Supporting information for

Tests of the RPBE, revPBE, τ-HCTHhyb, ωB97X-D, and MOHLYP density functional approximations and 29 others against representative databases for diverse bond energies and barrier heights in catalysis

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This supporting information contains the comparison of SCF and post-SCF results for the SOGGA functional, the spin quantum numbers of ground states of V and Zr as calculated by each functional, extended versions of Table 2 to 5, and the gradient enhancement factors F_X as a function the reduced gradient densities s for the TPSS, M06-L, VS98, and τ-HCTH meta-GGA functionals, and the expressions of exchange enhancement factors F_X of the GGA and meta-GGA exchange functionals in Figure 1 and Figure S1-S3.

The extended versions of Table 2 to 5 differ from those tables in the main text in two respects: (i) results are rounded to the hundredth of a kcal/mol rather than to the tenth of a kcal/mol; (ii) an additional functional, MOHLYP2, is included. Note that MOHLYP is the original MOHLYP functional of Ref. 4, and MOHLYP2 is a different version presented in Ref. 5; MOHLYP2 was mislabeled as MOHLYP in Ref. 5. MOHLYP2 gives a spin quantum number of 5/2 for the ground state of V and 2 for the ground state of Zr.

Note:

Some of the results differ quantitatively (not enough to change previous conclusions) from previously published numbers. The main sources of these differences are as follows: (i) In some previous work we used fine grids; in the present paper we always use ultrafine grids because we found that the results were not completely converged with fine grids. (ii) In some previous calculations (e.g., the BLYP calculations of the DBH24/08 paper[5]), we used the option SCF=(TIGHT,XQC), whereas in this article we used SCF=(XQC, MAXCONVENTIONALCYCLE=20,TIGHT,INTREP), which ensure the energies to converge to a threshold of 10^{-6} Hartree. (iii) Some of the previous calculations were done with a version of the computer code that had a small (10^{-3}–10^{-4} hartrees) bug in the SOGGA functional.

Contents:

Table S1. Comparison of the calculated bond energies (kcal/mol) by SCF calculations and post-SCF calculations with the SOGGA functional

	Bond energy[a]	Bond energy[b]
SCF (V_2)	82.59	119.05
Post-SCF (V_2)[c]	82.59	119.05
SCF (VS)	121.53	139.75
Post-SCF (VS)[c]	121.55	139.79
SCF for ($NiCH_2^+$)	98.08	98.08
Post-SCF ($NiCH_2^+$)[c]	98.07	98.07

[a] Bond energies calculated by using calculated atomic ground states (V, $S = 5/2$; Ni^+, $S = 1/2$)
[b] Bond energies calculated by using experimental atomic ground states (V, $S = 3/2$; Ni^+, $S = 1/2$).
[c] Post-SCF calculations were done by using the PBEsol densities.

Table S2. Spin quantum numbers of ground states of V and Zr as calculated by various functionals

Functional	V	Zr
BP86	5/2	1
BVP86	5/2	1
BLYP	5/2	1
PW91	5/2	2
B3PW91	5/2	2
B3LYP	5/2	1
B3V5LYP	5/2	1
PBE	5/2	2
B98	3/2	1
revPBE	5/2	2
VS98	5/2	1
PBEhole	5/2	2
PBE0	5/2	2
RPBE	5/2	1
τ-HCTH	3/2	1
τ-HCTHhyb	3/2	1
TPSS	5/2	1
TPSSKCIS	5/2	1
TPSSh	5/2	1
BMK	5/2	1
TPSS1KCIS	5/2	1
MOHLYP	5/2	1
MOHLYP2	5/2	2
MPWLYP1M	5/2	1
B97-3	3/2	1
M05	3/2	1
WC06	5/2	2
B97-D	3/2	1
M06-L	3/2	1
LC-ωPBE	5/2	2
M06	3/2	1
PBEsol	5/2	2
SOGGA	5/2	2
ωB97X-D	5/2	1
HSE	5/2	2

Table S3. Mean signed and unsigned errors in bond energies (kcal/mol per bond)[a, b]

Functional	AE6		ABDE4		TMAE4		MLBE4		DBE18	
	MSE	MUE	MSE	MUE	MSE[c]	MSE[c]	MSE[c]	MUE[c]	AMSE[d]	AMUE[d]
BP86	3.32	3.32	-6.07	6.07	7.44/13.77	7.44/13.77	12.49/15.66	12.49/15.66	5.24	7.94
BVP86	2.59	2.59	-7.16	7.16	3.86/10.65	5.12/11.91	10.90/14.30	10.90/14.30	3.68	7.15
BLYP	-0.50	1.40	-10.53	10.53	6.64/9.54	7.04/9.95	9.60/11.05	9.60/11.05	1.59	6.99
PW91	2.66	3.16	-3.71	3.71	5.83/13.76	6.55/14.48	12.99/16.71	12.99/16.71	5.54	7.51
B3PW91	-0.18	0.63	-7.28	7.28	-20.71/-12.45	20.71/12.45	-2.59/1.02	5.69/4.23	-5.54	6.61
B3LYP	-0.60	0.66	-8.62	8.62	-16.56/-14.33	16.56/14.33	-1.63/-0.52	5.52/4.41	-5.79	6.67
B3V5LYP	-0.89	0.92	-9.04	9.04	-17.06/-14.90	17.06/14.90	-2.00/-0.92	5.74/4.66	-6.18	7.02
PBE	2.39	3.04	-3.98	3.98	5.38/13.18	6.79/14.59	12.62/16.28	12.62/16.28	5.19	7.48
B98	-4.75	4.75	-3.15	3.15	-10.47	10.47	-0.04	0.04	-4.78	6.02
revPBE	-1.22	1.77	-10.46	10.46	-2.79/4.67	5.30/12.22	6.98/10.49	6.98/10.49	-0.58	6.80
VS98	-0.03	0.55	-7.87	7.87	4.09/7.64	6.77/10.31	5.42/7.19	5.42/7.19	0.95	5.23
PBEhole	1.93	2.63	-4.77	4.77	4.42/12.20	8.04/15.82	12.84/16.56	12.84/16.56	4.70	7.85
PBE0	-0.06	1.12	-4.98	4.98	-22.58/-15.69	22.58/15.69	-3.27/-0.11	6.35/3.97	-5.75	6.88
RPBE	-1.66	1.97	-11.08	11.08	-2.08/4.07	4.87/10.86	6.60/9.67	6.60/9.67	-0.99	6.67
τ-HCTH	-0.31	0.73	-7.91	7.91	22.28	22.28	7.94	7.94	4.85	8.72
τ-HCTHhyb	-0.25	0.82	-4.24	4.24	4.25	5.68	2.55	5.94	0.49	3.80
TPSS	0.71	1.09	-9.39	9.39	0.17/6.38	3.29/9.50	8.56/11.67	8.56/11.67	1.13	6.12
TPSSKCIS	0.89	0.99	-8.25	8.25	1.15/6.90	3.56/9.31	9.49/12.37	9.49/12.37	1.79	6.02
TPSSh	0.03	1.28	-9.35	9.35	-10.51/-4.69	10.51/4.69	0.28/3.18	7.09/8.69	-3.37	5.95
BMK	0.12	0.45	-1.36	1.68	-37.99/-29.64	37.99/29.64	-5.35/-1.17	9.87/10.32	-8.50	10.28
TPSS1KCIS	0.01	0.66	-8.13	8.13	-13.29/-8.04	13.29/8.04	1.54/4.16	4.50/5.21	-3.54	5.47
MOHLYP	-2.09	2.21	-13.93	13.93	-2.62/0.02	5.15/7.78	4.55/5.87	4.55/5.87	-2.92	6.43
MOHLYP2	-17.44	17.44	-32.09	32.09	-32.58/-27.08	32.58/27.08	-16.26/-13.54	16.26/13.54	-22.88	22.88

MPWLYP1M	0.09	0.97	-8.56	8.56	1.39/3.37	1.87/3.85	8.06/9.05	8.06/9.05	0.56	4.76
B97-3	-0.18	0.57	-4.63	4.63	-17.25	17.25	-3.11	8.07	-5.61	6.85
M05	-0.02	0.40	-5.78	5.78	-5.91	8.29	-1.62	4.93	-2.96	4.36
WC06[e]	5.17	5.54	1.48	2.34	8.39/19.84	8.39/19.84	17.20/22.00	17.20/22.00	9.54	9.86
B97-D	-0.11	0.38	-7.66	7.66	17.93	17.93	7.42	7.42	3.89	7.46
M06-L	0.49	0.72	-5.54	5.54	0.52	4.22	7.01	7.01	0.61	3.97
LC-ωPBE	-0.41	0.87	-4.70	4.70	-33.55/-26.46	33.55/26.46	-8.07/-4.80	10.09/6.82	-9.28	9.88
M06	0.43	0.57	-1.89	1.89	-8.92	8.92	-1.35	4.35	-2.56	3.56
PBEsol	7.25	7.25	4.15	4.15	13.6/22.93	13.6/22.93	19.41/23.62	19.41/23.62	12.18	12.18
SOGGA	6.97	7.26	5.22	5.22	10.76/21.43	11.79/22.46	19.91/24.46	19.91/24.46	11.99	12.31
ωB97X-D	-0.17	0.41	-2.15	2.15	-20.48/-19.84	20.84/19.84	-2.54/-2.22	6.14/5.83	-5.54	6.42
HSE	-0.56	0.88	-5.66	5.66	-21.95/-15.12	21.95/15.12	-4.72/-1.53	7.96/5.56	-6.26	7.17

[a] Basis set: Metals: TZQ; nonmetals: MG3 in MLBE4, MG3S in AE6, and 6-311+G(3df, 2p) in ABDE4.

[b] A positive MSE corresponds to the functional predicting too large of a bond strength. Note that in computing the mean errors per bond for AE6, as explained in ref. 2, we first compute the mean error in the atomization energy, and then we divide by 4.83, which is the mean number of bonds per molecule. It is not necessary to divide by the average number of bonds for TMAE4 because those data are for diatomics which have only a single bond. MLBE4 has three cases where a single bond is broken and one case where five bonds on broken; for that data set, as explained in ref. 4, we divide the error for $Fe(CO)_5$ by 5 before we compute the mean errors for MLBE4.

[c] The bond dissociation energies of molecules in TMAE4 and MLBE4 databases were calculated in two ways if the calculated atomic ground states are different than the experimental atomic ground states. The numbers before the slash "/" are the MSEs and MUEs calculated with the calculated atomic ground states; while the numbers after the slash are the MSEs and MUEs calculated with the experimental atomic ground states.

[d] AMSE and AMUE are the average of MSEs and MUEs for AE6, ABDE4, TMAE4, and MLBE4 databases weighted 6/18:4/18:4/18:4/18; for TMAE4 and MLBE4 databases, the MSEs and MUEs used in AMSE and AMUE are chosen to be the average of the pre-slash and post-slash values. As explained in footnote *b*, the mean errors averaged to obtain the final average values of this table are all on a per bond basis before we average them.

[e] The bond dissociation energy of V_2, $NiCH_2^+$, and VS were obtained by post-SCF calculations with PBEsol densities due to the convergence problems for V and Ni^+ atoms.

Table S4. Mean signed errors and mean unsigned errors in barrier heights (kcal/mol)[a]

Functional	HATBH6		NSBH6		UABH6		HTBH6		DBH24/08	
	MSE	MUE	MSE	MUE	MSE	MUE	MSE	MUE	AMSE[b]	AMUE[b]
BP86	-13.99	13.99	-7.12	7.12	-3.40	3.40	-9.22	9.22	-8.43	8.43
BVP86	-14.19	14.19	-7.02	7.02	-3.59	3.59	-9.29	9.29	-8.52	8.52
BLYP	-12.36	12.36	-7.53	7.53	-3.06	3.06	-7.76	7.76	-7.68	7.68
PW91	-13.90	13.90	-7.54	7.54	-2.82	2.82	-9.56	9.56	-8.46	8.46
B3PW91	-6.18	6.18	-2.59	2.59	-0.79	1.87	-4.35	4.35	-3.48	3.75
B3LYP	-6.73	6.73	-3.65	3.65	-1.21	1.69	-4.65	4.65	-4.06	4.18
B3V5LYP	-6.76	6.76	-3.63	3.63	-1.28	1.71	-4.64	4.64	-4.08	4.19
PBE	-13.61	13.61	-7.00	7.00	-2.88	2.88	-9.26	9.26	-8.19	8.19
B98	-4.75	4.75	-3.15	3.15	0.09	1.84	-3.93	3.93	-2.94	3.42
revPBE	-10.89	10.89	-5.84	5.84	-2.33	2.33	-6.52	6.52	-6.40	6.40
VS98	-6.88	6.88	-3.96	3.96	-0.05	1.49	-4.91	4.91	-3.95	4.31
PBEhole	-13.62	13.62	-7.35	7.35	-2.83	2.83	-9.11	9.11	-8.23	8.23
PBE0	-5.81	5.81	-2.06	2.06	-0.63	1.93	-4.55	4.55	-3.26	3.59
RPBE	-10.77	10.77	-5.87	5.87	-2.30	2.30	-6.34	6.34	-6.32	6.32
τ-HCTH	-9.18	9.18	-5.84	5.84	-0.57	1.99	-6.14	6.14	-5.43	5.79
τ-HCTHhyb	-6.23	6.23	-4.68	4.68	0.04	1.84	-4.78	4.78	-3.91	4.38
TPSS	-13.02	13.02	-7.93	7.93	-3.62	3.62	-8.23	8.23	-8.20	8.20
TPSSKCIS	-11.62	11.62	-7.66	7.66	-2.22	2.22	-7.02	7.02	-7.13	7.13
TPSSh	-10.11	10.11	-5.85	5.85	-2.81	2.86	-6.65	6.65	-6.36	6.37
BMK	-0.96	0.96	0.60	0.77	0.97	2.05	-1.12	1.12	-0.13	1.23
TPSS1KCIS	-7.80	7.80	-4.95	4.95	-1.16	1.59	-4.91	4.91	-4.71	4.81
MOHLYP	-10.24	10.24	-3.76	3.76	-3.06	3.06	-5.50	5.63	-5.64	5.67
MOHLYP2	-1.44	3.01	-0.79	3.11	-0.64	1.83	2.68	4.21	-0.05	3.04
MPWLYP1M	-11.85	11.85	-7.14	7.14	-2.75	2.75	-7.81	7.81	-7.39	7.39

B97-3	-2.29	2.49	-0.48	0.96	0.71	1.63	-2.16	2.20	-1.06	1.82
M05	-3.26	4.80	0.01	0.95	1.00	2.48	-0.63	1.74	-0.72	2.49
WC06	-15.70	15.70	-7.58	7.58	-3.36	3.36	-11.53	11.53	-9.54	9.54
B97-D	-9.40	9.40	-6.19	6.19	-1.25	1.71	-6.01	6.39	-5.71	5.92
M06-L	-5.85	6.87	-3.35	3.35	0.52	1.77	-4.11	4.21	-3.20	4.05
LC-ωPBE	1.07	2.42	2.82	2.82	1.30	2.09	-1.01	1.15	1.05	2.12
M06	-3.62	4.06	-1.61	1.64	0.54	1.91	-1.53	1.66	-1.56	2.32
PBEsol	-17.50	17.50	-7.40	7.40	-3.90	3.90	-12.69	12.69	-10.37	10.37
SOGGA	-17.04	17.04	-7.14	7.14	-3.87	3.87	-12.85	12.85	-10.23	10.23
ωB97X-D	-1.31	2.19	0.10	0.67	1.03	2.04	-2.04	2.24	-0.56	1.79
HSE	-6.10	6.10	-2.58	2.58	-0.65	1.87	-4.56	4.56	-3.47	3.78

[a] Single-point calculations with MG3S basis set with QCISD/MG3 geometries.

[b] AMSE and AMUE are the average of MSEs and MUEs for the HATBH6, NSBH6, UABH6, and HTBH6 databases.

Table S5. Average error for catalytical energies (AECE) of various functionals, weighting DBE18 and DBH24 equally

Functional	AECE
M06	2.94
M05	3.42
M06-L	4.01
τ-HCTHhyb	4.09
ωB97X-D	4.10
B97-3	4.33
B98	4.72
VS98	4.77
TPSS1KCIS	5.14
B3PW91	5.18
PBE0	5.23
B3LYP	5.43
HSE	5.47
B3V5LYP	5.60
BMK	5.75
LC-ωPBE	6.00
MOHLYP	6.05
MPWLYP1M	6.08
TPSSh	6.16
RPBE	6.50
TPSSKCIS	6.58
revPBE	6.60
B97-D	6.69
TPSS	7.16
τ-HCTH	7.25
BLYP	7.33
BVP86	7.84
PBE	7.84
PW91	7.98
PBEhole	8.04
BP86	8.19
WC06	9.70
SOGGA	11.27
PBEsol	11.28
MOHLYP2	12.96

Table S6. Mean signed errors and mean unsigned errors in barrier heights for two basis sets (kcal/mol)

Method	HATBH6		NSBH6		UABH6		HTBH6		DBH24/08
	MSE	MUE	MSE	MUE	MSE	MUE	MSE	MUE	AMUE
MG3S									
M06-2X	-0.02	0.73	0.60	0.86	0.37	1.09	-0.49	1.24	0.98
M08-SO	-0.57	1.08	0.19	0.69	0.23	1.43	-0.81	1.00	1.05
BMK	-0.96	0.96	0.60	0.77	0.97	2.05	-1.12	1.12	1.22
ωB97X-D	-1.31	2.19	0.10	0.67	1.03	2.04	-2.04	2.24	1.78
B97-3	-2.29	2.49	-0.48	0.96	0.71	1.63	-2.16	2.20	1.82
LC-ωPBE	1.07	2.42	2.82	2.82	1.30	2.09	-1.01	1.15	2.12
M06	-3.62	4.06	-1.61	1.64	0.54	1.91	-1.53	1.66	2.32
maug-cc-pV(T+d)Z									
M06-2X	-0.20	0.41	0.84	0.84	0.19	1.13	-0.50	1.26	0.91
M08-SO	-0.62	0.68	0.80	0.80	0.15	1.32	-0.77	0.91	0.93
BMK	-1.44	1.44	0.72	0.94	0.80	1.93	-1.07	1.47	1.45
ωB97X-D	-1.34	1.73	0.73	0.82	0.89	1.98	-1.87	2.31	1.71
B97-3	-2.65	2.69	-0.14	1.30	0.48	1.56	-2.16	2.27	1.95
LC-ωPBE	1.01	2.22	3.43	3.43	1.12	2.10	-0.90	1.16	2.23
M06	-3.55	3.99	-0.91	1.30	0.47	1.76	-1.36	1.69	2.18

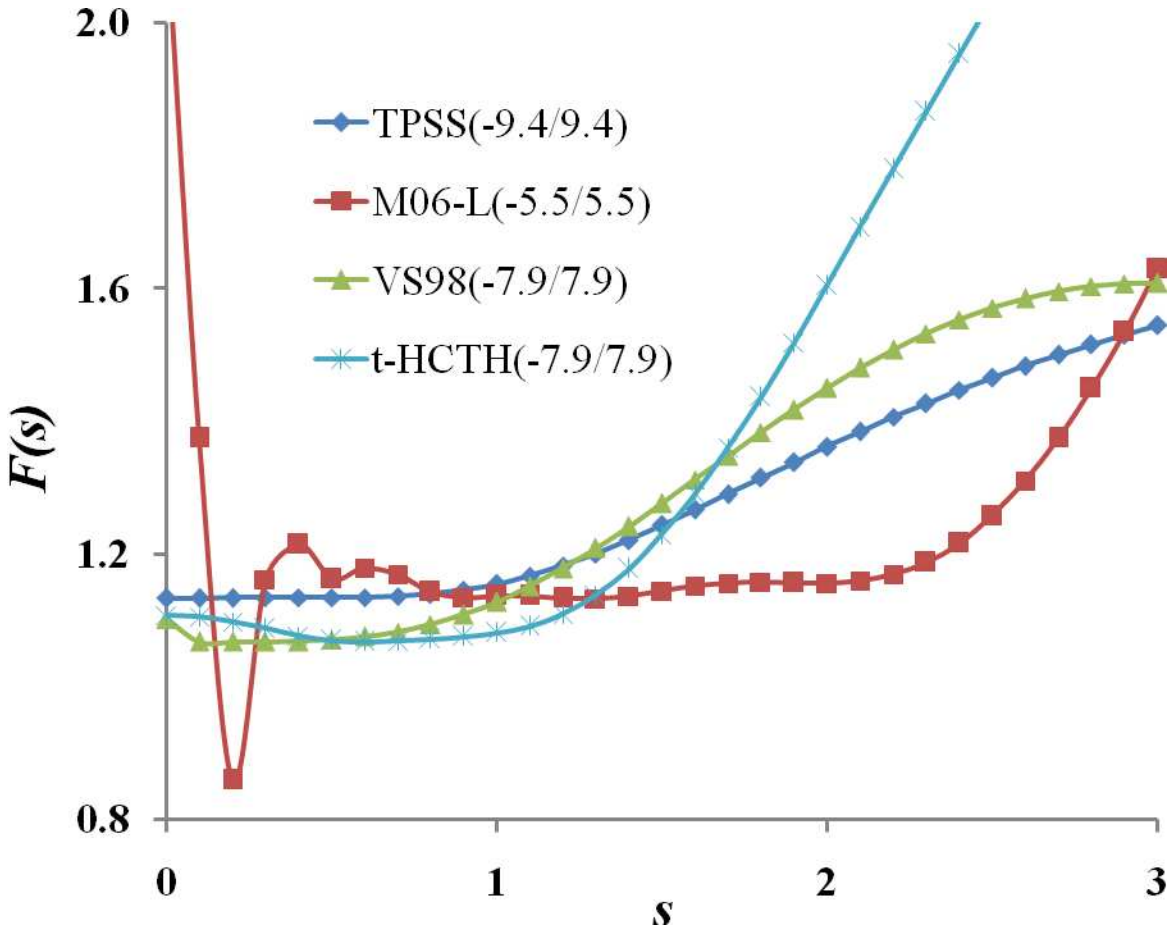

Figure S1. Exchange enhancements factors F_X as function of reduced gradient s ($\alpha = 0$). (the numbers in the parentheses are the MSEs and MUEs of meta-GGA functionals for the ABDE4 database in units of kcal/mol)

Note: s and α are two dimensionless variables defined as following:

$$s = \frac{|\nabla n|}{2(3\pi^2)^{1/3} n^{4/3}}$$

$$\alpha = \frac{\tau - \tau^W}{\tau^{LDA}}$$

where n is the electron density, τ is the kinetic energy density, τ^W is the von Weizsäcker kinetic energy density, and τ^{LDA} is the kinetic energy density of uniform electron gas.

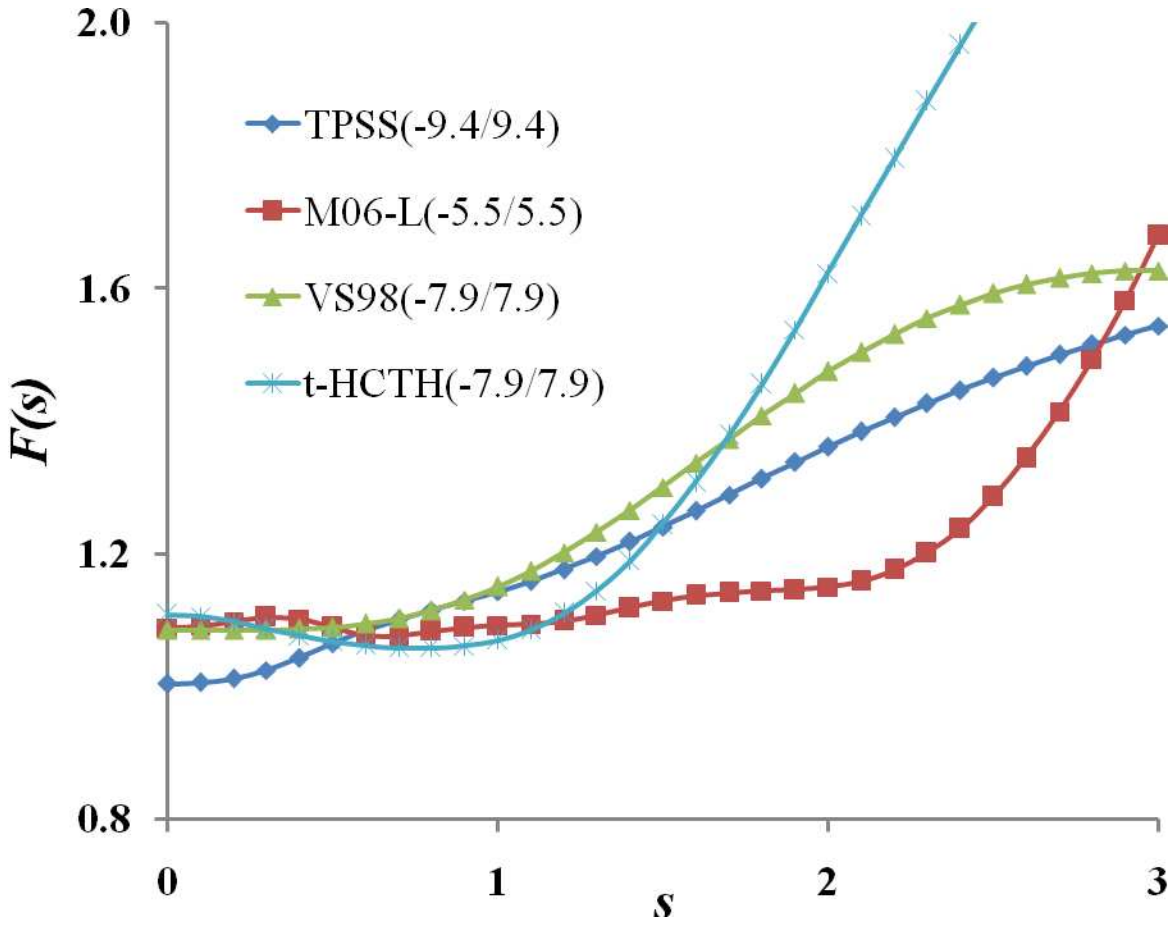

Figure S2. Exchange enhancements factors F_X as function of reduced gradient s ($\alpha = 0.5$). (the numbers in the parentheses are the MSEs and MUEs of meta-GGA functionals for the ABDE4 database in units of kcal/mol)

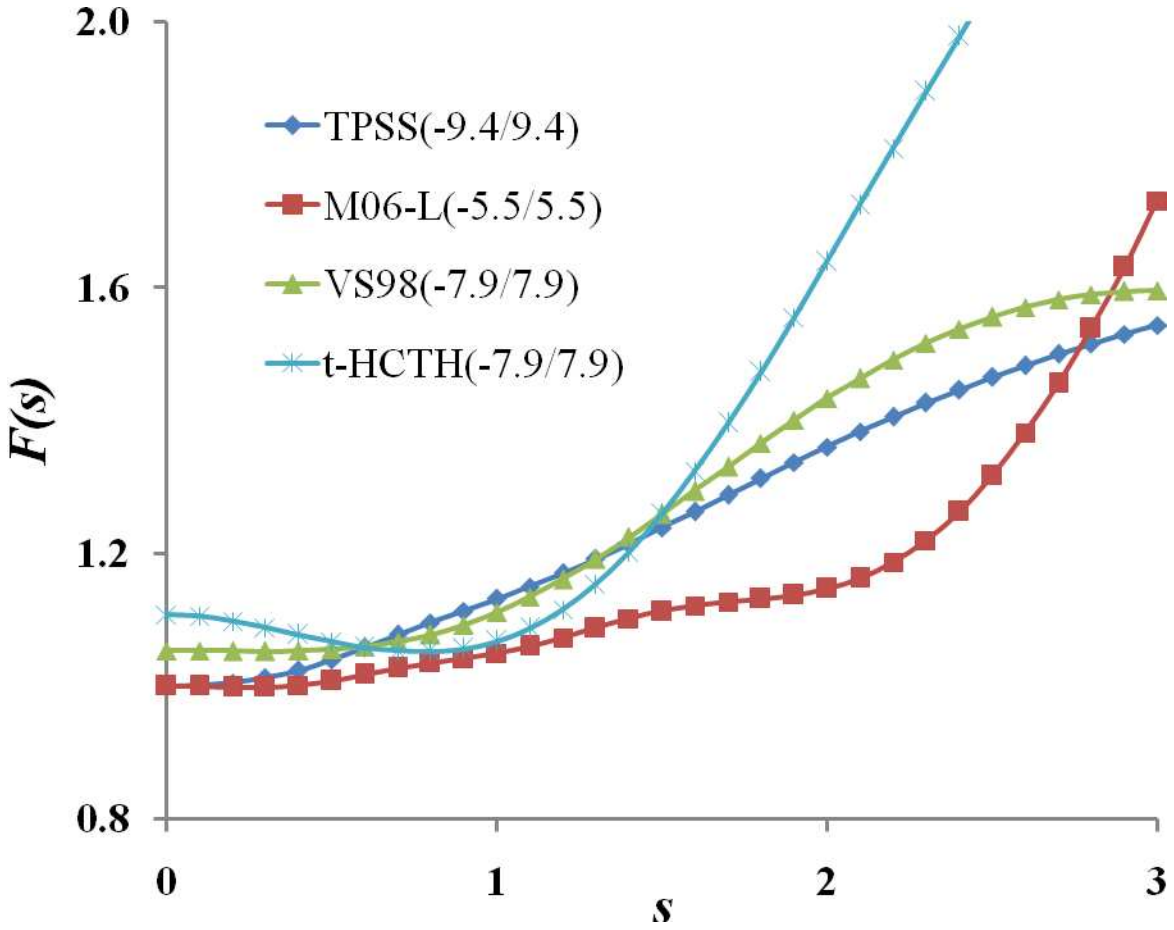

Figure S3. Exchange enhancements factors F_X as function of reduced gradient s (α = 1.0). (the numbers in the parentheses are the MSEs and MUEs of meta-GGA functionals for the ABDE4 database in units of kcal/mol)

Exchange enhancement factors F_X of popular GGAs:

$$F_X^{B88} = 1 + \frac{1.07466 \times 0.25237 s^2}{1 + 0.196448 s \sinh^{-1} 7.79555 s}$$

$$F_X^{PW91} = 1 + \frac{1.07466 \times \left(0.25237 s^2 - 0.14038024 s^2 e^{-100 s^2} - 0.00369307 s^4 \right)}{1 + 0.196448 s \sinh^{-1} 7.79555 s - 0.00369688 s^4}$$

$$F_X^{PBE} = 1 + 0.804 - \frac{0.804}{1 + 0.21951 s^2 / 0.804}$$

$$F_X^{revPBE} = 1 + 1.245 - \frac{1.245}{1 + 0.21951 s^2 / 1.245}$$

$$F_X^{RPBE} = 1 + 0.804 \left(1 - e^{-0.21951 s^2 / 0.804} \right)$$

$$F_X^{PBEsol} = 1 + 0.804 - \frac{0.804}{1 + 0.12346 s^2 / 0.804}$$

$$F_X^{SOGGA} = 1 + 0.552 \left(1 - \frac{0.5}{1 + 0.12346 s^2 / 0.552} - 0.5 e^{-0.12346 s^2 / 0.552} \right)$$

$$F_X^{WC06} = 1 + 0.804 - \frac{0.804}{1 + 0.21951 x / 0.804}$$

$$x = \frac{10}{81} s^2 + (0.21951 - \frac{10}{81}) s^2 e^{-s^2} + \ln(1 + 0.0079325 s^2)$$

Exchange enhancement factors F_X of 4 Meta-GGAs:

TPSS:

$$F_X^{TPSS} = 1 + 0.804 - \frac{0.804}{1 + 0.21951x/0.804}$$

$$x = \{[\frac{10}{81} + 1.5906\frac{z^2}{(1+z^2)^2}]s^2 + \frac{146}{2025}q_b^2 - \frac{73}{405}q_b\sqrt{\frac{1}{2}(\frac{3}{5}z)^2 + \frac{1}{2}s^4} + \frac{1}{0.804}(\frac{10}{81})^2 s^4$$
$$+ 2\sqrt{1.537}\frac{10}{81}(\frac{3}{5}z)^2 + 1.537 \times 0.21951s^6\}/(1 + \sqrt{1.537}s^2)^2$$

$$q_b = \frac{9}{20}\frac{\alpha - 1}{(1 + 0.40\alpha(\alpha - 1))^{1/2}} + \frac{2}{3}s^2$$

$$z = \frac{5s^2}{3\alpha + 5s^2}$$

M06-L:

$$F_X^{M06-L} = F_X^{PBE} f(\omega) + h(x,z)$$

$$\omega = 1 - \frac{2\alpha + 10s^2/3}{1 + \alpha + 5s^2/3}$$

$$x = 7.79555s$$

$$z = \frac{3}{5}(6\pi^2)^{2/3}(\alpha + 5s^2/3 - 1)$$

$$\gamma(x,z) = 1 + 0.001867(x^2 + z)$$

The expressions of $f(\omega)$ and $h(x,z)$ are in the M06-L paper.
See: Y. Zhao and D. G. Truhlar, J. Chem. Phys. **125**, 194101 (2006).

VS98:

$$F_X^{VS98} = -1.07466\left(\frac{-0.9800}{\gamma(x,z)} + \frac{-0.003557x^2 + 0.006250z}{\gamma^2(x,z)} + \frac{-0.00002354x^2 - 0.0001283x^2 z + 0.0003575z^2}{\gamma^3(x,z)}\right)$$

$$x = 7.79555s$$

$$z = \frac{3}{5}(6\pi^2)^{2/3}(\alpha + 5s^2/3 - 1)$$

$$\gamma(x,z) = 1 + 0.001867(x^2 + z)$$

τ-HCTH:

$$F_X^{\tau-HCTH} = g_{local} + g_{non-local} f(\omega)$$

$$u(s) = \frac{0.004 \times (7.795554s)^2}{1 + 0.004 \times (7.795554s)^2}$$

$$\omega = 1 - \frac{2\alpha + 10s^2/3}{1 + \alpha + 5s^2/3}$$

The expressions of g_{local} and $g_{non-local}$ is in the τ-HCTH paper.
See: A. D. Boese and N. C. Handy, J. Chem. Phys. **116**, 9559 (2002).