Density-corrected DFT explained: Questions and answers

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I. Supporting Information

CCSD	17.3
HF-PBE	15.6
PBE (un-conv.)	16.6
PBE (conv.)	23.9
S^{PBE} (un-conv.)	1.1
S^{PBE} (conv.)	8.4

Table S1: *Electron affinity information of hydrogen atom. CCSD/aug-cc-pV6Z is used as a reference. For standard PBE functional, 0.37 electrons are unbound and denoted as un-converged. For converged cases, where electrons are omitted to match HOMO equals 0, denoted as converged.*

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		$\tilde{S}_{avg.}$	SC	HF	DC(HF)	SC-D4	HF-D4	DC(HF)-D4
BH76	12 spinc	8.0	8.8 (5.0)	3.9 (3.7)	4.4 (5.0)	9.3 (5.1)	4.0 (3.7)	4.7 (5.1)
	w/o spinc	6.6	8.5 (3.8)	3.3 (2.6)	3.3 (2.4)	8.9 (3.9)	3.6 (2.7)	3.5 (2.6)
RC21	9 spinc	9.2	5.4 (3.2)	4.6 (3.5)	4.3 (3.1)	6.9 (3.7)	4.0 (2.7)	4.1 (2.9)
	w/o spinc	11.3	6.8 (2.8)	4.8 (3.2)	4.8 (3.2)	8.5 (2.9)	3.8 (2.4)	3.8 (2.4)
RSE43	8 spinc	3.7	3.1 (1.4)	2.0 (3.3)	2.0 (1.7)	3.0 (1.4)	2.0 (3.4)	1.9 (1.6)
	w/o spinc	2.0	2.9 (1.2)	1.0 (0.8)	1.5 (1.1)	2.8 (1.2)	0.9 (0.7)	1.5 (1.0)

Table S2: *PBE mean absolute errors (MAE, kcal/mol) on three datasets (BH76, RC21, and RSE43) self-consistently, with the HF density, and DC(HF). Root-mean-squared-displacement of absolute errors (RMSD) values are noted in the parenthesis. $\tilde{S}_{avg.}$ is the averaged density sensitivity (kcal/mol) for the given dataset. The deviation of HF's $\langle S^2 \rangle$ by more than 10% from the ideal $\langle S^2 \rangle$ value is taken as a criterion for spin-contamination [1]. The D4 parameters uses the same parameter as PBE-D4 of Ref. [2].*

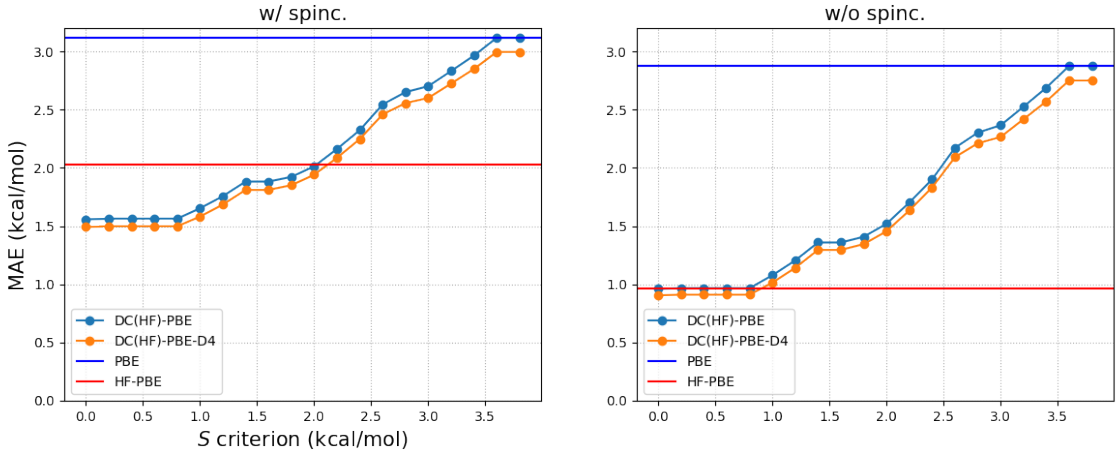

Figure S1: *MAE of RSE43 dataset with respect to the $\tilde{S}$ value cut-off criterion for DC(HF)-PBE. DC(HF)-PBE is SC-PBE for spin-contaminated cases and below the $\tilde{S}$ cut-off criterion value (the x-axis of the plots) and HF-PBE otherwise. The l.h.s. panel is the MAE of all cases in RSE43 and the r.h.s. panel is the MAE of non-spin-contaminated cases.*

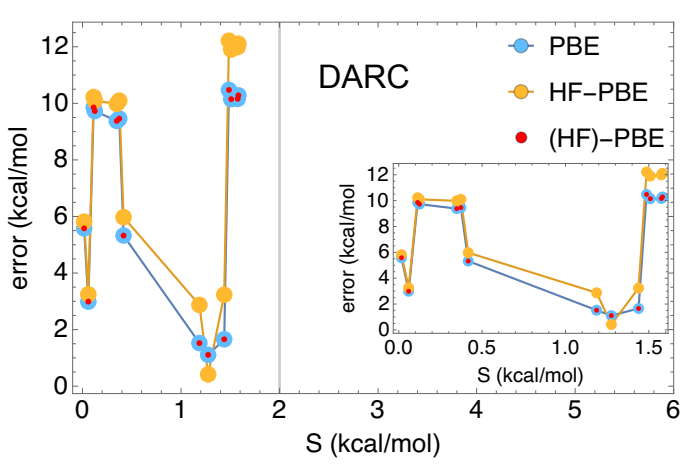

Figure S2: *Same as Fig. 2, but for the DARC dataset.*

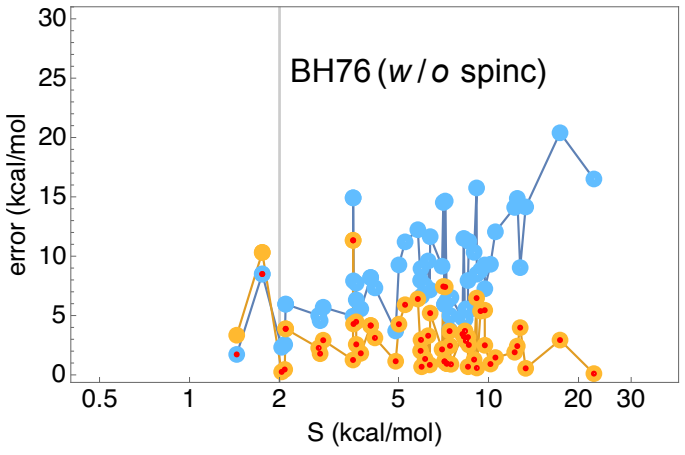

Figure S3: *Same as Fig. 2, but with spin-contaminated cases excluded.*

	Electron Affinity (kcal/mol)				ϵ_H (kcal/mol)			
	PBE		B3LYP					
name	SC	DC	SC	DC	PBE	B3LYP	HF	exact
CCH	7.5	5.5	1.5	-0.2	44.0	28.4	-49.3	-27.9
CH_2	3.6	1.8	1.8	0.8	44.5	29.5	-33.5	-13.4
CH_3	1.6	-0.2	-1.8	-2.8	48.7	34.0	-22.1	-1.2
NH	4.7	1.4	1.2	-1.2	64.3	46.7	1.0	-8.3
NH_2	2.6	0.7	-1.5	-2.6	57.0	38.2	-31.3	-16.8
OH	3.6	0.8	-1.2	-3.0	49.1	23.7	-68.6	-41.7
SiH	2.8	2.2	-1.9	-2.9	28.7	18.9	-35.7	-29.3
SiH_2	4.0	3.2	-0.2	-1.3	32.1	22.4	-30.4	-25.1
SiH_3	-0.2	-0.1	-1.9	-1.6	20.4	6.3	-44.2	-31.4
PH	1.0	0.6	-0.1	-0.3	38.0	24.4	-21.3	-23.5
PH_2	-0.2	0.0	-2.0	-1.8	35.1	21.4	-28.7	-28.8
HS	-0.6	-0.7	-2.5	-2.4	22.0	4.3	-59.7	-54.2
O_2	-0.2	-2.3	0.2	-1.0	77.7	48.1	-57.0	-9.5
NO	6.2	1.4	5.5	2.6	75.9	50.7	-60.2	0.2
CN	-2.8	17.3	1.6	19.1	0.0	-27.1	-120.9	-89.5
PO	3.8	2.6	1.9	0.8	39.2	23.5	-48.7	-24.9
S_2	-2.0	-1.5	-1.5	-1.1	28.5	10.4	-53.0	-38.0
Cl_2	5.4	5.2	8.4	7.9	-22.5	-46.0	-106.8	-54.7
MAE	2.9 (2.1)	2.6 (3.9)	2.0 (1.9)	3.0 (4.2)				
MAE*	2.9 (2.2)	1.8 (1.6)	2.1 (2.0)	2.0 (1.7)				

Table S3: *Same as the Table 2 but with aug-cc-pvqz basis set. Electron affinity errors for the G21EA dataset relative to GMTKN55 reference. HOMO energies (kcal/mol) for anions (ϵ_H). The exact value is the -EA of the reference energy. MAE is the mean absolute error of all electrons affinities while MAE* is the MAE without CN. RMSD values are given in the paraenthesis. CN is omitted due to large spin-contamination. See text for details.*

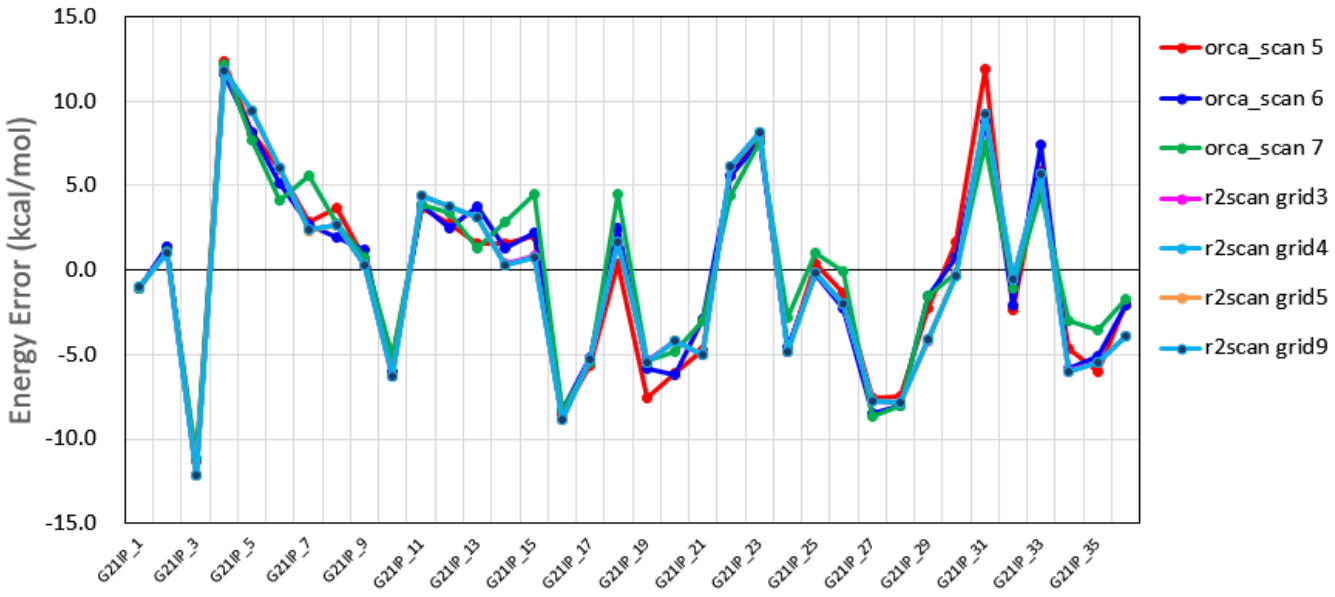

Figure S4: *G21IP reaction energy errors for SCAN and r2SCAN with various grid levels. SCAN shows a grid convergency issue (calculated by ORCA pacakge). Note that all r2SCAN results are very similar (almost no changes).*

References

[1] Adam Rettig, Diptarka Hait, Luke W Bertels, and Martin Head-Gordon. Third-order møller–plesset theory made more useful? the role of density functional theory orbitals. *Journal of Chemical Theory and Computation*, 16(12):7473–7489, 2020.

[2] Eike Caldeweyher, Sebastian Ehlert, Andreas Hansen, Hagen Neugebauer, Sebastian Spicher, Christoph Bannwarth, and Stefan Grimme. A generally applicable atomic-charge dependent london dispersion correction. *The Journal of Chemical Physics*, 150(15):154122, 2019.