handy, N. C. New exchange-correlation density functionals: The role of the kinetic-energy density. *J. Chem. Phys.* **2002**, *116*, 9559-9569.
- S41. Austin, A.; Petersson, G. A.; Frisch, M. J.; Dobek, F. J.; Scalmani, G.; Throssell, K. A Density Functional with Spherical Atom Dispersion Terms. *J. Chem. Theory Comput.* **2012**, *8*, 4989-5007.
- S42. Adamo, C.; Barone, V. Toward reliable adiabatic connection models free from adjustable parameters. *Chem. Phys. Lett.* **1997**, *274*, 242-250.
- S43. Stephens, P. J.; Devlin, F. J.; Chabalowski, C. F.; Frisch, M. J. Ab Initio Calculation of Vibrational Absorption and Circular Dichroism Spectra Using Density Functional Force Field Methods. *J. Phys. Chem.* **1994**, *98*, 11623-11627.
- S44. Becke, A. D. Density-functional thermochemistry. III. The role of exact exchange. *J. Chem. Phys.* **1993**, *98*, 5648-5652.
- S45. Hamprecht, F. A.; Cohen, A. J.; Tozer, D. J.; Handy, N. C. Development and assessment of new exchange-correlation functionals. *J. Chem. Phys.* **1998**, *109*, 6264-6271.
- S46. Wilson, P. J.; Bradley, T. J.; Tozer, D. J. Hybrid exchange-correlation functional determined from thermochemical data and *ab initio* potentials. *J. Chem. Phys.* **2001**, *115*, 9233-9242.

- S47. Schmider, H. L.; Becke, A. D. Optimized density functionals from the extended G2 test set. *J. Chem. Phys.* **1998**, *108*, 9624-9631.
- S48. Becke, A. D. A new mixing of Hartree-Fock and local density-functional theories. *J. Chem. Phys.* **1993**, *98*, 1372-1377.
- S49. Yanai, T.; Tew, D. P.; Handy, N. C. A new hybrid exchange–correlation functional using the Coulomb-attenuating method (CAM-B3LYP). *Chem. Phys. Lett.* **2004**, *393*, 51-57.
- S50. Verma, P.; Bartlett, R. J. Increasing the applicability of density functional theory. IV. Consequences of ionization-potential improved exchange-correlation potentials. *J. Chem. Phys.* **2014**, *140*, 18A543.
- S51. Jin, Y.; Bartlett, R. J. The QTP family of consistent functionals and potentials in Kohn-Sham density functional theory. *J. Chem. Phys.* **2016**, *145*, 034107.
- S52. Haiduke, R. L. A.; Bartlett, R. J. Non-empirical exchange-correlation parameterizations based on exact conditions from correlated orbital theory. *J. Chem. Phys.* **2018**, *148*, 184106.
- S53. Henderson, T. M.; Izmaylov, A. F.; Scuseria, G. E.; Savin, A. Assessment of a Middle-Range Hybrid Functional. *J. Chem. Theory Comput.* **2008**, *4*, 1254-1262.
- S54. Henderson, T. M.; Izmaylov, A. F.; Scuseria, G. E.; Savin, A. The importance of middle-range Hartree-Fock-type exchange for hybrid density functionals. *J. Chem. Phys.* **2007**, *127*, 221103.
- S55. Heyd, J.; Scuseria, G. E. Efficient hybrid density functional calculations in solids: Assessment of the Heyd–Scuseria–Ernzerhof screened Coulomb hybrid functional. *J. Chem. Phys.* **2004**, *121*, 1187-92.

- S56. Heyd, J.; Scuseria, G. E. Assessment and validation of a screened Coulomb hybrid density functional. *J. Chem. Phys.* **2004**, *120*, 7274-7280.
- S57. Heyd, J.; Peralta, J. E.; Scuseria, G. E.; Martin, R. L. Energy band gaps and lattice parameters evaluated with the Heyd-Scuseria-Ernzerhof screened hybrid functional. *J. Chem. Phys.* **2005**, *123*, 174101.
- S58. Heyd, J.; Scuseria, G. E.; Ernzerhof, M. Erratum: “Hybrid functionals based on a screened Coulomb potential” [J. Chem. Phys. 118, 8207 (2003)]. *J. Chem. Phys.* **2006**, *124*, 219906.
- S59. Izmaylov, A. F.; Scuseria, G. E.; Frisch, M. J. Efficient evaluation of short-range Hartree-Fock exchange in large molecules and periodic systems. *J. Chem. Phys.* **2006**, *125*, 104103.
- S60. Krukau, A. V.; Vydrov, O. A.; Izmaylov, A. F.; Scuseria, G. E. Influence of the exchange screening parameter on the performance of screened hybrid functionals. *J. Chem. Phys.* **2006**, *125*, 224106.
- S61. Henderson, T. M.; Izmaylov, A. F.; Scalmani, G.; Scuseria, G. E. Can short-range hybrids describe long-range-dependent properties? *J. Chem. Phys.* **2009**, *131*, 044108.
- S62. Vydrov, O. A.; Heyd, J.; Krukau, A.; Scuseria, G. E. Importance of short-range versus long-range Hartree-Fock exchange for the performance of hybrid density functionals. *J. Chem. Phys.* **2006**, *125*, 074106.
- S63. Vydrov, O. A.; Scuseria, G. E. Assessment of a long-range corrected hybrid functional. *J. Chem. Phys.* **2006**, *125*, 234109.

- S64. Vydrov, O. A.; Scuseria, G. E.; Perdew, J. P. Tests of functionals for systems with fractional electron number. *J. Chem. Phys.* **2007**, *126*, 154109.
- S65. Rohrdanz, M. A.; Martins, K. M.; Herbert, J. M. A long-range-corrected density functional that performs well for both ground-state properties and time-dependent density functional theory excitation energies, including charge-transfer excited states. *J. Chem. Phys.* **2008**, *130*, 054112.
- S66. Lynch, B. J.; Fast, P. L.; Harris, M.; Truhlar, D. G. Adiabatic Connection for Kinetics. *J. Phys. Chem. A* **2000**, *104*, 4811-4815.
- S67. Peverati, R.; Truhlar, D. G. Screened-exchange density functionals with broad accuracy for chemistry and solid-state physics. *Phys. Chem. Chem. Phys.* **2012**, *14*, 16187-16191.
- S68. Cohen, A. J.; Handy, N. C. Dynamic correlation. *Mol. Phys.* **2001**, *99*, 607-615.
- S69. Adamo, C.; Barone, V. Toward reliable density functional methods without adjustable parameters: The PBE0 model. *J. Chem. Phys.* **1999**, *110*, 6158-6170.
- S70. Hujo, W.; Grimme, S. Performance of the van der Waals Density Functional VV10 and (hybrid)GGA Variants for Thermochemistry and Noncovalent Interactions. *J. Chem. Theory Comput.* **2011**, *7*, 3866-3871.
- S71. Peverati, R.; Truhlar, D. G. Communication: A global hybrid generalized gradient approximation to the exchange-correlation functional that satisfies the second-order density-gradient constraint and has broad applicability in chemistry. *J. Chem. Phys.* **2011**, *135*, 191102.
- S72. Chai, J.-D.; Head-Gordon, M. Long-range corrected hybrid density functionals with damped atom–atom dispersion corrections. *Phys. Chem. Chem. Phys.* **2008**, *10*, 6615-6620.

S73. Lin, Y.-S.; Li, G.-D.; Mao, S.-P.; Chai, J.-D. Long-Range Corrected Hybrid Density Functionals with Improved Dispersion Corrections. *J. Chem. Theory Comput.* **2013**, *9*, 263-272.

S74. Mardirossian, N.; Head-Gordon, M. ω B97X-V: A 10-parameter, range-separated hybrid, generalized gradient approximation density functional with nonlocal correlation, designed by a survival-of-the-fittest strategy. *Phys. Chem. Chem. Phys.* **2014**, *16*, 9904-9924.

S75. Becke, A. D. Density-functional thermochemistry. IV. A new dynamical correlation functional and implications for exact-exchange mixing. *J. Chem. Phys.* **1996**, *104*, 1040-1046.

S76. Zhao, Y.; Lynch, B. J.; Truhlar, D. G. Development and Assessment of a New Hybrid Density Functional Model for Thermochemical Kinetics. *J. Phys. Chem. A* **2004**, *108*, 2715-2719.

S77. Boese, A. D.; Martin, J. M. L. Development of density functionals for thermochemical kinetics. *J. Chem. Phys.* **2004**, *121*, 3405-3416.

S78. Zhao, Y.; Truhlar, D. G. The M06 suite of density functionals for main group thermochemistry, thermochemical kinetics, noncovalent interactions, excited states, and transition elements: two new functionals and systematic testing of four M06-class functionals and 12 other functionals. *Theor. Chem. Acc.* **2008**, *120*, 215-241.

S79. Zhao, Y.; Truhlar, D. G. Density Functional for Spectroscopy: No Long-Range Self-Interaction Error, Good Performance for Rydberg and Charge-Transfer States, and Better Performance on Average than B3LYP for Ground States. *J. Phys. Chem. A* **2006**, *110*, 13126-13130.

- S80. Zhao, Y.; Truhlar, D. G. Exploring the Limit of Accuracy of the Global Hybrid Meta Density Functional for Main-Group Thermochemistry, Kinetics, and Noncovalent Interactions. *J. Chem. Theory Comput.* **2008**, *4*, 1849-1868.
- S81. Peverati, R.; Truhlar, D. G. Improving the Accuracy of Hybrid Meta-GGA Density Functionals by Range Separation. *J. Phys. Chem. Lett.* **2011**, *2*, 2810-2817.
- S82. Yu, H. S.; He, X.; Li, S. L.; Truhlar, D. G. MN15: A Kohn–Sham global-hybrid exchange–correlation density functional with broad accuracy for multi-reference and single-reference systems and noncovalent *Chem. Sci.* **2016**, *7*, 5032-5051.
- S83. Zhao, Y.; Truhlar, D. G. Hybrid Meta Density Functional Theory Methods for Thermochemistry, Thermochemical Kinetics, and Noncovalent Interactions: The MPW1B95 and MPWB1K Models and Comparative Assessments for Hydrogen Binding and van der Waals Interactions. *J. Phys. Chem. A* **2004**, *108*, 6908-6918.
- S84. Zhao, Y.; González-García, N.; Truhlar, D. G. Benchmark Database of Barrier Heights for Heavy Atom Transfer, Nucleophilic Substitution, Association, and Unimolecular Reactions and Its Use to Test Theoretical Methods. *J. Phys. Chem. A* **2005**, *109*, 2012-2018.
- S85. Zhao, Y.; Truhlar, D. G. Benchmark Databases for Nonbonded Interactions and Their Use To Test Density Functional Theory. *J. Chem. Theory Comput.* **2005**, *1*, 415-432.
- S86. Zhao, Y.; Truhlar, D. G. Design of Density Functionals That Are Broadly Accurate for Thermochemistry, Thermochemical Kinetics, and Nonbonded Interactions. *J. Phys. Chem. A* **2005**, *109*, 5656-5667.
- S87. Grimme, S. Accurate Calculation of the Heats of Formation for Large Main Group Compounds with Spin-Component Scaled MP2 Methods. *J. Phys. Chem. A* **2005**, *109*, 3067-3077.

- S88. Hui, K.; Chai, J.-D. SCAN-based hybrid and double-hybrid density functionals from models without fitted parameters. *J. Chem. Phys.* **2016**, *144*, 044114.
- S89. Zhao, Y.; Lynch, B. J.; Truhlar, D. G. Multi-coefficient extrapolated density functional theory for thermochemistry and thermochemical kinetics. *Phys. Chem. Chem. Phys.* **2005**, *7*, 43-52.
- S90. Mardirossian, N.; Head-Gordon, M. ω B97M-V: A combinatorially optimized, range-separated hybrid, meta-GGA density functional with VV10 nonlocal correlation. *J. Chem. Phys.* **2016**, *144*, 214110.
- S91. Karton, A.; Tarnopolsky, A.; Lamère, J.-F.; Schatz, G. C.; Martin, J. M. L. Highly Accurate First-Principles Benchmark Data Sets for the Parametrization and Validation of Density Functional and Other Approximate Methods. Derivation of a Robust, Generally Applicable, Double-Hybrid Functional for Thermochemistry and Thermochemical Kinetics. *J. Phys. Chem. A* **2008**, *112*, 12868-12886.
- S92. Tarnopolsky, A.; Karton, A.; Sertchook, R.; Vuzman, D.; Martin, J. M. L. Double-Hybrid Functionals for Thermochemical Kinetics. *J. Phys. Chem. A* **2008**, *112*, 3-8.
- S93. Yu, F. Double-Hybrid Density Functionals Free of Dispersion and Counterpoise Corrections for Non-Covalent Interactions. *J. Phys. Chem. A* **2014**, *118*, 3175-3182.
- S94. Grimme, S. Semiempirical hybrid density functional with perturbative second-order correlation. *J. Chem. Phys.* **2006**, *124*, 034108.
- S95. Kozuch, S.; Martin, J. M. L. Spin-Component-Scaled Double Hybrids: An Extensive Search for the Best Fifth-Rung Functionals Blending DFT and Perturbation Theory. *J. Comput. Chem.* **2013**, *34*, 2327–2344.

- S96. Santra, G.; Sylvetsky, N.; Martin, J. M. L. Minimally Empirical Double Hybrid Functionals Trained Against the GMTKN55 Database: revDSD-PBEP86-D4, revDOD-PBE-D4, and DOD-SCAN-D4. *J. Phys. Chem. A* **2019**, *Just Accepted Manuscripts*, DOI: 10.1021/acs.jpca.9b03157.
- S97. Kozuch, S.; Gruzman, D.; Martin, J. M. L. DSD-BLYP: A General Purpose Double Hybrid Density Functional Including Spin Component Scaling and Dispersion Correction. *J. Phys. Chem. C* **2010**, *114*, 20801-20808.
- S98. Kozuch, S.; Martin, J. M. L. DSD-PBEP86: in search of the best double-hybrid DFT with spin-component scaled MP2 and dispersion corrections. *Phys. Chem. Chem. Phys.* **2011**, *13*, 20104-20107.
- S99. Toulouse, J.; Sharkas, K.; Brémond, E.; Adamo, C. Communication: Rationale for a new class of double-hybrid approximations in density-functional theory. *J. Chem. Phys.* **2011**, *135*, 101102.
- S100. Schwabe, T.; Grimme, S. Towards chemical accuracy for the thermodynamics of large molecules: new hybrid density functionals including non-local correlation effects. *Phys. Chem. Chem. Phys.* **2006**, *8*, 4398-4401.
- S101. Chai, J.-D.; Mao, S.-P. Seeking for reliable double-hybrid density functionals without fitting parameters: The PBE0-2 functional. *Chem. Phys. Lett.* **2012**, *538*, 121-125.
- S102. Brémond, E.; Adamo, C. Seeking for parameter-free double-hybrid functionals: The PBE0-DH model. *J. Chem. Phys.* **2011**, *135*, 024106.
- S103. Brémond, É.; Sancho-García, J. C.; Pérez-Jiménez, Á.; Adamo, C. Communication: Double-hybrid functionals from adiabatic-connection: The QIDH model. *J. Chem. Phys.* **2014**, *141*, 031101.

- S104. Goerigk, L.; Grimme, S. Efficient and Accurate Double-Hybrid-Meta-GGA Density Functionals—Evaluation with the Extended GMTKN30 Database for General Main Group Thermochemistry, Kinetics, and Noncovalent Interactions. *J. Chem. Theory Comput.* **2011**, *7*, 291-309.
- S105. Alipour, M. Seeking for Spin-Opposite-Scaled Double-Hybrid Models Free of Fitted Parameters. *J. Phys. Chem. A* **2016**, *120*, 3726-3730.
- S106. Mardirossian, N.; Head-Gordon, M. Survival of the most transferable at the top of Jacob's ladder: Defining and testing the ω B97M(2) double hybrid density functional. *J. Chem. Phys.* **2018**, *148*, 241736.
- S107. Brandenberg, J. G.; Bannwarth, C.; Hansen, A.; Grimme, S. B97-3c: A revised low-cost variant of the B97-D density functional method. *J. Chem. Phys.* **2018**, *148*, 064104.
- S108. Sure, R.; Grimme, S. Corrected small basis set Hartree-Fock method for large systems. *J. Comput. Chem.* **2013**, *34*, 1672-1685.
- S109. Grimme, S.; Brandenberg, J. G.; Bannwarth, C.; Hansen, A. Consistent structures and interactions by density functional theory with small atomic orbital basis sets. *J. Chem. Phys.* **2015**, *143*, 054107.
- S110. Stewart, J. J. P. Optimization of parameters for semiempirical methods V: Modification of NDDO approximations and application to 70 elements. *J. Mol. Model.* **2007**, *13*, 1173-1213.
- S111. Grimme, S.; Antony, J.; Ehrlich, S.; Krieg, H. A consistent and accurate ab initio parametrization of density functional dispersion correction (DFT-D) for the 94 elements H-Pu. *J. Chem. Phys.* **2010**, *132*, 154104.

- S112. Korth, M. Third-Generation Hydrogen-Bonding Corrections for Semiempirical QM Methods and Force Fields. *J. Chem. Theory Comput.* **2010**, *6*, 3808-3816.
- S113. Korth, M.; Pitoňák, M.; Řezáč, J.; Hobza, P. A Transferable H-Bonding Correction for Semiempirical Quantum-Chemical Methods. *J. Chem. Theory Comput.* **2010**, *6*, 344-352.
- S114. Řezáč, J.; Fanfrlík, J.; Salahub, D.; Hobza, P. Semiempirical Quantum Chemical PM6 Method Augmented by Dispersion and H-Bonding Correction Terms Reliably Describes Various Types of Noncovalent Complexes. *J. Chem. Theory Comput.* **2009**, *5*, 1749-1760.
- S115. Řezáč, J.; Hobza, P. A halogen-bonding correction for the semiempirical PM6 method. *Chem. Phys. Lett.* **2011**, *506*, 286-289.
- S116. Řezáč, J.; Hobza, P. Advanced Corrections of Hydrogen Bonding and Dispersion for Semiempirical Quantum Mechanical Methods. *J. Chem. Theory Comput.* **2012**, *8*, 141-151.
- S117. Vorlová, B.; Nachtigallová, D.; Jiráskova-Vaníčková, J.; Ajani, H.; Jansa, P.; Řezáč, J.; Fanfrlík, J.; Otyepka, M.; Hobza, P.; Konvalinka, J., et al. Malonate-based inhibitors of mammalian serine racemase: Kinetic characterization and structure-based computational study. *Eur. J. Med. Chem.* **2015**, *89*, 189-197.
- S118. Stewart, J. J. P. Optimization of parameters for semiempirical methods VI: more modifications to the NDDO approximations and re-optimization of parameters. *J. Mol. Model.* **2013**, *19*, 1-32.

- S119. Brandenberg, J. G.; Bates, J. E.; Sun, J.; Perdew, J. P. Benchmark tests of a strongly constrained semilocal functional with a long-range dispersion correction. *Phys. Rev. B* **2016**, *94*, 115144.
- S120. Santra, G.; Martin, J. M. L. Some Observations on the Performance of the Most Recent Exchange-Correlation Functionals for the Large and Chemically Diverse GMTKN55 Benchmark. *arXiv.org* **2019**, 1905.60172v2.
- S121. Mehta, N.; Casanova-Páez, M.; Goerigk, L. Semi-empirical or non-empirical double-hybrid density functionals: which are more robust? . *Phys. Chem. Chem. Phys.* **2018**, *20*, 23175-23194.
- S122. Nehta, N.; Goerigk, L. personal communication.