Extrapolating DFT towards the complete basis set limit: Lessons from PBE

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Supplementary Material

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Additional supplemental files and archives in computer-readable form are available on Zenodo, see DOI: 10.5281/zenodo.4779488. An executable version of this archive is available on Binder.

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Table S1: List of methods used with the diet100 variant of the GMTKN55 database. References correspond to functionals and parametrizations of dispersion corrections.

Method name	**DFA type**	**Disp. type**	**Reference**
BLYP-D3(BJ)	GGA	D3(BJ)	1;2;3
PBE-D3(BJ)	GGA	D3(BJ)	4;3
revPBE-D3(BJ)	GGA	D3(BJ)	5;4;3
B97-D3(BJ)	GGA	D3(BJ)	6;3
SCAN-D3(BJ)	mGGA	D3(BJ)	7;8
M06L-D3	mGGA	D3(0)	9;10
B97M-V	mGGA	VV10	11
B97M-D3(BJ)	mGGA	D3(BJ)	11;12
B3LYP-D3(BJ)	single hyb.	D3(BJ)	13;14;3
ωB97X-V	single hyb.	VV10	15
M052X-D3	single hyb.	D3(0)	16;10
dlDF+D10	single hyb.	DAS2010	17;18
DSD-BLYP-D3(BJ)	double hyb.	D3(BJ)	19
B2PLYP-D3(BJ)	double hyb.	D3(BJ)	20;10
PWPB95-NL	double hyb.	VV10	21;22;23
PBE0DH-D3(BJ)	double hyb.	D3(BJ)	24;25

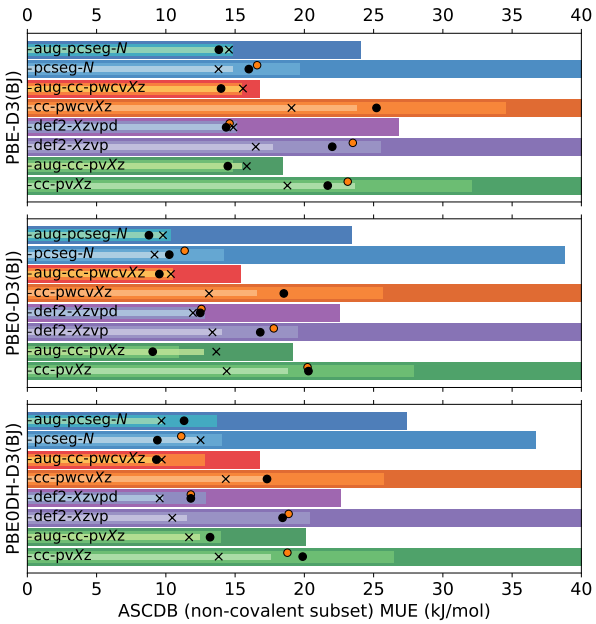

Figure S1: The total of the mean unsigned errors in the non-covalent subset of the ASCDB database. Calculations with 2-, 3-, and 4-ζ basis sets shown as bars. Results from the [2,3]-ζ extrapolation (•) and [3,4]-ζ extrapolation (×) from current work compared to previous [2,3]-ζ results (•), where available.

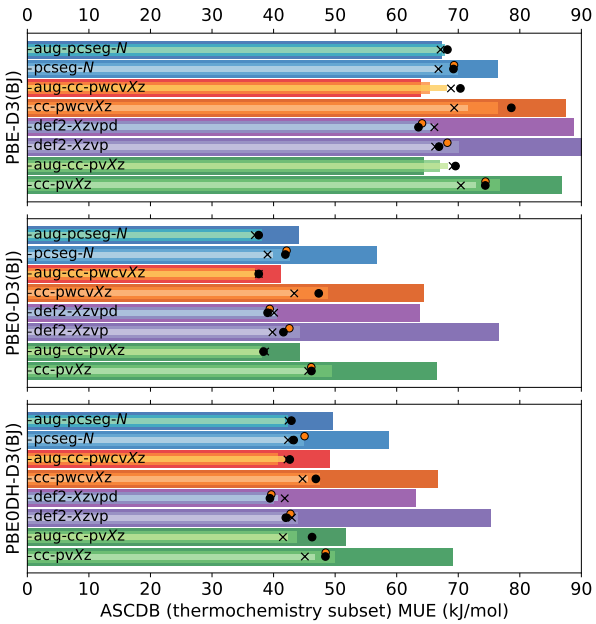

Figure S2: The total of the mean unsigned errors in the thermochemistry subset of the ASCDB database. Bars and symbols as in Fig. S1.

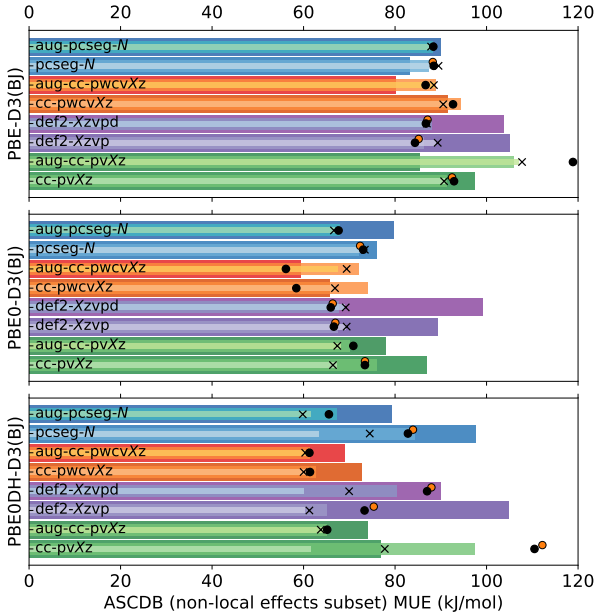

Figure S3: The total of the mean unsigned errors in the non-local subset of the ASCDB database. Bars and symbols as in Fig. S1.

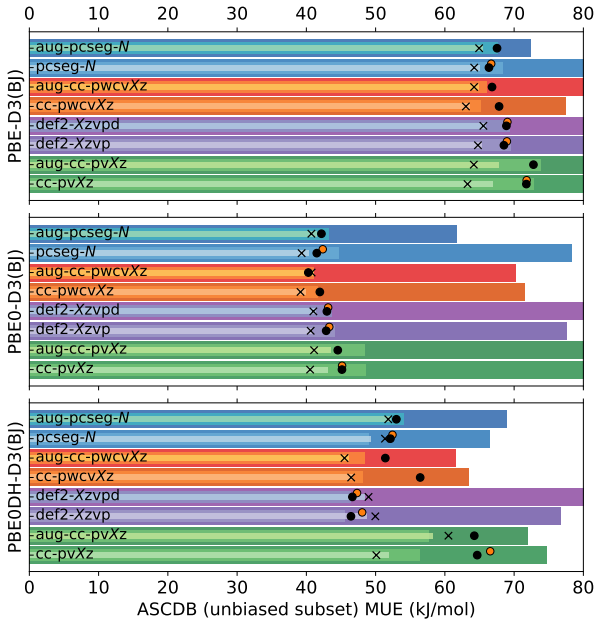

Figure S4: The total of the mean unsigned errors in the unbiased calculations subset of the ASCDB database. Bars and symbols as in Fig. S1.

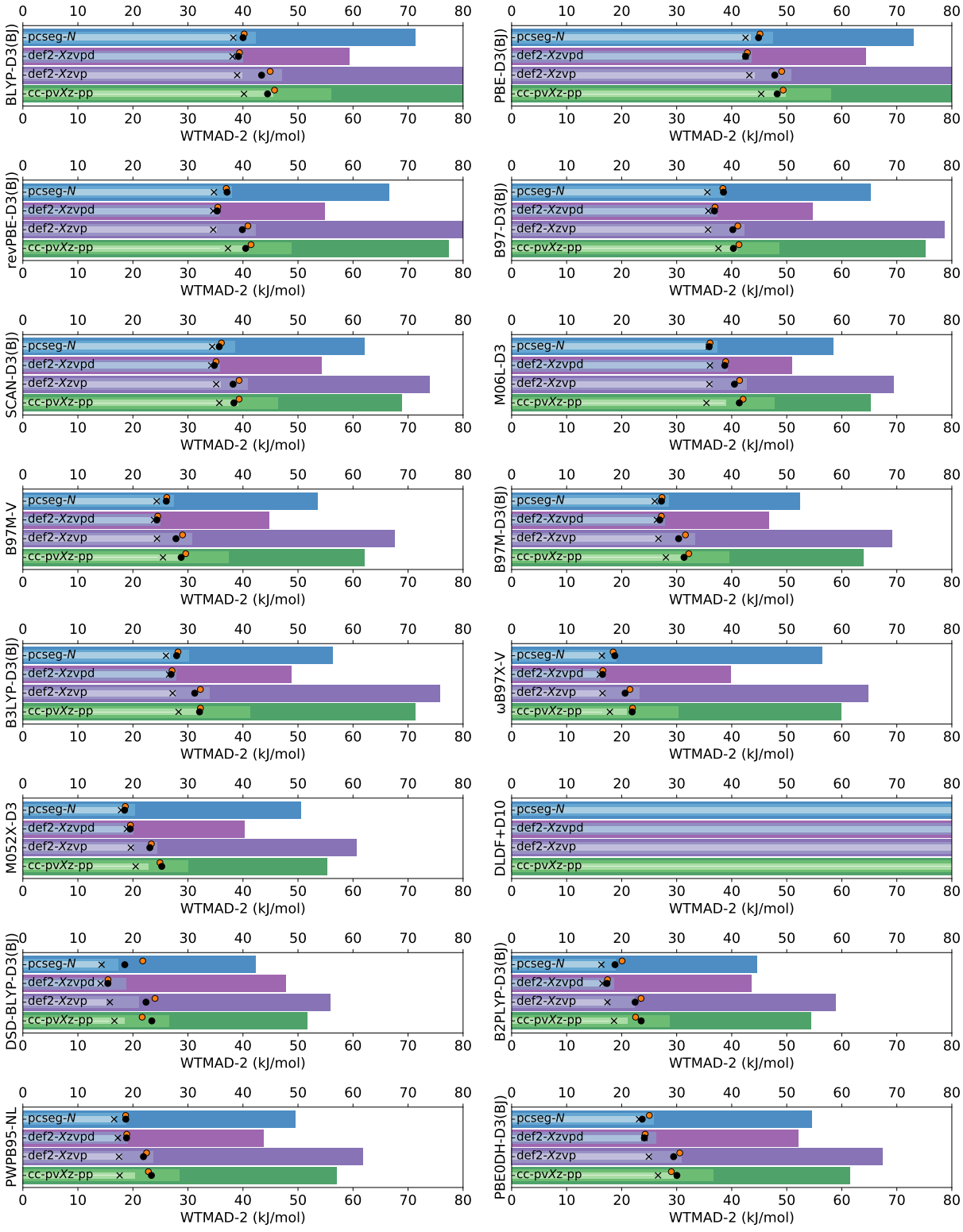

Figure S5: The WTMAD-2 measures of the diet100 subset of the GMTKN55 database. Bars and symbols as in Fig. S1.

References

[1] A. D. Becke, "Density-functional exchange-energy approximation with correct asymptotic behavior," *Phys. Rev. A*, vol. 38, pp. 3098–3100, Sept. 1988.

[2] C. Lee, W. Yang, and R. G. Parr, "Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density," *Phys. Rev. B*, vol. 37, pp. 785–789, Jan. 1988.

[3] S. Grimme, S. Ehrlich, and L. Goerigk, "Effect of the damping function in dispersion corrected density functional theory," *J. Comput. Chem.*, vol. 32, pp. 1456–1465, May 2011.

[4] J. P. Perdew, K. Burke, and M. Ernzerhof, "Generalized gradient approximation made simple," *Phys. Rev. Lett.*, vol. 77, pp. 3865–3868, Oct. 1996.

[5] Y. Zhang and W. Yang, "Comment on "Generalized gradient approximation made simple"," *Phys. Rev. Lett.*, vol. 80, pp. 890–890, Jan. 1998.

[6] S. Grimme, "Semiempirical GGA-type density functional constructed with a long-range dispersion correction," *Journal of computational chemistry*, vol. 27, no. 15, pp. 1787–1799, 2006.

[7] J. Sun, A. Ruzsinszky, and J. P. Perdew, "Strongly constrained and appropriately normed semilocal density functional," *Phys. Rev. Lett.*, vol. 115, p. 036402, July 2015.

[8] J. G. Brandenburg, J. E. Bates, J. Sun, and J. P. Perdew, "Benchmark tests of a strongly constrained semilocal functional with a long-range dispersion correction," *Phys. Rev. B*, vol. 94, p. 115144, Sept. 2016.

[9] Y. Zhao and D. G. Truhlar, "A new local density functional for main-group thermochemistry, transition metal bonding, thermochemical kinetics, and noncovalent interactions," *The Journal of Chemical Physics*, vol. 125, p. 194101, Nov. 2006.

[10] L. Goerigk and S. Grimme, "A thorough benchmark of density functional methods for general main group thermochemistry, kinetics, and noncovalent interactions," *Phys. Chem. Chem. Phys.*, vol. 13, no. 14, p. 6670, 2011.

[11] N. Mardirossian and M. Head-Gordon, "Mapping the genome of meta-generalized gradient approximation density functionals: The search for B97M-V," *The Journal of Chemical Physics*, vol. 142, p. 074111, Feb. 2015.

[12] A. Najibi and L. Goerigk, "The nonlocal kernel in van der Waals density functionals as an additive correction: An extensive analysis with special emphasis on the B97M-V and ωB97M-V approaches," *J. Chem. Theory Comput.*, vol. 14, pp. 5725–5738, Nov. 2018.

[13] A. D. Becke, "A new mixing of Hartree–Fock and local density-functional theories," *The Journal of Chemical Physics*, vol. 98, pp. 1372–1377, Jan. 1993.

[14] P. J. Stephens, F. J. Devlin, C. F. Chabalowski, and M. J. Frisch, "Ab initio calculation of vibrational absorption and circular dichroism spectra using density functional force fields," *J. Phys. Chem.*, vol. 98, pp. 11623–11627, Nov. 1994.

[15] N. Mardirossian and M. Head-Gordon, "ωB97X-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.*, vol. 16, no. 21, p. 9904, 2014.

[16] Y. Zhao, N. E. Schultz, and D. G. Truhlar, "Design of density functionals by combining the method of constraint satisfaction with parametrization for thermochemistry, thermochemical kinetics, and noncovalent interactions," *J. Chem. Theory Comput.*, vol. 2, pp. 364–382, Mar. 2006.

[17] K. Pernal, R. Podeszwa, K. Patkowski, and K. Szalewicz, "Dispersionless density functional theory," *Phys. Rev. Lett.*, vol. 103, p. 263201, Dec. 2009.

[18] R. Podeszwa, K. Pernal, K. Patkowski, and K. Szalewicz, "Extension of the Hartree-Fock plus dispersion method by first-order correlation effects," *J. Phys. Chem. Lett.*, vol. 1, pp. 550–555, Jan. 2010.

[19] S. Kozuch and J. M. L. Martin, "Spin-component-scaled double hybrids: An extensive search for the best fifth-rung functionals blending DFT and perturbation theory," *J. Comput. Chem.*, pp. 2327–2344, July 2013.

[20] S. Grimme, "Semiempirical hybrid density functional with perturbative second-order correlation," *Journal of Chemical Physics*, vol. 124, no. 3, pp. 034108–034108, 2006.

[21] L. Goerigk and S. Grimme, "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.*, vol. 7, pp. 291–309, Feb. 2011.

[22] W. Hujo and S. Grimme, "Performance of the van der waals density functional VV10 and (hybrid)GGA variants for thermochemistry and noncovalent interactions," *Journal of Chemical Theory and Computation*, vol. 7, no. 12, pp. 3866–3871, 2011.

[23] F. Yu, "Spin-component-scaled double-hybrid density functionals with nonlocal van der Waals correlations for noncovalent interactions," *J. Chem. Theory Comput.*, vol. 10, pp. 4400–4407, Oct. 2014.

[24] E. Brémond and C. Adamo, "Seeking for parameter-free double-hybrid functionals: The PBE0-DH model," *The Journal of Chemical Physics*, vol. 135, p. 024106, July 2011.

[25] D. Bousquet, E. Brémond, J. C. Sancho-García, I. Ciofini, and C. Adamo, "Non-parametrized functionals with empirical dispersion corrections: A happy match?," *Theor Chem Acc*, vol. 134, p. 1602, Jan. 2015.