SI APPENDIX

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A Hybrid Meta On-Top Functional for Multiconfiguration Pair-Density Functional Theory

Jie J. Bao,[†] Dayou Zhang,[†] Shaoting Zhang,[§] Laura Gagliardi,*[‡] Donald G. Truhlar*[†]

[†]*Department of Chemistry, Chemical Theory Center, and Minnesota Supercomputing Institute, University of Minnesota, Minneapolis, Minnesota 55455-0431, United States*

[‡]*Department of Chemistry, Pritzker School of Molecular Engineering, James Franck Institute, and Chicago Center for Theoretical Chemistry, The University of Chicago, Chicago, Illinois 60637, United States*

[§]*College of Chemistry, Nankai University, Tianjin 300071, China*

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S1. References for Kohn–Sham Density Functionals

This section lists all the KS functionals that are mentioned in the paper (in the introduction and/or later) and their reference(s).

Table S1. Functionals and their references

Functional Name	Reference(s)
GGAs	
PBE	1
BLYP	2, 3, 4
HCTH	5
NGA	
GAM	6
hybrid GGAs	
B1LYP	7
B3LYP	8
PBE0	9, 10
meta-GGAs	
τ-HCTH	11
M06-L	12
revM06-L	13
meta-NGAs	
MN12-L	14
MN15-L	15
hybrid meta-GGAs	
TPSSh	16
M06	17
revM06	13
revM11	18
hybrid meta-NGA	
MN15	19
hybrid meta-NGA with damped dispersion	
CF22D	20
other functionals	
Doubly hybrid functionals	21, 22, 23, 24, 25, 26
van der Waals (vdW) functionals	27, 28
rung-3.5 functionals	29, 30

S2. Databases with References, Systems, Reference Data, and Spin–Orbit Coupling

Table S2. Databases used in functional training and testing

database	description	parent database(s)	Reference(s)
Database DS2			
HTBH29	hydrogen-transfer barrier heights	HTBH38/18	31, 32, 33
NHTBH4	non-hydrogen-transfer barrier heights	NHTBH38/18	6, 31, 32, 33
MC-BE3	metal compound bond energies	MR-MGM-BE4, MR-TM-BE12, SR-TM-BE15	6, 34, 35, 36, 37
MR-MGN-BE8	multireference main-group nonmetal bond energies	MR-MGN-BE17	6
SR-MGM-BE2	single-reference main-group metal bond energies	SR-MGM-BE8	6, 34, 35
SR-MGN-BE17	single-reference main-group nonmetal bond energies	SR-MGN-BE107	6, 38
Database DS3			
NGD-CE5	noble gas complexation energies	NGD21/18	6, 20, 31, 39
G2-BE5	group-2 bond energies	[new]	40, 41, 42, 43
NC-CE9	noncovalent complexation energies	NCCE30/18	6, 31, 44, 45, 46, 47, 48, 49
PX-BH3	proton exchange barrier heights	PX13	50, 51
PERI-BH4	pericyclic reaction barrier heights	BHPERI	52, 53, 54
Lix-AE3	binding energies of Li_2, Li_4 and Li_5	[new]	55, 56
CH-BE5	C–H bond energies	SR-MGN-BE107 + [new]	20, 52, 57
DAC-DE5	di-aluminum complex dimerization energies	Al2X6	50, 58
PB-BE3	p-block bond energies	W4-08	59, 25
HP-BE6	heavy p-block bond energies	HeavySB11	50
MR-MGN-BE4	multireference main-group nonmetal bond energies	MR-MGN-BE17	6
MR-MGM-BE3	multireference main-group metal bond energies	MR-MGM-BE4	6, 34
ΣTMD-BE4	transition metal dimer; with Σ ground states; bond energies	MR-TMD-BE3, SR-TM-BE15	36, 37
ΣTML-BE17	transition metal–ligand bond energies of compounds with Σ ground states	SR-TM-BE15 + [new]	36, 37

database	description	parent database(s)	Reference(s)
IP10	ionization potentials	IP23	14, 60
NG-IP4	noble-gas ionization potentials	[new]	61
SIE4x4	energy of four points on the potential energy curve of dimmer cations	SIE4x4	50
PC-ED5	energy differences between two points on potential energy curves	[new]	62, 63, 64
IsoE6	isomerization energies	IsoL6/11, πTC13, 2pIsoE4	65, 66, 67
PA8	proton affinities	PA8	31, 65, 66
MG-SS26	main group spin splitting energies	[new]	68, 69, 70, 71, 72, 73, 74
TM-SS6	transition metal compound spin-splitting energies	[new]	61, 75, 76

Tables S3 and S4 provide the reference values of each system. Most reference values are accurate experimental values, and therefore they automatically contain the spin–orbit coupling (SOC), which, in our definition (which is the common usage), also contains the spin–spin terms.

To first order, SOC is zero by symmetry for closed-shell molecules, for linear molecules in Σ states, and for singlet and doublet molecules in A or B states. For systems where this rule does not yield zero SOC, the SOC was obtained from the Supporting Information (SI) of ref 13.

We note that there are two errors in the SOC values for NH and PH in the SI of ref 13. The correct values with spin–spin splittings included are −0.001 kcal/mol for NH and −0.002 kcal/mol for PH, when we approximate them as $-\lambda - \gamma$ from pages 556f and 564f of Herzberg.[77] The present work does not include PH, but it does include NH and we used the corrected value of the SOC for NH.

The SOC values used in this work are shown in Table S3. These signed SOC values are added to the calculated values prior to comparison to the experimental reference values. As an example, consider the bond energy of a singlet diatomic molecule dissociating to open-shell fragments, for example $Cl_2 \rightarrow 2Cl$, for which Table S1 shows a reference value of 58.07 kcal/mol (this is D_e in the notation of Herzberg[77]). The SOC is zero for the molecule and negative for the atoms, so it lowers the positive energy required to dissociate the molecule. Thus, the SOC value for the bond energy is negative.

In a few cases in Table S4, the reference values are from theoretical calculations[74–76] without SOC, and therefore we did not add SOC to our calculated values for these systems. These cases are indicated by "N.I." in the Δ*E*(SOC) column.

Table S3. Systems, their reference values (iun kcal/mol) with spin–orbit coupling included, SOC values, charges, and multiplicities for each system in the DS2 database

Database	System (molecule or reaction)	Reference Value	Δ*E*(SOC)	Charge	Multiplicity
HTBH29	V_f H + HCl → H_2 + Cl	5.7	0	0	2
	V_r H + HCl → H_2 + Cl	8.7	0.84	0	2
V_f is a forward classical barrier height, and V_r is a classical barrier height for the reverse reaction.	V_r OH + H_2 → H_2O + H	21.2	0	0	2
	V_r CH_3 + H_2 → CH_4 + H	15.3	0	0	2
	V_f OH + CH_4 → H_2O + CH_3	6.7	0.2	0	2
	V_r OH + CH_4 → H_2O + CH_3	19.6	0	0	2
	V_f H + H_2 → H_2 + H	9.6	0	0	2
	V_f OH + NH_3 → H_2O + NH_2	3.2	0.2	0	2
	V_r OH + NH_3 → H_2O + NH_2	12.7	0	0	2
	V_f OH + C_2H_6 → H_2O + C_2H_5	3.4	0.2	0	2
	V_r OH + C_2H_6 → H_2O + C_2H_5	19.9	0	0	2
	V_f F + H_2 → HF + H	1.8	0.38	0	2
	V_r F + H_2 → HF + H	33.4	0	0	2
	V_r O + CH_4 → OH + CH_3	8.1	0.2	0	3
	V_f H + PH_3 → H_2 + PH_2	3.1	0	0	2
	V_r H + PH_3 → H_2 + PH_2	23.2	0.002	0	2
	V_f H + HO → H_2 + O	10.7	0.2	0	3
	V_r H + HO → H_2 + O	13.1	0.22	0	3
	V_f H + H_2S → H_2 + HS	3.5	0	0	2
	V_r H + H_2S → H_2 + HS	17.3	0.54	0	2
	V_r O + HCl → OH + Cl	10.4	1.04	0	3

Database	System (molecule or reaction)	Reference Value	Δ*E*(SOC)	Charge	Multiplicity
	V_f $CH_3 + NH_2 \rightarrow CH_4 + NH$	8.0	0	0	3
	V_r $CH_3 + NH_2 \rightarrow CH_4 + NH$	22.4	0	0	3
	V_f $C_2H_5 + NH_2 \rightarrow C_2H_6 + NH$	7.5	0	0	3
	V_r $C_2H_5 + NH_2 \rightarrow C_2H_6 + NH$	18.3	0	0	3
	V_f $NH_2 + C_2H_6 \rightarrow NH_3 + C_2H_5$	10.4	0	0	2
	V_r $NH_2 + C_2H_6 \rightarrow NH_3 + C_2H_5$	17.4	0	0	2
	V_f $NH_2 + CH_4 \rightarrow NH_3 + CH_3$	14.5	0	0	2
	V_r $NH_2 + CH_4 \rightarrow NH_3 + CH_3$	17.8	0	0	2
MC-BE3	LiO^-	57.59	-0.16	-1	1
	CuCl	90.2	-0.84	0	1
	FeCl	80.5	-0.89	0	6
MR-MGN-BE8	SiO (multiplicity = 1)	192.4	-0.65	0	1
	CO	259.42	-0.31	0	1
	ClO	64.84	-0.6	0	2
	$O_3 \rightarrow O_2 + O$	26.61	-0.22	0	1
	N_2	228.48	0	0	1
	O_2	120.37	-0.44	0	5 and 3
	B_2	67.4	-0.06	0	3
	C_2	146.88	-0.18	0	1
NHTBH4	V_f $H + FH \rightarrow HF + H$	42.18	0	0	2
	V_f $H + ClH \rightarrow HCl + H$	18	0	0	2
	V_r $H + FCH_3 \rightarrow HF + CH_3$	57.02	0	0	2
	V_f $H + F_2 \rightarrow HF + F$	2.27	0	0	2

Database	System (molecule or reaction)	Reference Value	Δ*E*(SOC)	Charge	Multiplicity
SR-MGM-BE2	NaO	65.23	1.0	0	2
	ZnCl	53.48	-0.84	0	2
SR-MGN-BE17	CH_3–CH_3[a]	97.39	0	0	1
	CH_3O–CH_3	89.79	-0.19156	0	1
	Et–H	108.92	0	0	1
	Et–CH_3	95.89	0	0	1
	Et–OCH_3	95.26	-0.03	0	1
	Et–OH	100.29	-0.2	0	1
	CH ($^2\Pi$)	84.18	-0.05	0	2
	NH	83.1	0	0	3
	OH	107.19	-0.02	0	2
	HCl	106.66	-0.84	0	1
	Si_2 (multiplicity = 3)	75.72	-0.66	0	5 and 3
	P_2	117.59	0	0	1
	S_2	103.13	-1.12	0	5 and 3
	Cl_2	58.07	-1.68	0	1
	SC	171.11	-0.65	0	1
	H_2	109.49	0	0	1
	SH	86.98	-0.02	0	2

[a] A hyphen is used to indicate the bond(s) dissociated in a polyatomic molecule.

Table S4. Systems, their reference values (in kcal/mol) with spin–orbit coupling included, SOC values, charges, and multiplicities for each system in the DS3 database

Database	System (molecule or reaction)	Reference Value	Δ*E*(SOC)	Charge	Multiplicity
CH-BE5	C_2H–H[a]	140.9	0	0	1
	C_2H_3–H	119.5	0	0	1
	$C_2H_4 \rightarrow C_2H_2 + H_2$	49.06	0	0	1
	C^+–H	98.42	0.12	1	3 and 1
	tert-butyl–H (dissociation of isobutane)	103.9	0	0	3 and 1
DAC-DE5	$Al_2H_6 \rightarrow 2AlH_3$	38.5	0	0	1
	$Al_2F_6 \rightarrow 2AlF_3$	51.6	0	0	1
	$Al_2Cl_6 \rightarrow 2AlCl_3$	32.5	0	0	1
	$Al_2HMe_5 \rightarrow AlHMe_2 + AlMe_3$	31.2	0	0	1
	$Al_2Me_6 \rightarrow 2AlMe_3$	23.1	0	0	1
G2-BE5	Be_2	2.66	0	0	1
	Mg_2	1.24	0	0	1
	Ca_2	3.13	0	0	1
	Sr_2	3.02	0	0	1
	Ba_2	3.87	0	0	1
HP-BE6	H_3Ge–GeH_3	73.8	0	0	1
	Me_3Pb–$PbMe_3$	52.9	0	0	3 and 1
	Me_2As–$AsMe_2$	52.2	0	0	1
	HS–SH	67.9	-1.08	0	1
	Br_2	53.2	-7.02	0	1
	MeTe–TeMe	52.9	0	0	3 and 1

Database	System (molecule or reaction)	Reference Value	Δ*E*(SOC)	Charge	Multiplicity
IP10	Cl_2	265.3	-0.92	1 and 0	2 and 1
	SH	238.9	-0.0012	1 and 0	3 and 2
	PH_2	226.3	0.002	1 and 0	1 and 2
	O_2	278.9	-0.28	1 and 0	2 and 3
	Zn	216.6	0	1 and 0	2 and 1
	OH	299.1	0.2	1 and 0	3 and 2
	Mo	163.7	0	1 and 0	6 and 7
	Cu	178.2	0	1 and 0	1 and 2
	Cr	156	0	1 and 0	6 and 7
	Cl	299.1	0.82	1 and 0	3 and 2
IsoE6	C_3H_4 (propyne → allene in ref 66)	-1.4	0	0	1
	C_6NH_7 (7 in ref 67)	57.1	0	0	1
	$C_{14}H_{20}O$ (10 in ref 65)	6.8	0	0	1
	$C_{14}H_{12}F_2$ (20 in ref 65)	4.7	0	0	1
	$C_{12}N_2H_{12}$ (13 in ref 65)	33.5	0	0	1
	$C_{12}H_{20}$ (9 in ref 65)	21.8	0	0	1
Lix-AE3 (atomization energy per atom)	Li_2	12.18	0	0	1
	Li_4	17.37	0	0	5 and 1
	Li_5	18.47	0	0	6 and 2
MG-SS26	NH	35.93	0.001	0	1 and 3
	OH^+	50.5	0	1	1 and 3
	NF	34.32	0	0	1 and 3
	O_2	22.64	0.006	0	1 and 3

Database	System (molecule or reaction)	Reference Value	Δ*E*(SOC)	Charge	Multiplicity
	H_2CC	-48.6	0	0	1 and 3
	C_2H_5CHS	-53.7	0	0	1 and 3
	C_4H_3CHO	-3.6	0	0	1 and 3
	$C_4H_3NH_2$	-2.7	0	0	1 and 3
	$Me_2C{=}CH_2$	-104	0	0	1 and 3
	CH_3CHO	-91.6	0	0	1 and 3
	NH_2CHO	-124	0	0	1 and 3
	He	457.1	0	0	3 and 1
	acetone	95.2	0	0	3 and 1
	propynal	80	0	0	3 and 1
	pyrimidine	94.3	0	0	3 and 1
	cyanoformaldehyde	79.3	0	0	3 and 1
	butadiene	77.5	0	0	3 and 1
	cyclopropenone	90.6	0	0	3 and 1
	pyrrole	104	0	0	3 and 1
	CH_2	9	0	0	1 and 3
	NH_2	29	0	1	1 and 3
	SiH_2	-21	0	0	1 and 3
	PH_2	-17	0	1	1 and 3
	Be_2CO ^{3}6–^{1}6[b]	-10.4	N.I.[c]	0	3 and 1
	Be_2CO ^{5}6–^{1}6[b]	-10.5	N.I.	0	5 and 1
	Be_2CO ^{3}5–^{1}5[b]	-8.6	N.I.	0	3 and 1
MR-MGM-BE3	CaO	96.2	-0.22	0	3 and 1

Database	System (molecule or reaction)	Reference Value	Δ*E*(SOC)	Charge	Multiplicity
	BeO	106.57	-0.22	0	3 and 1
	MgS	55.7	-0.56	0	3 and 1
MR-MGN-BE4	CN	181.3	-0.09	0	2
	Cl_2–O	41.7	-0.22	0	3 and 1
	SO	125.7	-0.78	0	5 and 3
	NO	152.7	-0.04	0	2
NC-CE5	H_2O–H_2O	4.91	0	0	1
	C_2H_4–F_2	1.06	0	0	1
	parallel-displaced CO_2–CO_2	1.49	0	0	1
	sandwich C_6H_6–C_6H_6	1.65	0	0	1
	parallel-displaced C_6H_6–C_6H_6	2.59	0	0	1
NG-IP4	He	567.0	0	1 and 0	2 and 1
	Ne	497.29	0	1 and 0	2 and 1
	Ar	363.43	0	1 and 0	2 and 1
	Kr	322.84	0	1 and 0	2 and 1
NGD-CE5	He_2	0.02	0	0	1
	Ne_2	0.08	0	0	1
	Ar_2	0.29	0	0	1
	He_2	0.04	0	0	1
	He_2	0.06	0	0	1
PA8	NH_3	211.9	0	0 and 1	1
	H_2O	171.8	0	0 and 1	1
	C_2H_2	156.6	0	0 and 1	1

Database	System (molecule or reaction)	Reference Value	Δ*E*(SOC)	Charge	Multiplicity
	SiH_4	156.5	0	0 and 1	1
	PH_3	193.1	0	0 and 1	1
	H_2S	173.7	0	0 and 1	1
	HCl	137.1	0	0 and 1	1
	H_2	105.9	0	0 and 1	1
PB-BE4	BN	105.82	-0.03	0	5 and 3
	SiO	193.05	-0.65	0	5 and 1
	AlCl	122.62	-1.05	0	3 and 1
	H–P–H (atomization energy per bond)	76.6	0	0	6 and 2
PC-ED5	N_2	212.38	—[d]	0	1
	F_2	37.9	-0.64	0	1
	Li_2	21.87	—	0	1
	KH	39.39	—	0	1
	ClF	19.96	—	0	1
PERI-BH4	C_4H_6 (cyclobutene)	34.8	0	0	1
	C_6H_8 (*cis*-1,3,5-hexatriene)	30.8	0	0	1
	C_8H_8 (*ortho*-xylylene)	28.1	0	0	1
	C_5H_6 (1,3-cyclopentadiene)	28.5	0	0	1
PX-BH3	$4NH_3$	48.4	0	0	1
	$4H_2O$	26.6	0	0	1
	4HF	14.7	0	0	1
SIE4x4	H_2^+ at 1.0 r_e	64.4	0	1	2
	H_2^+ at 1.25 r_e	58.9	0	1	2

Database	System (molecule or reaction)	Reference Value	Δ*E*(SOC)	Charge	Multiplicity
	H_2^+ at 1.5 r_e	48.7	0	1	2
	H_2^+ at 1.75 r_e	38.3	0	1	2
	He_2^+ at 1.0 r_e	56.9	0	1	2
	He_2^+ at 1.25 r_e	46.9	0	1	2
	He_2^+ at 1.5 r_e	31.3	0	1	2
	He_2^+ at 1.75 r_e	19.1	0	1	2
	$(NH_3)_2^+$ at 1.0 r_e	35.9	0	1	2
	$(NH_3)_2^+$ at 1.25 r_e	25.9	0	1	2
	$(NH_3)_2^+$ at 1.5 r_e	13.4	0	1	2
	$(NH_3)_2^+$ at 1.75 r_e	4.9	0	1	2
	$(H_2O)_2^+$ at 1.0 r_e	39.7	0	1	2
	$(H_2O)_2^+$ at 1.25 r_e	29.1	0	1	2
	$(H_2O)_2^+$ at 1.5 r_e	16.9	0	1	2
	$(H_2O)_2^+$ at 1.75 r_e	9.3	0	1	2
ΣTMD-BE4 (atomization energy per atom)	Cr_2	18.0	0	0	13 and 1
	Cu_2	23.6	0	0	1
	Ag_2	19.2	0	0	1
	AgCu	20.4	0	0	1
ΣTML-BE17	$TiCl_2$–Cl	102.16	-0.84	0	4 and 2
	VCl–Cl	113.86	-0.84	0	6 and 4
	CrCl	90.16	-0.84	0	8 and 6
	$CrO_3 \rightarrow Cr + 3O$ (atomization energy per bond)	117.88	-0.22	0	13 and 1
	MnCl–Cl	107.96	-0.84	0	8 and 6

Database	System (molecule or reaction)	Reference Value	Δ*E*(SOC)	Charge	Multiplicity
	MnCl	80.76	-0.84	0	7
	CuH	68.7	0	0	3 and 1
	ZnH	21.6	0	0	2
	ZnO	37.9	-0.22	0	3 and 1
	ZnCl–Cl	99.66	-0.84	0	3 and 1
	Cu–H_2O	38.8	0	1	1
	Cr–CH_3	28.8	0	1	7 and 5
	CrH	46.8	0	0	8 and 6
	CrN	87.6	0	0	10 and 4
	MnH	31.1	0	0	7
	Mn–CH_3^+	51.9	0	1	6
	AgH	54	0	0	3 and 1
TM-SS6	CoC_2H_4	-32.4	N.I.	1	3 and 1
	$Fe(H_2O)_6^{2+}$	-43.9	N.I.	2	5 and 1
	$Fe(H_2O)_6^{3+}$	-48.4	N.I.	3	6 and 4
	$FeO(NH_3)_5$	-0.4	N.I.	2	5 and 3
	Fe^{3+}	92.2	-0.1	3	4 and 6
	Mn^{2+}	76.7	-0.1	2	4 and 6

[a]a hyphen is used to indicate the bond(s) dissociated in a polyatomic molecule.
[b]5 and 6 mean two structures of Be_2CO in ref 74. Superscripts on the upper left mean the spin state of the corresponding structure.
[c]not included, as the reference values are theoretical calculations without SOC included.
[d]not found but is small enough so that we treat them as zero.

S3. More Discussion of Translating Meta Functionals

In MC-PDFT with translated gradient-approximation (tGA) functionals, the following two equations are used to convert one-electron density, ρ, and on-top density, Π, to translated effective densities $\rho^{\mathrm{t}}_{a/b}$, and effective translated density gradients $g^{\mathrm{t}}_{a/b}$,[78]

$$\rho^{\mathrm{t}}_{a/b} = \frac{\rho}{2}(1 \pm \zeta^{\mathrm{t}}) \tag{S1}$$

$$g^{\mathrm{t}}_{a/b} = \frac{\nabla_{\mathbf{r}}\rho}{2}(1 \pm \zeta^{\mathrm{t}}) \tag{S2}$$

where

$$\zeta^{\mathrm{t}} = \begin{cases} \sqrt{1-R}, R \leq 1 \\ 0 \qquad\quad , R > 1 \end{cases} \tag{S3}$$

and

$$R = \frac{4\Pi}{\rho^2} \tag{S4}$$

Equation S2 is obtained by taking the first derivative of eq S1 and dropping the derivative of ζ^{t}, which is unsmooth at $R = 1$. This is the standard translation that has been used in our previous work, and we continue to use it here. Note that $g^{\mathrm{t}}_{a/b}$ is not the gradient of $\rho^{\mathrm{t}}_{a/b}$ because we dropped the derivative of ζ^{t}; $g^{\mathrm{t}}_{a/b}$ is simply an ingredient in the funcional form used for the on-top functional.

Next, we define the mathematical intermediate quantities used to include kinetic energy densities in our parametrizations, and we explain the way in which these definitions are analogous to those used previously for translated gradient approximations. The kinetic energy density used as the starting point for obtaining the translated kinetic energy density can be computed, in any orbital basis (*p, q,* …), by:

$$\tau = \frac{1}{2}\sum_{pq} D_{pq}\nabla_{\mathbf{r}}\phi_p \nabla_{\mathbf{r}}\phi_q \tag{S5}$$

where D_{pq} is an element of the 1-electron reduced density matrix (1-RDM), ϕ_p and ϕ_q are molecular orbitals (note that eq S5 can also be expressed in the atomic-orbital basis), and $\nabla_{\mathbf{r}}\phi_p$ is the gradient vector with three Cartesian components.

Note that the τ of eq S5 can also be computed from the second derivative of the electronic density by dropping the second derivatives of orbitals ($\nabla^2_{\mathbf{r}}\phi_p$). The second derivative is

$$\nabla^2_{\mathbf{r}}\rho^{\mathrm{t}}_{\alpha/\beta} = \frac{(1 \pm \zeta^{\mathrm{t}})}{2}\nabla^2_{\mathbf{r}}\rho \pm \nabla_{\mathbf{r}}\rho \cdot \nabla_{\mathbf{r}}\zeta^{\mathrm{t}} \pm \frac{1}{2}\rho\nabla^2_{\mathbf{r}}\zeta^{\mathrm{t}} \tag{S6}$$

Then, we drop the terms containing second derivatives of orbitals ($\nabla^2_{\mathbf{r}}\phi_p$), and, analogous to the way we obtained eq S2, we drop the derivatives of ζ^{t}. These steps yield

$$\tau^{\mathrm{t}}_{a/b} = \frac{(1 \pm \zeta^{\mathrm{t}})}{2}\tau \tag{S7}$$

Note that the terms dropped in the formulations presented above are not approximations because the effective spin densities are not physical quantities; they are simply intermediate variables that we use to obtain parametrizable forms for the meta on-top functionals, and we have the freedom to define them in any convenient way.

The article presents the MC23 meta on-top functional, which is based on the functional form of the M06-L exchange–correlation functional. This new functional can be classified as a revised translated hybrid version of the M06-L exchange–correlation functional, which is indicated as rtM06-Lh if we name it in by our standardized notation. In the standardized notation, the prefix "t" denotes translating the functional and retaining the original parameters of the Kohn–Sham exchange–correlation functional, the prefix "rt" (an abbreviation of "revised translated") denotes reoptimization of the parameters in the context of MC-PDFT, and the suffix "h" denotes mixing of a CASSCF energy term (a "hybrid" term) to translated local functionals. Besides MC23, this article also presents results for the translated functionals tPBE, tPBE0, tτ-HCTH, and tM06-L, which are translations of PBE, PBE0, τ-HCTH, and M06-L, respectively. Note that PBE, τ-HCTH, and M06-L are local functionals, whereas PBE0 is a hybrid functional. In translating hybrid functionals,[79] we translate the percentage X of Hartree–Fock exchange into a percentage X of CASSCF wave-function energy. As a result of the various translations, tPBE is an on-top functional, tPBE0 is a hybrid on-top functional, tτ-HCTH and tM06-L are meta on-top functionals, and MC23 is a hybrid meta on-top functional that could have been called rtM06-Lh.

S4. Active Spaces for Each System

One reason why MC-PDFT is more accurate than KS-DFT on systems with strong multireference characters is that MC-PDFT uses better densities than the best a single Slater determinant can provide when optimized with available exchange–correlation functionals; this is important to describe strongly correlated systems. However, to achieve these better densities, one must make a good choice of active space, and this can be challenging.

The previously proposed correlated participating orbitals (CPO) schemes[80] provide one possible systematic way to generate active spaces. Previous experience shows that the mod-CPO scheme is the most efficient one among the three CPO schemes. The mod-CPO scheme usually involves the p subshells for non-transition metals and the d subshells for transition metals therefore, we use these two subshells in our calculations for most systems. Sometimes, a compromise active space is required to keep the active space size manageable, and the precise details of our active space choices are provided in this section.

We note that in the long run, it would be desirable to proceed with a uniquely defined active-space choice (yielding a "theoretical model" or "quantum chemical model" in the language of Pople[81]). In this work, we proceed with a combination of systematically defined active spaces (DS2) and active spaces based on human judgment (DS3). The systematic active space selection scheme of DS2 has been discussed in ref 62. Below are the details of the active spaces based on human judgment that we used in DS3.

S4.1. Systems Using Restricted Hartree–Fock References

We use the notation (*m, n*) to denote an active space with *m* active electrons in *n* active orbitals.

Restricted Hartree–Fock (RHF) theory may be considered to be a special case of MCSCF using a (2,1) active space, and in a few cases, we found that RHF theory already provides a reasonable reference wave function. Thus, RHF reference wave functions are used for the noble gas dataset (NGD-BE5), the di-aluminum cluster (DAC-BE5) dataset, the proton-exchange dataset (PX-BH3), and the water dimerization energy in the NCCE5 dataset. The choice of RHF references for noble gas dimers and water dimers is clear-cut since these are well known to have negligible static correlation. For the DAC-BE5 and the PX-BH3 datasets, we used the RHF reference wave functions because the unoptimized tM06-L functional was found to give accurate energies with an RHF reference wave function, and therefore we anticipated that the (2,1) active space would be sufficient.

The rest of the systems use multiconfigurational wave functions as the references, as described next. Note that all active space choices were made prior to optimizing the new functionals, and in no case is the active space chosen to improve the results with the optimized functionals.

S4.2. Systems with No More Than Five Atoms

For H atoms, the valence shell is put in the active space.

For p-block atoms, we put the valence s and p subshells in the active space for group-14 and group-15 elements, which are also called "early p-block elements", including B, C, N, and P; we

put the valence p subshell in the active space for group-16 and group-15 elements, which are also called “late p-block elements”, including O, F, S, Cl, and Br.

As an exception, for Cl_2O, we used the full valence active space, because the orbital optimization moves out-of-plane valence p orbitals on Cl and O out of the active space, replacing them with valence s orbitals of Cl when a smaller active space is used. However, we find that if we move these out-of-plane p orbitals into the active space to have only 9 active orbitals, the MC-PDFT results are different from the full valence active space by no more than 0.6 kcal/mol.

We also used a full-valence active space for H_2S_2 in the HP-BE5 dataset because the p subshell is more easily identified when one uses the full-valence active space.

For transition metals with incomplete d subshells, we put the s and the d subshells in the active space. This was done for Cr and Mn.

Ag and Cu atoms have a full d subshell, and further considerations were made to choose a good active space. In particular, for AgH bond energies, we tested two active spaces, namely (12, 7) with the d subshell of Ag included and (2, 2) with only the s subshell included; we found that MC-PDFT energies between for two active spaces differ by less than 0.4 kcal/mol. Therefore, for Ag, Cu, and Zn, we only include the s subshell in our calculations. However, for dissociation of one Zn–Cl bond in $ZnCl_2$, it is difficult to include only the p orbitals of Cl without introducing the d orbitals of Zn, so we choose the size of the active space to be (2, 2) instead of (12, 7). At the equilibrium structure of Cl–Zn–Cl, three atomic orbitals are important in describing the bonding of the system, namely the Zn 4s orbital and the p_z orbitals of two Cl atoms. Putting the linear $ZnCl_2$ in the z axis, the molecule is symmetric with respect to the reflection of the x-y plane where Zn is in. Therefore, two p_z orbitals, each from one Cl atom, form two auxiliary orbitals, one is symmetric after the reflection operation, called orbital *S*, and the other is antisymmetric after the reflection, called orbital *AS*. Because the Zn 4s orbital is also symmetric to the reflection, a bonding orbital (*B*) and an antibonding orbital (*AB*) between Zn 4s and orbital *S* can be formed. As a result, there are three molecular orbitals in this system, *B*, *AB*, and *AS*. The (2, 2) active space includes 2 electrons in orbitals *AB* and *AS*. At the dissociated structure, this is a ZnCl molecule and a Cl atom. For the ZnCl molecule, the Cl p_z orbital and the Zn 4s orbital form a pair of σ and σ^* orbitals, so the (2, 2) active space for the dissociated structure include the σ^* orbital and the p_z orbital of the dissociated Cl.

The systems whose active spaces are selected less systematically are the alkaline earth (AE) metals. For their dimers, we use the CPO active space as we did previously,[40] and as we mentioned in ref 40, all nom-CPO, mod-CPO, and ext-CPO schemes give the same active space because there are no occupied p or d orbitals. The active-space choice for AE compounds in the MR-MGM-BE3 dataset, namely BeO, MgS, and CaO, is more difficult than for the p-block compounds, and we chose their active spaces by trying various possibilities and then selecting a reasonable one, as discussed in the next paragraph.

MR-MGM-BE3 database. We considered three active spaces for the MR-MGM-BE3 database, namely (8, 5), (8, 6), and (8, 8). For dissociated geometries, all three active spaces contain the whole valence shell of O or S and the s subshell of the AE metal; they differ by the number of unoccupied p orbitals of the AE metal that is included, namely 0, 1, and 3. Including no unoccupied p orbitals of the AE metals is similar to the previously used rule for the H atom. Including one unoccupied p orbital can be thought of as employing the mod-CPO scheme, where

the unoccupied p orbital is used as the correlating orbital of the σ bond that is formed. Including three unoccupied orbitals corresponds to including the whole valence shell of three dimers. These three active spaces (mainly the active orbitals) can be obtained relatively easily when the dimers are dissociated (except for MgS, where we did not obtain all three degenerate p orbitals on Mg at dissociation), and we failed to maintain the characters of the active orbitals even when we use the active orbitals at dissociation as the initial guess for the orbitals at equilibrium. By characters we mean whether the orbital is a σ orbital or a π orbital, and whether a σ orbital is mainly formed by an s, p, or d orbital.

In deciding which active spaces among three can be used at equilibrium geometries, we used two rules: (1) when there are degenerate orbitals, both or none should be in the active space; (2) the M diagnostics should be similar to the one with the largest active space.

The (8, 6) active space does not follow the first rule for CaO. More precisely speaking, the CASSCF calculation favors an active space where the degenerate orbitals are not both within the active space, even when we start with degenerate orbitals in the active space as the initial guess.

The (8, 5) active space does not follow the second rule. As it can be seen in Table S4 for CaO, the M diagnostics of the (8, 5) active space wave function gives 0.62, which is much more different from the M diagnostics of the other two active spaces.

We conclude that the (8, 8) active space is a reasonably good active space for BeO, MgS, and CaO in describing the wave function at their equilibrium geometries.

The active orbitals at equilibrium geometries for BeO, MgS, and CaO can be found in Figure S1.

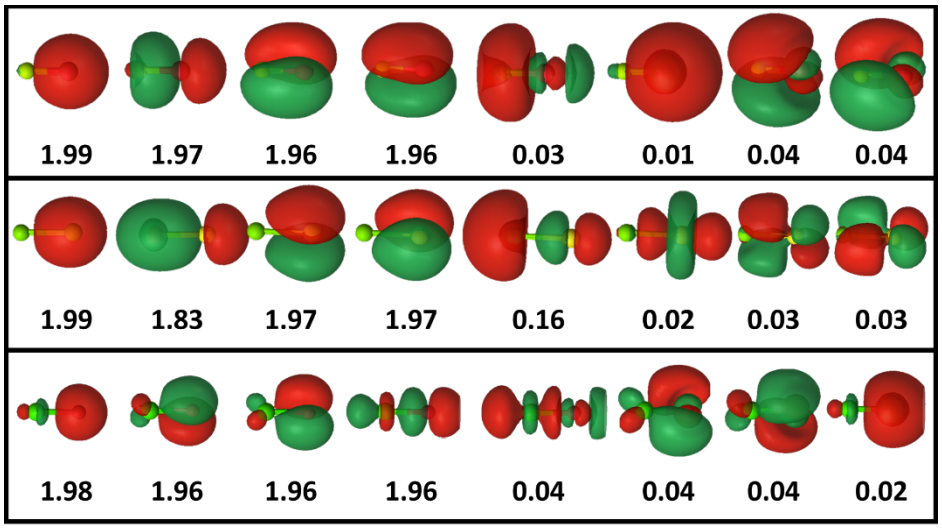

Figure S1. Natural orbitals of BeO (top row), MgS (middle row), and CaO (bottom row). The number below each orbital is the natural orbital occupation number.

Table S5. M diagnostics for BeO, MgS, and CaO at equilibrium with three choices of active spaces

	BeO	**MgS**	**CaO**
(8, 5)	0.07	0.19	0.62
(8, 6)	0.05	0.14	0.05
(8, 8)	0.03	0.16	0.04

Table S6. Bond energies (kcal/mol) for BeO, MgS, and CaO with three choices of active spaces

	BeO			**MgS**			**CaO**		
	tPBE	**tM06-L**	**tτ-HCTH**	**tPBE**	**tM06-L**	**tτ-HCTH**	**tPBE**	**tM06-L**	**tτ-HCTH**
(8, 5)	114.8	116.0	115.4	53.9	58.9	54.1	77.5	76.2	82.8
(8, 6)	110.7	110.2	113.1	53.3	57.7	55.8	105.6	105.5	115.9
(8, 8)	97.6	98.3	103.6	47.8	52.9	52.7	93.3	96.2	105.7

Be_2CO molecules in the MG-SS26 dataset. Another set of molecules that have nonsystematic active spaces are the Be_2CO molecules in MG-SS26. The "Be_2CO 5" system includes the valence shell of C, and the sp-hybridized orbitals from Be, giving a (6, 6) active space. For the linear BeOBeC structure, assuming the molecule is on the z axis, we chose our active space to include the p_x, p_y, p'_x, and p'_y orbitals of O (orbitals with a prime ($'$) are orbitals of a similar shape, but having one more node), the p subshells of C, and the sp_z-hybridized orbital of the terminal Be. These orbitals were chosen through a set of trial and error, rather than being selected systematically.

S4.3. Systems with More Than 5 Atoms

For larger systems, it is impractical to use an active space with all p subshells included, therefore the active space needs to be constructed less systematically with greater dependence on understanding the valence shell of the particular system.

For Te_2Me_2, Ge_2H_6, Pb_2Me_6, and As_2Me_4 in the HPBE6 dataset, we use (2, 2) active spaces to include the bonding and the anti-bonding orbitals of the bonds that are dissociated. Note that H_2S_2 and Br_2 in this dataset still use the rule for systems with no more than five atoms.

In the PERI-BH4 dataset, the active spaces contain all the valence π and π* orbitals. For cyclobutene, although it has only one π bond, the σ and σ^* orbitals of the bond that breaks to yield 1,3-butadiene are also included in the active space.

In the NCCE5 dataset, the water dimer uses the RHF reference as mentioned in Section S4.1. For ethylene, CO_2, and benzene, we used the active space with all valence π and π* orbitals. This yields (8, 12) for CO_2 dimers and (12, 12) for benzene dimers. For F_2, our active space includes the σ_{pz} and σ^*_{pz} orbitals, and the active space for the ethylene–F_2 system is (4, 4).

In the CH-BE5 dataset, we use a full valence active space, as the valence s orbitals of C are important in forming the C-H bond. This yields (10, 10) and (12, 12) active spaces for C_2H_2 and C_2H_4 dissociating to the C_2H_3–H pair, and C_2H_2–H_2 pair. For *tert*-butane C–H bond dissociation,

we use a (2, 2) active space that includes the CH bonding and antibonding orbitals. For CH^+, an active space containing the value shell of C and H is used.

The proton affinities in PA8 are calculated using the same active space for the molecule and the protonated molecule, and the active space follows the general rule for H, N, O, Si, P, S, and Cl as mentioned in Section S4.2. For C_2H_2, a (4, 4) active space is used to only include the π and π^* orbitals.

In IsoE6, we use the Hartree–Fock reference (namely (2, 1) active space) for $C_{12}H_{20}$, in which all bonds are single bonds. For the systems whose chemical formulas are $C_{12}N_2H_{12}$, $C_{14}H_{12}F_2$, C_6NH_7, and $C_{14}H_{20}O$, respectively, we include the π and π^* orbitals in the benzene ring, the C=C bond, C=O bond, and N=N bond. For C_3H_4, the active space contains the p subshell of C and the s subshell of H.

For molecules from references 69 and 70 in the MG-SS26, the active spaces are the same as those in two references.

In TM-SS6, $Fe(H_2O)_6^{2+}$ and $Fe(H_2O)_6^{3+}$ use the d-subshell active space for Fe; for $FeO(NH_3)_5$, the active space includes the d subshell of Fe and the p subshell of O; for CoC_2H_4, the active space contains the s and d subshells of Co, and the π and π^* orbitals from C_2H_4.

In SIE4x4, we use the CPO scheme as in our previous work in ref. 82.

The sizes of all active spaces can be found in Table S7.

S4.4. Multireference and Non-Single-Determinant Diagnostics

Table S7 also presents the multireference diagnostics that are calculated using the original formula[80] and a modified version.

According to the original definition, M diagnostics is computed as

$$M = \frac{1}{2}\left[2 - N_{\mathrm{MCDOMO}} + N_{\mathrm{MCUMO}} + \sum_{i}^{n_{\mathrm{SOMO}}} \left|N_{\mathrm{SOMO},i} - 1\right|\right] \tag{S8}$$

where N_{MCDOMO} is the natural orbital occupation number (NOON) of the most correlated doubly-occupied orbital, N_{MCUMO} is the NOON of the most correlated unoccupied orbital, $N_{\mathrm{SOMO},i}$ is the NOON of a singly occupied orbital with an index i, and n_{SOMO} is the total number of singly occupied orbitals. The most correlated doubly occupied molecular orbitals (MCDOMO), most correlated unoccupied molecular orbitals (MCUMO), and singly occupied molecular orbitals (SOMO) are determined from nominally doubly occupied or singly occupied orbitals. Given a system of n electrons and spin quantum number S, the number of nominally doubly occupied orbitals is computed as $n_{\mathrm{D}} = (n - 2S)/2$, the number of nominally singly occupied orbitals is computed as $n_{\mathrm{S}} = 2S$, and all the rest of the orbitals are nominally empty. The MCDOMO is defined as the nominally doubly occupied orbital whose NOON deviates the most from 2, and the MCUMO is the nominally empty orbital whose NOON deviates the most from 0.

This definition, although it is well-defined, is not appropriate for discussing the performance of KS-DFT functionals. For example, a multiconfiguration wave function that correctly describes dissociated H_2 or nearly dissociated H_2 is

$$\Psi = \frac{1}{\sqrt{2}}\left(\sigma_g^2 + \sigma_u^2\right)\frac{1}{\sqrt{2}}(\alpha\beta - \beta\alpha) \tag{S9}$$

where σ_g^2 and σ_u^2 are respectively the electronic configurations with two electrons occupying the σ_g orbital and two electrons occupying the σ_u orbital, where σ_g and σ_u are symmetric and antisymmetric with respect to the reflection plane that separates two H atoms in H_2, and where $\frac{1}{\sqrt{2}}(\alpha\beta - \beta\alpha)$ is a singlet spin function. In this wave function, the NOONs are 1 and 1 for the two orbitals. Using eq. S8, one concludes that the M diagnostics for dissociated H_2 is 1, and that dissociated H_2 has a strong multireference (MR) character. This is definitely a correct statement, however, KS-DFT calculations with approximate functionals can easily handle this strong MR system by using a broken-symmetry solution. Next, we discuss a more nuanced characterization of multireference character.

Most currently available KS-DFT calculations obtain reasonable bond energies and potential energy curves for the dissociation of H_2 by breaking symmetry and using the following Slater determinant to describe the electronic wave function:

$$\Psi^{\mathrm{UKS}} = \mathsf{A}s_{\mathrm{l}}\alpha s_{\mathrm{r}}\beta \tag{S10}$$

where A is an antisymmetrizer, s_{l} and s_{r} are respectively the $1s$ functions of the left-side H atom and the right-side H atom, and α and β are spin functions. Such broken-symmetry solutions are called unrestricted Kohn–Sham (UKS), analogous to unrestricted Hartree–Fock (UHF).

To provide a better analysis of whether the present multiconfiguration calculations with MC23 are better for strongly correlated systems than KS-DFT calculations with approximate functionals, we propose a new diagnostic, called the N diagnostic. We obtain this by modifying (as compared to the M diagnostic) how to classify orbitals when identifying the MCDOMO, MCUMO, and singly occupied orbitals, respectively.

In calculating N diagnostics, the doubly occupied orbitals are defined as those whose NOON is greater than or equal to 1.5, the empty orbitals are defined as those whose NOON is less than or equal to 0.5, and the singly occupied orbitals are orbitals whose NOON is between 0.5 and 1.5. Using these definitions, the N diagnostics of the wave function in eq. S9 is 0, indicating using the spin-unrestricted KS (UKS) formalism with approximate functionals can describe the dissociation of H_2. Therefore, the N diagnostics measure if a system can be qualitatively accurately described by the UHF method or by most currently available UKS functionals.

According to the N diagnostics in Table S7, the strong correlation of C_2H_5–H, Et–CH_3, NH, HCl, and other systems in the SR-MGN-BE17 from DS2 can be well described by UKS-DFT.

We do not present diagnostics for systems in the SIE4x4 database. This is because we use the diagnostics to characterize whether a system cannot be well-described by a single spin-restricted Slater determinant or by UHF. Because the difficulties for systems in SIE4x4, are due to the competition between localized holes and delocalized holes rather than from multireference character, we consider that categorizing them by multireference diagnostics would give a false impression.

Table S7. Active space size, basis set, M diagnostics, and N diagnostics of the reference wave function for each at datum

Database	System	active space	M diagnostics[a]		N diagnostics[a]		Basis set[b]
HTBH29	V_f H + HCl → H_2 + Cl	(3, 3)	0.01	0.01	0.01	0.01	ma-TZVP
	V_r H + HCl → H_2 + Cl	(3, 3)	0.01	0.01	0.01	0.01	ma-TZVP
	V_r OH + H_2 → H_2O + H	(1, 1)	0.00	0.00	0.00	0.00	ma-TZVP
	V_r CH_3 + H_2 → CH_4 + H	(1, 1)	0.00	0.00	0.00	0.00	ma-TZVP
	V_f OH + CH_4 → H_2O + CH_3	(3, 3)	0.02	0.00	0.02	0.00	ma-TZVP
	V_r OH + CH_4 → H_2O + CH_3	(3, 3)	0.02	0.00	0.02	0.00	ma-TZVP
	V_f H + H_2 → H_2 + H	(1, 1)	0.00	0.00	0.00	0.00	ma-TZVP
	V_f OH + NH_3 → H_2O + NH_2	(3, 3)	0.03	0.02	0.03	0.02	ma-TZVP
	V_r OH + NH_3 → H_2O + NH_2	(3, 3)	0.03	0.01	0.03	0.01	ma-TZVP
	V_f OH + C_2H_6 → H_2O + C_2H_5	(3, 3)	0.03	0.00	0.03	0.00	ma-TZVP
	V_r OH + C_2H_6 → H_2O + C_2H_5	(3, 3)	0.03	0.02	0.03	0.02	ma-TZVP
	V_f F + H_2 → HF + H	(1, 1)	0.00	0.00	0.00	0.00	ma-TZVP
	V_r F + H_2 → HF + H	(1, 1)	0.00	0.00	0.00	0.00	ma-TZVP
	V_r O + CH_4 → OH + CH_3	(6, 6)	0.04	0.02	0.04	0.02	ma-TZVP
	V_f H + PH_3 → H_2 + PH_2	(3, 3)	0.03	0.03	0.03	0.03	ma-TZVP
	V_r H + PH_3 → H_2 + PH_2	(3, 3)	0.03	0.02	0.03	0.02	ma-TZVP
	V_f H + HO → H_2 + O	(4, 4)	0.04	0.00	0.04	0.00	ma-TZVP
	V_r H + HO → H_2 + O	(4, 4)	0.04	0.01	0.04	0.01	ma-TZVP
	V_f H + H_2S → H_2 + HS	(3, 3)	0.02	0.00	0.02	0.00	ma-TZVP
	V_r H + H_2S → H_2 + HS	(3, 3)	0.02	0.02	0.02	0.02	ma-TZVP
	V_r O + HCl → OH + Cl	(6, 6)	0.04	0.02	0.04	0.02	ma-TZVP
	V_f CH_3 + NH_2 → CH_4 + NH	(6, 6)	0.03	0.02	0.03	0.02	ma-TZVP

Database	System	active space	M diagnostics[a]		N diagnostics[a]		Basis set[b]
	V_r $CH_3 + NH_2 \rightarrow CH_4 + NH$	(6, 6)	0.03	0.03	0.03	0.03	ma-TZVP
	V_f $C_2H_5 + NH_2 \rightarrow C_2H_6 + NH$	(6, 6)	0.04	0.02	0.04	0.02	ma-TZVP
	V_r $C_2H_5 + NH_2 \rightarrow C_2H_6 + NH$	(6, 6)	0.04	0.02	0.04	0.02	ma-TZVP
	V_f $NH_2 + C_2H_6 \rightarrow NH_3 + C_2H_5$	(3, 3)	0.03	0.02	0.03	0.02	ma-TZVP
	V_r $NH_2 + C_2H_6 \rightarrow NH_3 + C_2H_5$	(3, 3)	0.03	0.02	0.03	0.02	ma-TZVP
	V_f $NH_2 + CH_4 \rightarrow NH_3 + CH_3$	(3, 3)	0.01	0.01	0.01	0.01	ma-TZVP
	V_r $NH_2 + CH_4 \rightarrow NH_3 + CH_3$	(3, 3)	0.01	0.01	0.01	0.01	ma-TZVP
MC-BE3	LiO^-	(6, 6)	1.00	1.00	0.03	0.02	ma-TZVP
	CuCl	(4, 4)	1.00	0.02	0.00	0.02	ma-TZVP
	FeCl	(11, 11)	0.09	0.03	0.09	0.03	ma-TZVP
MR-MGN-BE8	SiO (multiplicity = 1)	(8, 8)	1.00	0.04	0.03	0.04	ma-TZVP
	CO	(10, 10)	1.00	0.05	0.05	0.05	ma-TZVP
	ClO	(7, 7)	1.00	0.05	0.02	0.05	ma-TZVP
	$O_3 \rightarrow O_2 + O$	(12, 12)	0.99	0.21	0.06	0.21	ma-TZVP
	N_2	(10, 10)	1.00	0.06	0.01	0.06	ma-TZVP
	O_2	(8, 8)	0.01	0.06	0.01	0.06	ma-TZVP
	B_2	(6, 6)	0.07	0.33	0.07	0.33	ma-TZVP
	C_2	(8, 8)	0.76	0.41	0.98	0.41	ma-TZVP
NHTBH4	V_f $H + FH \rightarrow HF + H$	(1, 1)	0.00	0.00	0.00	0.00	ma-TZVP
	V_f $H + ClH \rightarrow HCl + H$	(1, 1)	0.00	0.00	0.00	0.00	ma-TZVP
	V_r $H + FCH_3 \rightarrow HF + CH_3$	(3, 3)	0.06	0.02	0.06	0.02	ma-TZVP
	V_f $H + F_2 \rightarrow HF + F$	(3, 3)	0.18	0.01	0.18	0.01	ma-TZVP
SR-MGM-BE2	NaO	(5, 5)	1.00	0.03	0.01	0.03	ma-TZVP

Database	System	active space	M diagnostics[a]		N diagnostics[a]		Basis set[b]
	ZnCl	(3, 3)	0.06	0.01	0.06	0.01	ma-TZVP
SR-MGN-BE17	CH_3–CH_3	(6, 6)	1.00	0.02	0.02	0.02	ma-TZVP
	CH_3O–CH_3	(6, 6)	1.00	0.02	0.02	0.02	ma-TZVP
	Et–H	(4, 4)	1.00	0.02	0.02	0.02	ma-TZVP
	Et–CH_3	(6, 6)	1.00	0.02	0.02	0.02	ma-TZVP
	Et–OCH_3	(6, 6)	1.00	0.02	0.02	0.02	ma-TZVP
	Et–OH	(6, 6)	1.00	0.02	0.02	0.02	ma-TZVP
	CH ($^2\Pi$)	(5, 5)	1.00	0.07	0.05	0.07	ma-TZVP
	NH	(6, 6)	1.00	0.03	0.01	0.03	ma-TZVP
	OH	(5, 5)	1.00	0.03	0.00	0.03	ma-TZVP
	HCl	(4, 4)	1.00	0.02	0.01	0.02	ma-TZVP
	Si_2 (multiplicity = 3)	(8, 8)	0.76	0.13	0.98	0.13	ma-TZVP
	P_2	(6, 6)	1.00	0.08	0.00	0.08	ma-TZVP
	S_2	(8, 8)	0.02	0.05	0.02	0.05	ma-TZVP
	Cl_2	(6, 6)	1.00	0.04	0.02	0.04	ma-TZVP
	SC	(8, 8)	1.00	0.06	0.05	0.06	ma-TZVP
	H_2	(2, 2)	1.00	0.02	0.00	0.02	ma-TZVP
	SH	(5, 5)	1.00	0.03	0.01	0.03	ma-TZVP
CH-BE5	C_2H–H	(10, 10)	1.00	0.06	0.08	0.06	jun-cc-pVTZ
	C_2H_3–H	(12, 12)	1.00	0.07	0.09	0.07	jun-cc-pVTZ
	$C_2H_4 \rightarrow C_2H_2 + H_2$	(12, 12)	0.06	0.07	0.06	0.07	ma-TZVP
	C^+–H	(4, 5)	0.07	0.10	0.07	0.10	ma-TZVP
	tert-butyl–H	(2, 2)	0.00	0.02	0.00	0.02	ma-TZVP

Database	System	active space	M diagnostics[a]		N diagnostics[a]		Basis set[b]
DAC-DE5	$Al_2H_6 \rightarrow 2AlH_3$	(2, 1)	0.00	0.00	0.00	0.00	jun-cc-pVTZ
	$Al_2F_6 \rightarrow 2AlF_3$	(2, 1)	0.00	0.00	0.00	0.00	jun-cc-pVTZ
	$Al_2Cl_6 \rightarrow 2AlCl_3$	(2, 1)	0.00	0.00	0.00	0.00	jun-cc-pVTZ
	$Al_2HMe_5 \rightarrow AlHMe_2 + AlMe_3$	(2, 1)	0.00	0.00	0.00	0.00	jun-cc-pVTZ
	$Al_2Me_6 \rightarrow 2AlMe_3$	(2, 1)	0.00	0.00	0.00	0.00	jun-cc-pVTZ
G2-BE5	Be_2	(4, 4)	0.11	0.31	0.11	0.31	ma-TZVP
	Mg_2	(4, 4)	0.08	0.09	0.08	0.09	ma-TZVP
	Ca_2	(4, 4)	0.11	0.16	0.11	0.16	ma-TZVP
	Sr_2	(4, 4)	0.10	0.14	0.10	0.14	ma-TZVP
	Ba_2	(4, 4)	0.10	0.14	0.10	0.14	ma-TZVP
HP-BE6	$H_3Ge–GeH_3$	(2, 2)	1.00	0.02	0.00	0.02	ma-TZVP
	$Me_3Pb–PbMe_3$	(2, 2)	0.00	0.02	0.00	0.02	ma-TZVP
	$Me_2As–AsMe_2$	(2, 2)	1.00	0.03	0.00	0.03	ma-TZVP
	HS–SH	(14, 10)	1.00	0.03	0.03	0.03	ma-TZVP
	Br_2	(10, 6)	1.00	0.06	0.00	0.06	ma-TZVP
	MeTe–TeMe	(2, 2)	0.00	0.04	0.00	0.04	ma-TZVP
IP10	Cl_2	(9, 6) and (10, 6)	0.07	0.05	0.07	0.05	jun-cc-pVTZ
	SH	(4, 4) and (5, 4)	0.03	0.03	0.03	0.03	jun-cc-pVTZ
	PH_2	(4, 5) and (5, 5)	0.09	0.02	0.09	0.02	jun-cc-pVTZ
	O_2	(7, 6) and (8, 6)	0.11	0.08	0.11	0.08	jun-cc-pVTZ
	Zn	(1, 1) and (2, 1)	0.00	0.00	0.00	0.00	ma-TZVP
	OH	(4, 4) and (5, 4)	0.03	0.02	0.03	0.02	ma-TZVP
	Mo	(5, 6) and (6, 6)	0.00	0.00	0.00	0.00	ma-TZVP

Database	System	active space	M diagnostics[a]		N diagnostics[a]		Basis set[b]
	Cu	(10, 6) and (11, 6)	0.00	0.00	0.00	0.00	ma-TZVP
	Cr	(5, 6) and (6, 6)	0.00	0.00	0.00	0.00	ma-TZVP
	Cl	(4, 3) and (5, 3)	0.00	0.00	0.00	0.00	ma-TZVP
IsoE6	C_3H_4	(12, 12)	0.06	0.07	0.06	0.07	ma-TZVP
	C_6NH_7	(6, 6)	0.10	0.09	0.10	0.09	ma-TZVP
	$C_{14}H_{20}O$	(8, 8)	0.10	0.10	0.10	0.10	ma-TZVP
	$C_{14}H_{12}F_2$	(12, 12)	0.10	0.10	0.10	0.10	ma-TZVP
	$C_{12}N_2H_{12}$	(12, 12)	0.10	0.11	0.10	0.11	ma-TZVP
	$C_{12}H_{20}$	(2, 1)	0.00	0.00	0.00	0.00	ma-TZVP
Lix-AE3	Li_2	(2, 2)	1.00	0.09	0.00	0.09	ma-TZVP
	Li_4	(4, 4)	0.00	0.18	0.00	0.22	ma-TZVP
	Li_5	(5, 5)	0.00	0.14	0.00	0.14	ma-TZVP
MG-SS26	NH	(4, 4)	1.00	0.03	0.02	0.03	jun-cc-pVTZ
	OH^+	(4, 4)	1.00	0.03	0.02	0.03	jun-cc-pVTZ
	NF	(8, 6)	1.00	0.05	0.05	0.05	jun-cc-pVTZ
	O_2	(8, 6)	1.00	0.08	0.11	0.08	jun-cc-pVTZ
	H_2CC	(6, 8)	0.07	0.11	0.07	0.11	jun-cc-pVTZ
	C_2H_5CHS	(6, 5)	0.08	0.02	0.08	0.02	jun-cc-pVTZ
	C_4H_3CHO	(12, 14)	0.88	0.07	0.20	0.07	maug-cc-pVTZ
	$C_4H_3NH_2$	(12, 14)	0.77	0.07	0.32	0.07	maug-cc-pVTZ
	$Me_2C{=}CH_2$	(4, 4)	0.12	0.00	0.12	0.00	jun-cc-pVTZ
	CH_3CHO	(6, 5)	0.06	0.02	0.06	0.02	jun-cc-pVTZ
	NH_2CHO	(10, 8)	0.04	0.02	0.04	0.02	jun-cc-pVTZ

Database	System	active space	M diagnostics[a]		N diagnostics[a]		Basis set[b]
	He	(2, 2)	0.00	0.01	0.00	0.01	aug-cc-pVTZ
	acetone	(6, 5)	0.02	0.06	0.02	0.06	ma-TZVP
	propynal	(8, 7)	0.06	0.09	0.06	0.09	ma-TZVP
	pyrimidine	(10, 8)	0.19	0.10	0.19	0.10	ma-TZVP
	cyanoformaldehyde	(8, 7)	0.07	0.10	0.07	0.10	ma-TZVP
	butadiene	(10, 10)	0.15	0.11	0.15	0.11	ma-TZVP
	cyclopropenone	(6, 7)	0.02	0.04	0.02	0.04	ma-TZVP
	pyrrole	(6, 5)	0.18	0.08	0.18	0.08	ma-TZVP
	CH_2	(6, 6)	0.09	0.02	0.09	0.02	jun-cc-pVTZ
	NH_2	(6, 6)	0.08	0.03	0.08	0.03	jun-cc-pVTZ
	SiH_2	(6, 6)	0.10	0.03	0.10	0.03	jun-cc-pVTZ
	PH_2	(6, 6)	0.09	0.03	0.09	0.03	jun-cc-pVTZ
	Be_2CO ^{3}6–^{1}6	(8, 8)	0.98	1.00	0.04	0.07	ma-TZVP
	Be_2CO ^{5}6–^{1}6	(8, 8)	0.02	1.00	0.02	0.07	ma-TZVP
	Be_2CO ^{3}5–^{1}5	(6, 6)	0.05	0.09	0.05	0.09	ma-TZVP
MR-MGM-BE3	CaO	(8, 8)	0.12	0.04	0.12	0.04	ma-TZVP
	BeO	(8, 8)	0.13	0.04	0.13	0.04	ma-TZVP
	MgS	(8, 8)	0.09	0.16	0.09	0.16	ma-TZVP
MR-MGN-BE4	CN	(5, 6)	1.00	0.08	0.00	0.08	jun-cc-pVTZ
	Cl_2–O	(20, 12)	0.05	0.06	0.05	0.06	jun-cc-pVTZ
	SO	(8, 6)	0.00	0.06	0.00	0.06	jun-cc-pVTZ
	NO	(7, 6)	1.00	0.08	0.00	0.08	jun-cc-pVTZ
NC-CE5	H_2O–H_2O	(2, 1)	0.00	0.00	0.00	0.00	jun-cc-pVTZ

Database	System	active space	M diagnostics[a]		N diagnostics[a]		Basis set[b]
	C_2H_4–F_2	(4, 4)	0.14	0.14	0.14	0.14	jun-cc-pVTZ
	parallel-displaced CO_2–CO_2	(8, 12)	0.03	0.04	0.03	0.04	jun-cc-pVTZ
	sandwich C_6H_6–C_6H_6	(12, 12)	0.10	0.10	0.10	0.10	jun-cc-pVTZ
	parallel-displaced C_6H_6–C_6H_6	(12, 12)	0.10	0.10	0.10	0.10	jun-cc-pVTZ
NG-IP4	He	(1, 2) and (2, 2)	0.00	0.01	0.00	0.01	ma-TZVP
	Ne	(5, 6) and (6, 6)	0.01	0.01	0.01	0.01	ma-TZVP
	Ar	(5, 6) and (6, 6)	0.00	0.01	0.00	0.01	ma-TZVP
	Kr	(5, 6) and (6, 6)	0.00	0.01	0.00	0.01	ma-TZVP
NGD-CE5	He_2	(2, 1)	0.00	0.00	0.00	0.00	jun-cc-pVTZ
	Ne_2	(2, 1)	0.00	0.00	0.00	0.00	jun-cc-pVTZ
	Ar_2	(2, 1)	0.00	0.00	0.00	0.00	jun-cc-pVTZ
	He_2	(2, 1)	0.00	0.00	0.00	0.00	jun-cc-pVTZ
	He_2	(2, 1)	0.00	0.00	0.00	0.00	jun-cc-pVTZ
PA8	NH_3	(8, 7)	0.02	0.02	0.02	0.02	ma-TZVP
	H_2O	(6, 5)	0.02	0.02	0.02	0.02	ma-TZVP
	C_2H_2	(4, 4)	0.06	0.06	0.06	0.06	ma-TZVP
	SiH_4	(8, 8)	0.02	0.03	0.02	0.03	ma-TZVP
	PH_3	(8, 7)	0.03	0.02	0.03	0.02	ma-TZVP
	H_2S	(6, 5)	0.02	0.03	0.02	0.03	ma-TZVP
	HCl	(8, 5)	0.02	0.02	0.02	0.02	ma-TZVP
	H_2	(2, 2)	0.02	0.02	0.02	0.02	ma-TZVP
PB-BE4	BN	(4, 6)	0.00	0.08	0.00	0.08	jun-cc-pVTZ
	SiO	(6, 6)	0.01	0.04	0.01	0.04	jun-cc-pVTZ

Database	System	active space	M diagnostics[a]		N diagnostics[a]		Basis set[b]
	AlCl	(10, 8)	0.07	0.09	0.07	0.09	jun-cc-pVTZ
	H–P–H	(7, 6)	0.00	0.03	0.00	0.03	ma-TZVP
PC-ED5	N_2	(10, 8)	0.82	0.06	0.84	0.06	jun-cc-pVTZ
	F_2	(10, 6)	0.95	0.13	0.05	0.13	jun-cc-pVTZ
	Li_2	(2, 2)	0.67	0.09	0.33	0.09	ma-TZVP
	KH	(2, 2)	0.60	0.06	0.40	0.06	ma-TZVP
	ClF	(14, 8)	0.19	0.05	0.19	0.05	ma-TZVP
PERI-BH4	C_4H_6 (cyclobutene)	(4, 4)	0.13	0.08	0.13	0.08	jun-cc-pVTZ
	C_6H_8 (*cis*-1,3,5-hexatriene)	(6, 6)	0.13	0.13	0.13	0.13	jun-cc-pVTZ
	C_8H_8 (*ortho*-xylylene)	(8, 8)	0.22	0.18	0.22	0.18	jun-cc-pVTZ
	C_5H_6 (1,3-cyclopentadiene)	(4, 4)	0.06	0.11	0.06	0.11	jun-cc-pVTZ
PX-BH3	$4NH_3$	(2, 1)	0.00	0.00	0.00	0.00	jun-cc-pVTZ
	$4H_2O$	(2, 1)	0.00	0.00	0.00	0.00	jun-cc-pVTZ
	4HF	(2, 1)	0.00	0.00	0.00	0.00	jun-cc-pVTZ
SIE4x4[c]	H_2^+ at 1.0 r_e	(1, 2)	–	–	–	–	ma-TZVP
	H_2^+ at 1.25 r_e	(1, 2)	–	–	–	–	ma-TZVP
	H_2^+ at 1.5 r_e	(1, 2)	–	–	–	–	ma-TZVP
	H_2^+ at 1.75 r_e	(1, 2)	–	–	–	–	ma-TZVP
	He_2^+ at 1.0 r_e	(3, 4)	–	–	–	–	ma-TZVP
	He_2^+ at 1.25 r_e	(3, 4)	–	–	–	–	ma-TZVP
	He_2^+ at 1.5 r_e	(3, 4)	–	–	–	–	ma-TZVP
	He_2^+ at 1.75 r_e	(3, 4)	–	–	–	–	ma-TZVP
	$(NH_3)_2^+$ at 1.0 r_e	(3, 4)	–	–	–	–	ma-TZVP

Database	System	active space	M diagnostics[a]		N diagnostics[a]		Basis set[b]
	$(NH_3)_2^+$ at 1.25 r_e	(3, 4)	–	–	–	–	ma-TZVP
	$(NH_3)_2^+$ at 1.5 r_e	(3, 4)	–	–	–	–	ma-TZVP
	$(NH_3)_2^+$ at 1.75 r_e	(3, 4)	–	–	–	–	ma-TZVP
	$(H_2O)_2^+$ at 1.0 r_e	(7, 8)	–	–	–	–	ma-TZVP
	$(H_2O)_2^+$ at 1.25 r_e	(7, 8)	–	–	–	–	ma-TZVP
	$(H_2O)_2^+$ at 1.5 r_e	(7, 8)	–	–	–	–	ma-TZVP
	$(H_2O)_2^+$ at 1.75 r_e	(7, 8)	–	–	–	–	ma-TZVP
ΣTMD-BE4	Cr_2	(12, 12)	0.00	0.40	0.00	0.40	jun-cc-pVTZ-DK
	Cu_2	(2, 2)	1.00	0.06	0.00	0.06	ma-TZVP
	Ag_2	(2, 2)	1.00	0.07	0.00	0.07	ma-TZVP
	AgCu	(2, 2)	1.00	0.06	0.00	0.06	ma-TZVP
ΣTML-BE17	$TiCl_2$–Cl	(7, 9)	0.01	0.02	0.01	0.02	ma-TZVP
	VCl–Cl	(7, 8)	0.01	0.03	0.01	0.03	ma-TZVP
	CrCl	(7, 7)	0.00	0.00	0.00	0.00	ma-TZVP
	$CrO_3 \rightarrow Cr + 3O$	(18, 15)	0.00	0.13	0.00	0.13	ma-TZVP
	MnCl–Cl	(9, 8)	0.00	0.00	0.00	0.00	ma-TZVP
	MnCl	(8, 7)	0.00	0.00	0.00	0.00	ma-TZVP
	CuH	(2, 2)	0.00	0.04	0.00	0.04	ma-TZVP
	ZnH	(3, 2)	0.00	0.00	0.00	0.00	ma-TZVP
	ZnO	(6, 4)	0.00	0.36	0.00	0.36	ma-TZVP
	ZnCl–Cl	(2, 2)	0.00	0.00	0.00	0.00	ma-TZVP
	$Cu–H_2O^+$	(2, 2)	0.00	0.01	0.00	0.01	ma-TZVP
	$Cr–CH_3$	(12, 13)	0.03	0.07	0.03	0.07	ma-TZVP

Database	System	active space	M diagnostics[a]		N diagnostics[a]		Basis set[b]
	CrH	(7, 7)	0.00	0.06	0.00	0.06	ma-TZVP
	CrN	(11, 10)	0.00	0.16	0.00	0.16	ma-TZVP
	MnH	(8, 7)	0.00	0.00	0.00	0.00	ma-TZVP
	$Mn–CH_3^+$	(13, 13)	1.00	0.08	0.02	0.08	ma-TZVP
	AgH	(12, 7)	0.00	0.00	0.00	0.00	ma-TZVP
TM-SS6	CoC_2H_4	(10, 8)	0.06	0.92	0.06	0.59	ma-TZVP
	$Fe(H_2O)_6^{2+}$	(6, 5)	0.00	0.07	0.00	0.07	ma-TZVP
	$Fe(H_2O)_6^{3+}$	(5, 5)	0.00	0.04	0.00	0.04	ma-TZVP
	$FeO(NH_3)_5$	(10, 8)	0.28	0.21	0.28	0.21	ma-TZVP
	Fe^{3+}	(5, 5)	1.00	0.00	0.00	0.00	ma-TZVP
	Mn^{2+}	(5, 5)	1.00	0.00	0.00	0.00	ma-TZVP

[a]This column lists the two M diagnostic values or the two N diagnostic values of the two CASSCF wave functions before and after a chemical or physical process for each system. We present the order of the two wave functions in a way that the energy of the first wave function minus that of the second wave function gives an energy that is comparable to the reference value in Tables S3 and S4. We do not present two diagnostics for systems in SIE4x4 because these systems are difficult for approximate density functionals.

[b]The second-order Douglas−Kroll−Hess scalar relativistic Hamiltonian is used for calculations that employed the jun-cc-pVTZ-DK basis set. All other basis sets are used with the nonrelativistic Hamiltonians, but the ma-TZVP basis set includes the scalar relativistic effect by using a relativistic effective core potential for atoms in row 5 and later.

[c]The SIE4x4 systems are difficult for both KS-DFT and MC-PDFT for reasons other than multireference character, so they are not sorted by multireference character.

S5. Computational Details

S5.1. Data Generation

We implemented kinetic energy densities in *OpenMolcas*,[83,84,85] commit dbe66bdde53f6d0bc4e9e5bcc0243922b3559a66 on GitLab (where it is available as open-source software), and we tested this new version of the program with tPBE,[78] tPBE0,[79] tM06-L (see Section 2.1), tτ-HCTH (see Section 2.1), and CASPT2.[86]

The CASPT2 calculations use an imaginary shift[87] of 0.25 a.u. and an IPEA shift[88] of 0.25 a.u. The MC-PDFT calculations are performed with the MHL grid[89] (99 radial × 590 angular), 10^{10} for the crowding factor, and 10.0 for the fading factor. We employ density fitting based on Cholesky decomposition[90] to avoid exact two-electron integral calculations. Because the results for data in DS2 in ref 62 did not use density fitting, we reran all multireference calculations in DS2 with the default initial guess and with the above setup so that all DS3 results in the present study are done consistently.

All CASSCF wave functions are obtained by minimizing the ground-state energies for each system (they are not state averaged).

The active spaces and basis sets are summarized in Table S7. The active space choices are discussed above in Section S4; the basis sets are discussed below in this section.

In the CASSCF, MC-PDFT, and CASPT2 calculations, we mainly use two basis sets, namely jun-cc-pVTZ[91,92] and ma-TZVP.[93,94] The exceptions are as follows. For Cr_2, we used the jun-cc-pVTZ-DK[95] basis set with the second-order Douglas−Kroll−Hess (DKH) Hamiltonian[96,97] to be consistent with our previous work.[62] For C_4H_3CHO and $C_4H_3NH_2$, we used maug-cc-pVTZ[91,92] to stay consistent with refs 67 and 69. For all systems in DS2, we used ma-TZVP to be consistent with ref 62.

Because the CASPT2 results are expected to converge more slowly with basis set than do the PDFT calculations, and our previous tests[40] do show changes upon increasing the basis set to the quadruple-zeta (QZ) level, practical CASPT2 calculations are more affordable with the TZ basis sets, especially for large systems. The CASPT2 calculations with a given TZ basis set are already more expensive than the PDFT calculations with the same basis set. Our goal here is to compare CASPT2 with the same basis set and same active space as used for PDFT calculations. Therefore, we use CASSCF with TZ basis sets as the reference wave function for both MC-PDFT and CASPT2 calculations. The reader should, however, keep in mind that CASPT2 performance might be improved by using a QZ basis set.

All calculations used augmented (typically minimally augmented or jun- augmented) polarized valence-triple-zeta basis sets, either from the of the correlation-consistent family[91] (maug-cc-,[98] jun-cc,[92] and aug-cc-) or from the Karlsruhe family (ma-TZVP,[94] which adds diffuse functions to the def2-TZVP[93] basis sets for nonhydrogenic atoms). For many data the choice between the families was based on consistency with previous calculations to allow convenient comparisons. However, with the exception of Cr_2, all calculations on systems containing an atom from the fourth row or higher of the periodic table (atoms heavier than Ar) used the ma-TZVP basis set. We generally prefer this basis set family for systematic calculations on molecules with element from these rows because it is available in well-balanced form for the whole periodic table through the sixth row (i.e., up to Rn). A possible disadvantage of this basis set, though, is that it does not include the scalar relativistic effect for the first four rows. These effects small for the first three rows, but they can be important for quantitative work on transition metals in the

fourth row.[99] To check whether this significantly affects our parametrization, we performed some post-parametrization tests, as discussed next.

First, we calculated *D* for each datum involving a 3d transition metal, where *D* is defined as the mean unsigned error (MUE) of all 19 methods without scalar relativistic effects for that datum. Then, using Kohn-Sham density functional theory (KS-DFT) with the PBE density functional, we calculated the datum by three basis sets: two nonrelativistic basis sets used without scalar relativistic terms in the Hamiltonian and one relativistic basis set used with the second-order Douglass-Kroll-Hess (DKH2) scalar relativistic Hamiltonian. For the relativistic calculations, we used the jun-cc-pVTZ-DK basis set. For the nonrelativistic calculations we used both the ma-TZVP basis set that was used in the article for parametrization and testing and the jun-cc-pVTZ basis set, which is the nonrelativistic analog of jun-cc-pVTZ-DK. The KS-PBE/jun-cc-pVTZ calculation is used to show directly whether it is important to include scalar relativistic effects, whereas switching from ma-TZVP to jun-cc-pVTZ-DK calculations includes both the basis-set-family difference and the relativistic effect. Then we calculated the deviations of the nonrelativistic calculations from the relativistic one and compared the magnitudes of the deviations to the *D* values. The results are shown in Table S8. In 30 of the 31 cases, the magnitudes of both of the nonrelativistic deviations from the relativistic one are smaller than *D*; in the only case where this is not so, Cu_2, the differences from *D* are small. For example, the ma-TZVP estimate of the relativistic effect is only 0.1 kcal/mol greater than the MUE.

We conclude that the error of not including relativistic effects for 3d transition metals is less than the error in the electronic structure methods, and, therefore, it does not invalidate our parametrization and our tests.

Because the CASPT2 results are expected to converge more slowly with basis set than do the PDFT calculations, and our previous tests[40] do show changes upon increasing the basis set to the quadruple-zeta (QZ) level, practical CASPT2 calculations are more affordable with the TZ basis sets, especially for large systems. The CASPT2 calculations with a given TZ basis set are already more expensive than the PDFT calculations with the same basis set. Our goal here is to compare CASPT2 with the same basis set and same active space as used for PDFT calculations. Therefore, we use CASSCF with TZ basis sets as the reference wave function for both MC-PDFT and CASPT2 calculations. The reader should, however, keep in mind that CASPT2 performance might be improved by using a QZ basis set.

Table S8. KS-PBE signed errors with and without using the second-order DKH scalar-relativistic Hamiltonian for all systems containing fourth-row transition metals (3d transition metals). The table also contains the deviation of nonrelativistic calculations from the calculations with the scalar-relativistic effect, the mean unsigned error (*D*) over 19 nonrelativistic methods for each system, and the results of the comparisons of relativistic effects to *D*. All numerical values are in kcal/mol.

Database	System	KS-DFT-PBE error			Deviation from DK		$D \equiv$ MUE[d]	Deviation < *D*?	
		ma-TZVP	jun-cc-pVTZ[b]	jun-cc-pVTZ-DK[c]	ma-TZVP	jun-cc-pVTZ[b]		ma-TZVP	jun-cc-pVTZ[b]
MC-BE3	CuCl	-4.9	-3.8	-3.1	1.7	0.7	7.2	yes	yes
MC-BE3	FeCl	3.5	4.3	4.9	1.5	0.6	3.6	yes	yes
SR-MGM-BE2	ZnCl	-2.1	-1.2	-4.0	1.8	2.7	4.5	yes	yes
IP10	Cr	11.6	11.6	14.6	3.1	3.0	4.5	yes	yes
IP10	Cu	10.0	9.7	15.1	5.1	5.4	6.4	yes	yes
IP10	Zn	0.3	-0.2	4.8	4.5	5.0	6.8	yes	yes
ΣTML-BE17	AgCu	1.5	2.3	3.9	2.4	1.6	2.5	yes	yes
ΣTML-BE17	Cr_2	-3.6	-1.5	1.6	5.3	3.1	13.7	yes	yes
ΣTML-BE17	Cu_2	0.9	1.9	5.2	4.3	3.3	3.2	no	no
ΣTML-BE17	$CrCH_3$	14.8	15.1	17.7	2.9	2.6	7.2	yes	yes
ΣTML-BE17	CrCl	-1.1	-0.6	-0.1	1.0	0.5	5.7	yes	yes
ΣTML-BE17	CrH	5.2	5.6	6.6	1.5	1.1	6.9	yes	yes
ΣTML-BE17	CrN	18.0	18.1	21.2	3.3	3.1	12.5	yes	yes
ΣTML-BE17	CrO_3	37.3	39.1	45.7	8.4	6.6	11.7	yes	yes
ΣTML-BE17	CuH	-5.3	-4.1	-1.3	4.0	2.8	8.0	yes	yes
ΣTML-BE17	CuH_2O	6.0	6.1	9.8	3.9	3.7	4.2	yes	yes
ΣTML-BE17	$MnCH_3^+$	9.8	9.9	9.3	0.5	0.6	7.2	yes	yes
ΣTML-BE17	MnCl	10.3	11.2	9.2	1.1	1.9	5.1	yes	yes
ΣTML-BE17	$MnCl_2$	0.4	0.6	0.4	0.1	0.3	7.5	yes	yes
ΣTML-BE17	MnH	13.7	14.3	12.8	0.9	1.4	6.8	yes	yes
ΣTML-BE17	$TiCl_3$	8.9	8.8	9.7	0.7	0.9	7.6	yes	yes
ΣTML-BE17	VCl_2	16.0	16.0	17.1	1.1	1.1	9.8	yes	yes
ΣTML-BE17	$ZnCl_2$	0.2	1.3	1.2	1.0	0.1	4.6	yes	yes
ΣTML-BE17	ZnH	0.7	1.4	0.1	0.6	1.3	2.6	yes	yes
ΣTML-BE17	ZnO	2.3	4.4	1.9	0.5	2.5	11.3	yes	yes
TM-SS6	CoC_2H_4	17.9	18.0	18.2	0.3	0.2	12.8	yes	yes
TM-SS6	$Fe(H_2O)_6^{2+}$	23.8	24.0	23.4	0.5	0.6	16.4	yes	yes
TM-SS6	$Fe(H_2O)_6^{3+}$	21.4	21.6	21.4	0.0	0.2	12.4	yes	yes
TM-SS6	Fe^{3+}	-32.2	-33.0	-33.1	0.9	0.2	17.5	yes	yes
TM-SS6	$FeO(NH_3)_5$	10.5	10.6	11.0	0.5	0.4	7.0	yes	yes
TM-SS6	Mn^{2+}	-25.2	-26.0	-26.1	0.9	0.2	14.1	yes	yes

[a]calculations using the ma-TZVP basis set without the scalar relativistic effect included
[b]calculations using the jun-cc-pVTZ basis set without the scalar relativistic effect included
[c]calculations using the jun-cc-pVTZ-DK basis set and second-order DKH Hamiltonian
[d]mean unsigned error of 19 methods for each system

All energetics calculated at CASSCF, MC-PDFT, and CASPT2 levels are carried out by two separate multireference calculations. For bond dissociation energies, atomization energies, and reaction barrier heights, we calculate the dissociated fragments, reactants, or products as a super-molecule where individual fragments are placed far apart. The charges and multiplicities of each calculation are summarized in Table S3.

We have also carried out several KS-DFT calculations to compare their performance for the databases used here. The KS exchange–correlation functionals tested are PBE, PBE0, BLYP, B1LYP, B3LYP, HCTH, τ-HCTH, M06, M06-L, MN15, MN15-L, and CF22D. For DS2, we reuse the KS calculations from our previous work[62] for PBE, BLYP, HCTH, M06-L, MN15, and MN15-L. The KS-DFT calculations are performed in *Gaussian 16*.[100] An internal stability check[101] is performed for all KS-DFT calculations.

For KS-DFT calculations, we use the ma-TZVP basis set for all systems. All energetics calculated at KS-DFT level are carried out by two or more separate KS-DFT calculations. Unlike multireference calculations, we calculate dissociated fragments, reactants, or products as individual calculations (rather than supermolecules) with KS-DFT.

The spin–orbit coupling (SOC) is included in all theoretical calculations by all methods for cases where the reference data is from experiment, because experimental results automatically include SOC. We define the SOC energy (E^{SOC}) as the energy difference between the lowest-energy state including SOC and the degeneracy-weighted mean of the spin–orbit manifold, as obtained (usually) from experiment. More details of SOC energies are provided in the previous Section S2 and Table S3.

S5.2. Functional Parameterization and Optimization

We use a Python program based on *PyTorch*,[102] *Numpy*,[103] and *Pandas*[104] to perform functional optimization and data analysis.

The new MC-PDFT functional is optimized by minimizing the objective function of eq 7 of the main manuscript. The methods used for comparison are CASSCF, CASPT2, tPBE, tPBE0, tτ-HCTH, tM06-L, and the twelve KS-DFT functionals mentioned in Section 4.

The fractional rank appearing is equal to the integer rank if the RMSE is equal to the RMSE of one of 18 comparing methods, and it interpolates smoothly between them otherwise. The interpolating polynomial also needs two endpoints, which are taken as

$$R_d(0) = 0$$
$$R_d(10^{100}) = 10^{100} \tag{S12}$$

We used the BFGS algorithm[105,106,107,108] for functional optimization. The automatic differentiation feature of *PyTorch*[102] is utilized to produce gradients of U with respect to the functional parameters while invoking the BFGS algorithm. In cases when BFGS does not converge due to precision loss, we continue to minimize U using the Nelder–Mead algorithm.[109] We use the *SciPy*[110] implementation of BFGS and Nelder–Mead algorithms in this study. Because there are many possible local minimums of the objective function, we tried multiple initial guess functional parameters to find the best set of parameters that gives the lowest sum of integer ranks.

To obtain the final parameters of the new functional, we round all optimized parameters to 7 significant figures, except for X, which is rounded to 4 significant figures.

S6. MUE of Each Method on Databases

Table S9. Mean unsigned error (MUE, kcal/mol) for each database, mean root mean squared errors (RMSE, kcal/mol) over databases, mean MUE over databases and data points, for CASSCF and the multireference methods

Database	HMC-PDFT	CASSCF	CASPT2	MC-PDFT			
	MC23			tPBE	tPBE0	tτ-HCTH	tM06-L
DS2							
HTBH29	2.7	12.1	3.0	2.9	2.4	2.8	3.5
NHTBH4	1.1	22.3	3.1	8.9	2.0	6.8	3.8
MC-BE3	1.5	5.0	2.2	7.1	6.6	6.2	3.7
MR-MGN-BE8	3.6	11.8	5.5	6.4	2.4	5.8	6.5
SR-MGM-BE2	2.3	13.0	4.8	5.1	7.0	3.8	1.5
SR-MGN-BE17	2.0	15.2	4.6	2.5	4.8	2.5	3.4
DS3							
NGD-CE5	0.01	0.17	0.03	0.07	0.09	0.09	0.06
G2-BE5	0.8	5.2	1.4	0.4	1.1	0.6	0.3
NC-CE5	0.11	2.7	1.2	1.9	2.1	2.7	0.4
PX-BH3	0.9	17.7	3.2	7.2	1.0	4.5	2.5
PERI-BH4	1.3	10.5	1.8	3.0	1.7	2.5	3.6
Lix-AE3	1.1	9.1	6.3	3.5	4.9	7.1	4.6
CH-BE5	2.0	12.9	4.1	1.3	3.3	1.9	1.7
DAC-DE5	0.9	11.8	0.9	6.6	7.9	11.8	1.7
PB-BE4	1.1	15.7	3.7	3.6	6.0	2.8	5.5
HP-BE6	1.7	18.0	5.2	3.1	6.2	3.6	3.0
MR-MGN-BE4	2.5	31.3	6.3	4.0	6.3	7.4	5.1
MR-MGM-BE3	3.8	7.8	14.4	6.9	6.3	5.4	4.0
ΣTMD-BE4	0.8	19.2	2.8	5.0	8.6	2.7	6.9
ΣTML-BE17	4.6	20.0	5.1	7.6	9.8	5.3	8.7
IP10	2.4	28.6	6.3	4.0	6.0	5.6	3.2
NG-IP4	1.9	15.8	3.6	1.4	3.0	9.4	3.2
SIE4x4	9.4	7.2	3.3	15.0	10.2	15.2	11.5
PC-ED5	3.0	11.5	5.5	4.7	3.2	8.9	6.7
IsoE6	1.2	5.4	0.6	3.7	3.0	4.4	3.0
PA8	0.7	2.1	1.4	1.2	0.8	3.3	3.0
MG-SS26	4.7	6.9	3.5	4.2	3.8	4.9	4.9
TM-SS6	4.6	17.5	11.6	9.7	5.1	5.4	12.2
average MUE by database	2.2	12.7	4.1	4.7	4.5	5.1	4.2
average RMSD by database	2.8	14.0	4.8	5.5	5.2	5.9	5.2
MUE by data points	3.1	12.5	3.9	4.9	4.7	5.2	4.8

Table S10. MUE (kcal/mol) for each database, RMSE (kcal/mol) over databases, mean MUE over databases and data points for KS functionals without kinetic energy density as ingredients

Database	KS-DFT					
	PBE	**PBE0**	**B1LYP**	**B3LYP**	**BLYP**	**HCTH**
DS2						
HTBH29	9.2	4.2	3.4	4.5	7.8	5.8
NHTBH4	12.7	6.6	7.5	8.7	13.2	6.8
MC-BE3	4.4	4.5	6.1	4.7	6.9	6.4
MR-MGN-BE8	12.0	6.2	9.6	5.3	5.8	6.4
SR-MGM-BE2	2.3	2.6	6.2	4.4	6.8	5.5
SR-MGN-BE17	3.9	3.4	5.9	4.1	4.4	4.2
DS3						
NGD-CE5	0.09	0.06	0.17	0.17	0.25	0.25
G2-BE5	2.9	1.9	1.9	1.6	1.9	1.2
NC-CE5	1.7	1.5	2.2	2.1	2.7	1.9
PX-BH3	11.5	6.5	2.1	3.8	6.8	3.6
PERI-BH4	4.7	2.7	1.1	0.9	3.0	2.7
Lix-AE3	2.4	2.9	3.4	3.1	3.3	1.3
CH-BE5	3.8	4.3	2.7	1.8	3.4	3.8
DAC-DE5	4.7	3.0	9.9	9.5	12.8	12.7
PB-BE4	5.0	5.3	5.5	5.0	5.1	4.1
HP-BE6	3.7	4.8	10.5	8.9	9.5	10.2
MR-MGN-BE4	14.7	1.4	6.1	1.6	8.9	1.9
MR-MGM-BE3	11.0	4.1	7.8	3.8	10.5	8.2
ΣTMD-BE4	1.1	9.3	8.6	6.7	1.4	1.8
ΣTML-BE17	7.5	6.6	6.7	5.3	6.4	6.2
IP10	5.3	3.3	2.6	4.6	4.9	4.9
NG-IP4	1.8	2.2	2.4	4.1	3.0	7.0
SIE4x4	23.2	13.9	15.4	17.4	24.5	23.3
PC-ED5	7.5	4.3	3.5	3.1	6.7	3.4
IsoE6	3.5	2.8	4.8	4.8	5.6	4.8
PA8	1.2	1.3	1.0	0.9	1.5	2.9
MG-SS26	7.5	7.8	7.6	7.2	7.9	7.9
TM-SS6	21.8	14.6	17.8	18.8	25.1	8.2
mean MUE by database	6.8	4.7	5.8	5.2	7.1	5.6
mean RMSD by database	7.7	5.6	6.9	6.3	8.1	6.4
MUE by data points	7.9	5.5	6.3	6.0	8.0	6.8

Table S11. MUE (kcal/mol) for each database, RMSE (kcal/mol) over databases, mean MUE over databases and data points for six KS-DFT methods that include kinetic energy density as an ingredient

Database	KS-DFT					
	τ-HCTH	**M06-L**	**M06**	**MN15-L**	**MN15**	**CF22D**
DS2						
HTBH29	5.3	4.4	1.9	1.4	1.1	1.3
NHTBH4	5.0	3.6	2.2	3.0	3.5	3.6
MC-BE3	2.4	7.0	7.4	2.8	2.6	3.3
MR-MGN-BE8	4.1	4.6	3.9	2.7	3.4	3.7
SR-MGM-BE2	4.1	4.6	7.3	1.4	1.9	1.0
SR-MGN-BE17	2.7	3.8	2.3	2.8	1.4	1.3
DS3						
NGD-CE5	0.08	0.05	0.11	0.01	0.03	0.05
G2-BE5	1.4	1.8	1.1	0.9	1.0	1.4
NC-CE5	1.7	0.4	0.5	1.2	0.2	0.1
PX-BH3	7.0	0.9	1.2	5.9	1.6	0.9
PERI-BH4	2.1	2.0	1.4	2.3	1.4	1.0
Lix-AE3	2.2	0.4	0.9	1.0	1.4	1.0
CH-BE5	3.2	5.1	2.7	2.8	1.4	1.0
DAC-DE5	6.0	1.0	3.0	1.3	2.0	1.3
PB-BE3	2.2	3.5	1.5	3.3	2.1	1.0
HP-BE6	3.8	4.0	3.0	8.1	6.6	3.7
MR-MGN-BE4	2.1	2.2	3.1	0.9	2.2	2.5
MR-MGM-BE3	5.1	5.4	1.8	4.5	4.5	5.6
ΣTMD-BE4	2.9	2.7	4.5	4.9	5.0	7.2
ΣTML-BE17	5.4	7.0	7.1	6.0	5.7	5.9
IP10	3.3	2.6	3.1	2.7	3.0	1.8
NG-IP4	4.0	3.6	2.1	4.6	2.5	2.2
SIE4x4	18.1	17.6	14.0	10.9	11.5	10.9
PC-ED5	1.5	2.1	2.7	3.3	2.6	2.7
IsoE6	3.7	3.8	2.2	1.9	1.9	1.7
PA8	2.0	2.4	1.8	2.2	1.2	0.9
MG-SS26	6.5	7.4	6.0	5.1	6.6	5.4
TM-SS6	15.4	9.3	5.7	17.3	18.5	15.3
mean MUE by database	4.4	4.0	3.4	3.8	3.5	3.1
mean RMSD by database	5.0	5.0	4.2	4.6	4.3	4.1
MUE by data points	5.4	5.3	4.1	4.1	4.0	3.6

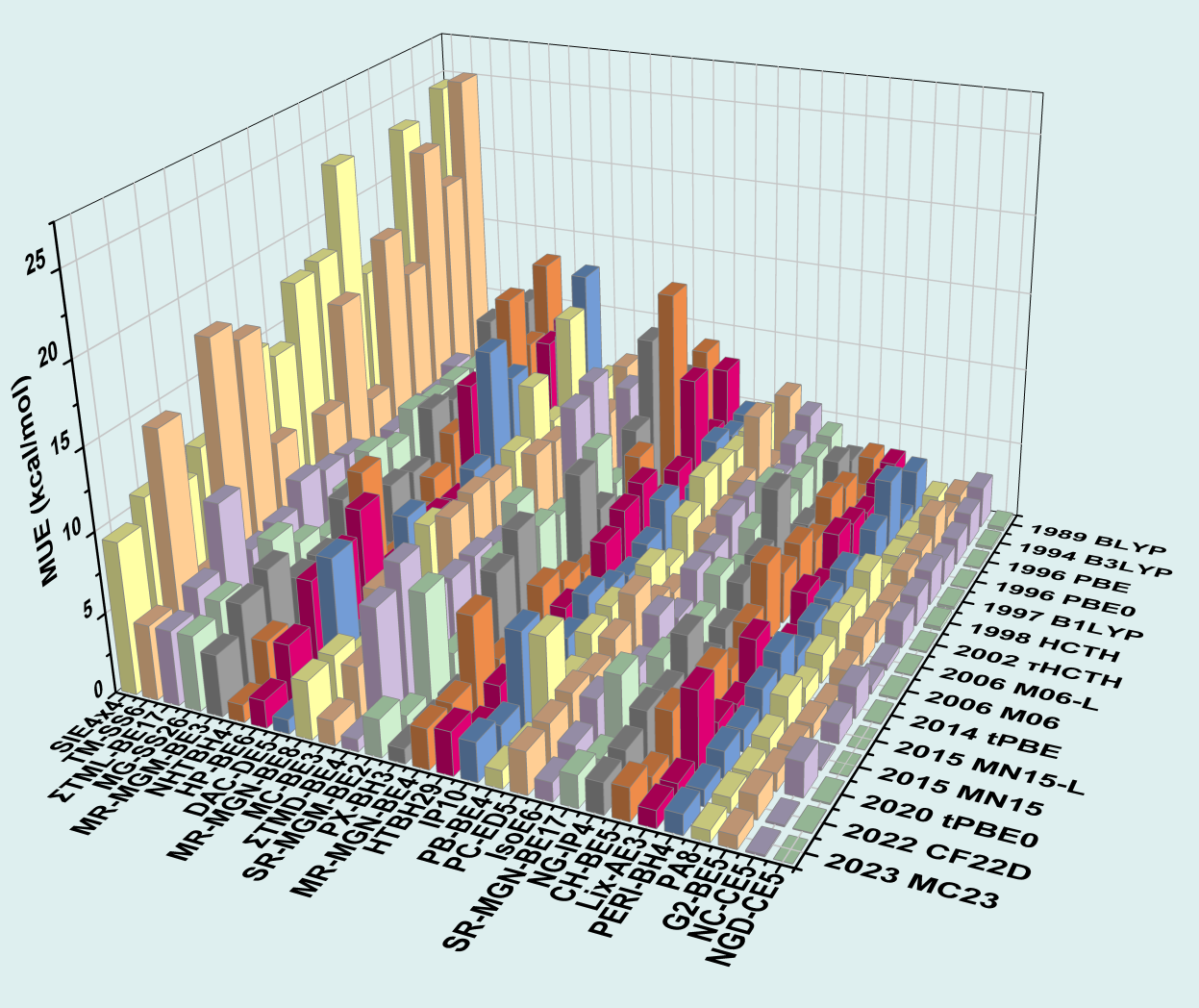

Figure S2. Mean unsigned error (kcal/mol) on each database for each KS-DFT or MC-PDFT density functional, with the year of each functional indicated. Data are obtained from Tables S9–S11.

S7. MUE Ranks for Each Method

The final ranks for evaluation of the functionals are based on mean unsigned error because it is a simple, robust quality indicator for distributions that do not necessarily have a normal error distribution,[111,112] and its use is especially preferred on smaller databases.

Table S12. Ranks of the mean unsigned error for the multiconfigurational methods of Table S9

Database	HMC-PDFT	CASSCF	CASPT2	MC-PDFT			
	MC23			tPBE	tPBE0	tτ-HCTH	tM06-L
DS2							
HTBH29	6	19	9	8	5	7	11
NHTBH4	1	19	5	16	2	13	9
MC-BE3	1	11	2	18	15	13	7
MR-MGN-BE8	4	18	10	14	1	11	16
SR-MGM-BE2	6	19	12	13	17	8	3
SR-MGN-BE17	3	19	16	5	17	6	9
DS3							
NGD-CE5	1	15	3	9	12	13	7
G2-BE5	4	19	11	2	7	3	1
NC-CE5	2	19	7	13	15	17	5
PX-BH3	2	19	9	17	4	12	8
PERI-BH4	4	19	8	16	7	12	17
Lix-AE3	5	19	17	14	16	18	15
CH-BE5	7	19	16	2	12	6	4
DAC-DE5	1	17	2	12	13	16	6
PB-BE4	2	19	10	9	18	6	16
HP-BE6	1	19	11	4	12	5	2
MR-MGN-BE4	9	19	14	11	15	16	12
MR-MGM-BE3	3	15	19	13	12	10	4
ΣTMD-BE4	1	19	7	12	16	6	14
ΣTML-BE17	1	19	2	16	18	3	17
IP10	2	19	18	11	17	16	8
NG-IP4	3	19	12	1	9	18	11
SIE4x4	3	2	1	11	4	12	7
PC-ED5	6	19	14	13	8	18	16
IsoE6	2	18	1	11	8	14	9
PA8	1	14	10	6	2	19	18
MG-SS26	4	12	1	3	2	6	5
TM-SS6	1	14	8	7	2	3	9
average MUE by database	1	19	7	11	10	13	8
average RMSD by database	1	19	6	11	9	13	10
MUE by data points	1	19	3	9	7	10	8
average rank by database	3.0	17.0	9.1	9.7	10.4	11.3	9.6

Table S13. The ranking of the MUE for KS-DFAs without using kinetic energy densities

Database	KS-DFT					
	PBE	**PBE0**	**B1LYP**	**B3LYP**	**BLYP**	**HCTH**
DS2						
HTBH29	18	12	10	14	17	16
NHTBH4	17	11	14	15	18	12
MC-BE3	8	9	12	10	16	14
MR-MGN-BE8	19	13	17	9	12	15
SR-MGM-BE2	5	7	15	10	16	14
SR-MGN-BE17	12	10	18	13	15	14
DS3						
NGD-CE5	11	8	17	16	19	18
G2-BE5	18	17	15	13	16	9
NC-CE5	11	9	16	14	18	12
PX-BH3	18	14	7	11	15	10
PERI-BH4	18	14	3	1	15	13
Lix-AE3	9	10	13	11	12	6
CH-BE5	15	17	8	5	13	14
DAC-DE5	10	8	15	14	19	18
PB-BE3	12	15	17	13	14	11
HP-BE6	7	10	18	15	16	17
MR-MGN-BE4	18	2	13	3	17	4
MR-MGM-BE3	18	5	14	2	17	16
ΣTMD-BE4	2	18	17	13	3	4
ΣTML-BE17	15	11	12	4	10	9
IP10	15	9	4	12	13	14
NG-IP4	2	6	7	15	10	17
SIE4x4	17	9	13	14	19	18
PC-ED5	17	12	11	7	15	10
IsoE6	10	7	17	15	19	16
PA8	8	9	5	4	11	17
MG-SS26	15	17	16	13	18	19
TM-SS6	18	10	15	17	19	5
mean MUE by database	17	12	16	14	18	15
mean RMSD by database	17	12	16	14	18	15
MUE by data points	17	13	15	14	18	16
average rank by database	12.9	10.8	12.4	10.5	14.9	12.6

Table S14. The ranking of the mean unsigned error (MUE) for KS-DFAs using kinetic energy densities.

Database	KS-DFT					
	τ-HCTH	**M06-L**	**M06**	**MN15-L**	**MN15**	**CF22D**
DS2						
HTBH29	15	13	4	3	1	2
NHTBH4	10	8	3	4	6	7
MC-BE3	3	17	19	5	4	6
MR-MGN-BE8	7	8	6	2	3	5
SR-MGM-BE2	9	11	18	2	4	1
SR-MGN-BE17	7	11	4	8	2	1
DS3						
NGD-CE5	10	6	14	2	4	5
G2-BE5	10	14	8	5	6	12
NC-CE5	10	4	6	8	3	1
PX-BH3	16	1	5	13	6	3
PERI-BH4	10	9	5	11	6	2
Lix-AE3	8	1	2	4	7	3
CH-BE5	11	18	9	10	3	1
DAC-DE5	11	3	9	5	7	4
PB-BE3	5	8	3	7	4	1
HP-BE6	8	9	3	14	13	6
MR-MGN-BE4	5	6	10	1	7	8
MR-MGM-BE3	8	9	1	7	6	11
ΣTMD-BE4	8	5	9	10	11	15
ΣTML-BE17	5	13	14	8	6	7
IP10	10	3	7	5	6	1
NG-IP4	14	13	4	16	8	5
SIE4x4	16	15	10	6	8	5
PC-ED5	1	2	5	9	3	4
IsoE6	12	13	6	5	4	3
PA8	13	16	12	15	7	3
MG-SS26	10	14	9	7	11	8
TM-SS6	12	6	4	13	16	11
mean MUE by database	9	6	3	5	4	2
mean RMSD by database	8	7	3	5	4	2
MUE by data points	12	11	5	6	4	2
average rank by database	9.7	8.5	7.0	8.2	6.9	5.4

S8. MUE and Ranks for Seven Databases According to Data Types

In this section, we present the MUE and the rankings for all methods over seven larger databases that are mentioned in Section 5.3 of the paper.

Table S15. MUE (in kcal/mol) of all methods for seven larger databases

	CASPT2	CASSCF	tM06-L	tPBE	tPBE0	tτHCTH	MC23
MG-BE55	5.0	15.0	3.7	4.0	5.1	4.5	2.1
TM-BE19	4.8	18.5	8.3	7.7	9.6	5.4	4.4
MC-AE7	4.3	14.9	6.0	4.4	7.0	4.6	0.9
BH40	2.9	13.4	3.4	3.8	2.2	3.3	2.3
WB15	0.9	2.7	0.3	0.8	1.1	1.1	0.3
SS32	5.0	8.9	6.3	5.2	4.0	5.0	4.7
Other(49)	3.5	11.6	6.2	7.0	5.6	8.9	4.3
	PBE	PBE0	B1LYP	B3LYP	BLYP	HCTH	
MG-BE55	6.3	3.9	7.0	4.9	6.7	6.0	
TM-BE19	7.1	6.6	6.9	5.4	6.5	6.3	
MC-AE7	1.6	6.5	6.4	5.1	2.2	1.6	
BH40	9.3	4.5	3.5	4.5	7.8	5.4	
WB15	1.6	1.2	1.4	1.3	1.6	1.1	
SS32	10.2	9.1	9.5	9.4	11.1	8.0	
Other(49)	10.2	6.4	6.9	8.0	10.9	10.6	
	τHCTH	M06-L	M06	MN15-L	MN15	CF22D	
MG-BE55	3.4	4.0	2.9	3.1	2.6	2.2	
TM-BE19	5.2	6.4	7.2	5.8	5.3	5.6	
MC-AE7	2.6	1.7	3.0	3.2	3.5	4.6	
BH40	5.0	3.8	1.9	2.0	1.4	1.4	
WB15	1.0	0.7	0.6	0.7	0.4	0.5	
SS32	8.2	7.7	5.9	7.4	8.8	7.3	
Other(49)	7.8	7.6	6.2	5.4	5.3	4.8	

Table S16. Ranking of MUEs of all methods for seven composite databases

	CASPT2	CASSCF	tM06-L	tPBE	tPBE0	tτHCTH	MC23
MG-BE55	13	19	7	9	14	11	1
TM-BE19	2	19	17	16	18	5	1
MC-AE7	10	19	15	11	18	13	1
BH40	7	19	9	12	5	8	6
WB15	9	19	1	8	11	12	2
SS32	3	14	7	5	1	4	2
Other(49)	1	19	8	11	6	15	2
	PBE	PBE0	B1LYP	B3LYP	BLYP	HCTH	
MG-BE55	16	8	18	12	17	15	
TM-BE19	14	12	13	6	11	9	
MC-AE7	3	17	16	14	5	2	
BH40	18	13	10	14	17	16	
WB15	17	14	16	15	18	13	
SS32	18	15	17	16	19	11	
Other(49)	16	9	10	14	18	17	
	τHCTH	M06-L	M06	MN15-L	MN15	CF22D	
MG-BE55	6	10	4	5	3	2	
TM-BE19	3	10	15	8	4	7	
MC-AE7	6	4	7	8	9	12	
BH40	15	11	3	4	1	2	
WB15	10	7	5	6	3	4	
SS32	12	10	6	9	13	8	
Other(49)	13	12	7	5	4	3	

S9. MUE and Rankings for Databases According to M and N Diagnostics

This section shows the tables of regrouped databases according to the M or N diagnostics of the data. Tables in this section are complete versions of Table 3 in the paper.

Table S17. MUE (in kcal/mol) of all methods for databases according to their M or N diagnostics

	CASPT2	CASSCF	tM06-L	tPBE	tPBE0	tτHCTH	MC23
SmallM85	3.2	13.0	3.6	4.1	3.9	4.5	2.2
ModerateM31	3.1	11.2	4.5	3.4	3.7	4.3	3.3
LargeM85	5.1	13.5	4.9	4.4	4.9	4.3	2.6
SmallN108	3.5	12.9	3.7	4.3	4.2	4.3	2.2
ModerateN50	4.4	13.2	4.6	3.7	4.7	4.5	3.1
LargeN43	4.7	12.6	5.4	4.1	3.9	4.5	2.7

	PBE	PBE0	B1LYP	B3LYP	BLYP	HCTH
SmallM85	6.2	3.8	4.0	4.5	6.2	5.3
ModerateM31	7.5	4.8	5.5	5.0	7.3	6.1
LargeM85	6.9	5.8	7.2	5.7	6.8	5.4
SmallN108	6.5	4.6	5.4	5.5	7.1	5.7
ModerateN50	7.3	4.6	5.7	4.5	6.7	6.0
LargeN43	6.4	5.6	5.9	4.7	5.4	4.2

	τHCTH	M06-L	M06	MN15-L	MN15	CF22D
SmallM85	4.2	3.6	2.5	3.1	2.5	2.0
ModerateM31	4.9	5.1	3.5	3.3	3.5	2.4
LargeM85	4.3	4.6	4.1	4.2	4.3	4.3
SmallN108	4.7	4.3	2.8	3.8	3.1	2.6
ModerateN50	4.6	4.9	3.6	3.2	3.6	2.8
LargeN43	3.3	3.6	4.4	3.6	4.1	4.7

Table S18. Ranking of MUEs of all methods for databases according to their M or N diagnostics

	CASPT2	CASSCF	tM06-L	tPBE	tPBE0	tτHCTH	MC23
SmallM85	6	19	7	12	10	14	2
ModerateM31	2	19	10	5	8	9	3
LargeM85	12	19	11	8	10	5	1
SmallN108	5	19	6	10	8	11	1
ModerateN50	7	19	11	6	13	8	2
LargeN43	13	19	14	6	5	10	1

	PBE	PBE0	B1LYP	B3LYP	BLYP	HCTH
SmallM85	17	9	11	15	18	16
ModerateM31	18	11	15	13	17	16
LargeM85	17	15	18	14	16	13
SmallN108	17	12	14	15	18	16
ModerateN50	18	10	15	9	17	16
LargeN43	18	16	17	12	15	8

	τHCTH	M06-L	M06	MN15-L	MN15	CF22D
SmallM85	13	8	3	5	4	1
ModerateM31	12	14	7	4	6	1
LargeM85	4	9	2	3	7	6
SmallN108	13	9	3	7	4	2
ModerateN50	12	14	5	3	4	1
LargeN43	2	3	9	4	7	11

S10. Signed Errors for Each System

Table S19. Signed error (in kcal/mol) of CASSCF, CASPT2, and MC-PDFT with various functionals for all systems

Database	System	CASPT2	CASSCF	tM06-L	tPBE	tPBE0	tτHCTH	MC23
HTBH29	V_f H + HCl → H_2 + Cl	4.5	14.9	3.9	-0.7	3.2	-0.8	3.4
	V_r H + HCl → H_2 + Cl	3.5	18.7	-4.3	-7.1	-0.6	-6.0	0.1
	V_r OH + H_2 → H_2O + H	9.1	9.9	8.0	5.2	6.4	5.7	8.3
	V_r CH_3 + H_2 → CH_4 + H	4.9	15.2	2.2	-2.4	2.0	-2.3	3.3
	V_f OH + CH_4 → H_2O + CH_3	2.5	14.2	-0.6	-3.7	0.8	-1.8	0.9
	V_r OH + CH_4 → H_2O + CH_3	2.9	2.9	-2.6	-2.1	-0.9	0.4	-0.3
	V_f H + H_2 → H_2 + H	5.1	14.8	-1.5	-3.8	0.9	-1.6	1.7
	V_f OH + NH_3 → H_2O + NH_2	3.3	27.3	4.4	-1.4	5.7	-1.2	6.3
	V_r OH + NH_3 → H_2O + NH_2	2.7	14.0	2.2	-0.9	2.8	0.8	2.5
	V_f OH + C_2H_6 → H_2O + C_2H_5	1.4	8.6	0.7	-1.8	0.8	-1.4	0.6
	V_r OH + C_2H_6 → H_2O + C_2H_5	2.4	6.1	2.7	1.4	2.6	2.1	3.8
	V_f F + H_2 → HF + H	4.9	13.4	2.4	0.8	4.0	1.8	4.3
	V_r F + H_2 → HF + H	9.3	-3.5	9.7	9.2	6.0	10.8	7.2
	V_r O + CH_4 → OH + CH_3	0.5	8.9	0.2	-1.3	1.2	-1.7	2.2
	V_f H + PH_3 → H_2 + PH_2	4.2	10.2	4.4	0.7	3.1	3.8	1.7
	V_r H + PH_3 → H_2 + PH_2	3.4	6.1	-1.4	-0.4	1.2	3.4	0.4
	V_f H + HO → H_2 + O	1.1	-4.5	0.0	-0.5	-1.5	1.6	-2.5
	V_r H + HO → H_2 + O	0.1	13.8	-3.3	-6.8	-1.7	-4.2	-2.4
	V_f H + H_2S → H_2 + HS	3.7	6.7	5.4	1.6	2.8	4.9	1.2
	V_r H + H_2S → H_2 + HS	2.6	9.9	-2.9	-3.7	-0.3	0.7	-0.7
	V_r O + HCl → OH + Cl	4.4	12.3	-6.2	-5.2	-0.8	-3.0	-1.2

Database	System	CASPT2	CASSCF	tM06-L	tPBE	tPBE0	tτHCTH	MC23
	V_f $CH_3 + NH_2 \rightarrow CH_4 + NH$	0.3	10.8	-0.4	-1.7	1.4	-2.1	2.0
	V_r $CH_3 + NH_2 \rightarrow CH_4 + NH$	1.3	12.1	7.1	-0.9	2.4	-1.4	4.1
	V_f $C_2H_5 + NH_2 \rightarrow C_2H_6 + NH$	1.3	12.0	1.9	0.5	3.3	0.2	3.6
	V_r $C_2H_5 + NH_2 \rightarrow C_2H_6 + NH$	1.6	11.9	6.5	-0.6	2.5	-1.1	3.5
	V_f $NH_2 + C_2H_6 \rightarrow NH_3 + C_2H_5$	0.8	17.3	4.6	-1.3	3.4	-1.1	4.1
	V_r $NH_2 + C_2H_6 \rightarrow NH_3 + C_2H_5$	1.3	11.3	4.1	0.5	3.2	0.7	3.9
	V_f $NH_2 + CH_4 \rightarrow NH_3 + CH_3$	-1.6	23.1	-3.1	-9.6	-1.4	-8.0	-0.7
	V_r $NH_2 + CH_4 \rightarrow NH_3 + CH_3$	-1.8	17.5	-3.7	-8.6	-2.1	-7.0	-1.1
MC-BE3	LiO^-	-2.5	-3.3	-0.8	-4.2	-4.0	-5.9	0.0
	CuCl	-3.8	-10.6	-2.3	-14.6	-13.6	-10.0	-3.1
	FeCl	-0.3	-1.1	8.0	-2.7	-2.3	2.6	-1.4
MR-MGN-BE8	SiO (multiplicity=1)	-8.1	3.5	-7.1	-7.9	-5.0	-0.4	1.7
	CO	-5.8	3.6	-6.2	-5.9	-3.5	-0.1	2.3
	ClO	-6.9	-19.3	3.3	9.4	2.3	11.3	4.3
	$O_3 \rightarrow O_2 + O$	-7.3	-24.3	5.4	12.4	3.2	13.4	6.3
	N_2	-9.4	-7.3	-11.2	-1.9	-3.2	8.3	0.6
	O_2	-4.2	-17.0	-4.6	5.1	-0.5	9.6	3.0
	B_2	1.6	-17.5	1.9	7.1	1.0	-2.0	3.5
	C_2	0.5	-2.2	11.9	1.4	0.5	-0.9	7.1
NHTBH4	V_f $H + FH \rightarrow HF + H$	4.2	21.9	0.6	-11.9	-3.5	-7.2	-0.4
	V_f $H + ClH \rightarrow HCl + H$	5.0	23.5	1.9	-5.4	1.8	-2.0	0.9
	V_r $H + FCH_3 \rightarrow HF + CH_3$	2.3	5.9	1.4	-5.5	-2.6	-2.0	-0.1
	V_f $H + F_2 \rightarrow HF + F$	0.7	-37.7	11.4	12.9	0.2	16.2	-3.0

Database	System	CASPT2	CASSCF	tM06-L	tPBE	tPBE0	tτHCTH	MC23
SR-MGM-BE2	NaO	-7.8	-18.2	0.4	-7.3	-10.0	-5.3	0.3
	ZnCl	-1.8	-7.8	2.5	-2.8	-4.0	2.3	-4.4
SR-MGN-BE17	CH_3–CH_3	-1.5	-11.7	4.7	0.6	-2.5	1.8	1.7
	CH_3O–CH_3	-1.8	-1.0	-4.9	-4.5	-3.6	-2.1	1.1
	Et–H	-5.4	-20.2	-0.1	-2.4	-6.9	1.1	-4.7
	Et–CH_3	-0.4	-12.4	4.9	0.5	-2.7	1.1	2.8
	Et–OCH_3	-3.7	-17.6	-5.3	-5.2	-8.3	-3.5	-3.2
	Et–OH	-3.8	-12.2	0.3	-0.9	-3.7	2.9	0.1
	CH ($^2\Pi$)	-5.0	-12.6	1.7	-0.6	-3.6	0.7	0.6
	NH	-6.6	-14.2	-6.6	-2.2	-5.2	-1.6	-2.3
	OH	-6.9	-10.2	-4.8	-2.0	-4.1	-0.6	-1.4
	HCl	-6.9	-16.3	-4.6	-5.0	-7.8	-3.2	-4.0
	Si_2 (multiplicity=3)	0.9	-10.4	4.5	-2.0	-4.1	-1.9	2.7
	P_2	-8.9	-28.6	-1.6	-1.8	-8.5	5.7	-1.7
	S_2	-6.1	-29.7	3.8	5.4	-3.4	7.4	1.9
	Cl_2	-4.9	-20.3	3.5	3.8	-2.2	3.6	1.7
	SC	-3.7	-12.6	-0.8	-0.5	-3.5	3.3	1.2
	H_2	-6.1	-14.5	-2.1	-1.8	-5.0	-1.5	0.4
	SH	-5.2	-13.7	-3.2	-3.1	-5.7	-1.2	-2.1
CH-BE5	C_2H–H	-5.3	-17.3	0.8	-0.4	-4.6	2.9	-1.2
	C_2H_3–H	-4.2	-14.0	0.8	-1.8	-4.9	1.0	-1.3
	$C_2H_4 \rightarrow C_2H_2 + H_2$	-3.0	-12.4	0.1	0.2	-3.0	0.3	-2.2
	C^+–H	-4.9	-8.6	4.5	3.5	0.4	4.9	3.8

Database	System	CASPT2	CASSCF	tM06-L	tPBE	tPBE0	tτHCTH	MC23
	tert-butyl–H	-3.4	-12.1	2.5	-0.9	-3.7	-0.6	1.6
DAC-DE5	$Al_2H_6 \rightarrow 2AlH_3$	-0.2	-10.3	-1.0	-3.0	-4.8	-7.1	-0.1
	$Al_2F_6 \rightarrow 2AlF_3$	-0.5	-2.7	-1.5	-7.1	-6.0	-10.7	1.1
	$Al_2Cl_6 \rightarrow 2AlCl_3$	1.7	-12.8	-2.4	-7.6	-8.9	-11.8	-0.9
	$Al_2HMe_5 \rightarrow AlHMe_2 + AlMe_3$	0.7	-14.8	-1.7	-6.9	-8.9	-12.7	0.4
	$Al_2Me_6 \rightarrow 2AlMe_3$	1.6	-18.5	-1.6	-8.6	-11.1	-16.4	2.0
G2-BE5	Be_2	-0.3	-4.9	-0.4	1.5	-0.1	0.9	1.4
	Mg_2	0.6	-3.3	-0.5	-0.3	-1.1	0.2	-0.1
	Ca_2	-2.1	-5.7	0.0	0.1	-1.3	0.8	0.5
	Sr_2	-1.9	-5.6	0.4	0.1	-1.3	0.9	0.7
	Ba_2	-2.2	-6.6	0.0	0.1	-1.6	0.0	1.4
HP-BE6	$H_3Ge–GeH_3$	-4.3	-15.2	2.9	-1.0	-4.5	1.6	-0.1
	$Me_3Pb–PbMe_3$	5.1	-13.1	-6.7	-6.9	-8.5	-5.8	-3.5
	$Me_2As–AsMe_2$	-2.0	-17.3	0.4	-4.9	-8.0	-6.1	0.5
	HS–SH	-4.6	-18.1	4.9	2.3	-2.8	2.6	1.3
	Br_2	-14.1	-25.9	-2.2	-3.1	-8.8	-3.7	-4.2
	MeTe–TeMe	-1.1	-18.5	-0.9	-0.5	-5.0	-2.1	0.7
IP10	Cl_2	-5.7	-20.6	0.3	-2.8	-7.2	2.3	-4.0
	SH	-5.0	-25.7	-0.4	1.2	-5.5	6.7	-2.8
	PH_2	-4.1	-23.8	1.4	2.5	-4.1	4.4	0.4
	O_2	-1.2	-42.8	-6.0	0.8	-10.1	3.6	-6.6
	Zn	-13.7	-40.3	-5.8	-6.3	-14.8	-7.6	-0.6
	OH	-5.4	-36.3	-2.1	4.1	-6.0	9.8	-2.6

Database	System	CASPT2	CASSCF	tM06-L	tPBE	tPBE0	tτHCTH	MC23
	Mo	-1.5	-19.4	1.8	8.4	1.5	0.1	-0.1
	Cu	-10.5	-31.1	-10.9	3.4	-5.2	-6.3	-4.7
	Cr	-2.4	-19.5	1.1	8.3	1.4	-6.8	1.1
	Cl	-13.3	-26.4	2.6	2.6	-4.6	8.8	-1.5
IsoE6	C_3H_4	0.3	-13.8	5.4	8.3	2.8	6.3	3.7
	C_6NH_7	-0.3	5.5	4.4	4.7	4.9	7.2	1.6
	$C_{14}H_{20}O$	0.5	-7.0	-3.3	-0.8	-2.4	-2.6	-0.7
	$C_{14}H_{12}F_2$	0.6	0.3	-1.3	0.7	0.6	0.8	-0.1
	$C_{12}N_2H_{12}$	0.5	-3.3	-0.8	-3.0	-3.0	-3.7	-0.1
	$C_{12}H_{20}$	1.6	-2.4	-2.7	-4.7	-4.2	-6.1	-0.8
Lix-AE3	Li_2	-5.5	-7.7	-4.7	-3.1	-4.2	-6.0	-1.1
	Li_4	-5.9	-8.6	-4.6	-3.8	-5.0	-7.5	-1.0
	Li_5	-7.3	-11.1	-4.7	-3.6	-5.5	-7.7	-1.1
MG-SS26	NH	0.7	6.8	-1.0	-9.9	-5.8	-9.4	-4.5
	OH^+	0.2	5.8	-3.6	-15.7	-10.3	-13.9	-8.3
	NF	-2.2	2.6	-3.6	-11.5	-8.0	-10.5	-7.1
	O_2	-0.5	-2.2	-0.6	-4.7	-4.1	-3.7	-4.0
	H_2CC	4.0	5.5	-4.9	-2.9	-0.8	-8.6	-2.8
	C_2H_5CHS	0.3	-5.7	-3.3	-0.1	-1.5	-1.3	-2.7
	C_4H_3CHO	-0.2	-3.4	0.4	2.5	1.0	1.7	0.4
	$C_4H_3NH_2$	0.6	-4.7	1.0	3.1	1.1	2.0	0.6
	$Me_2C{=}CH_2$	-21.8	8.7	-0.1	2.2	3.8	1.3	3.0
	CH_3CHO	-0.3	-12.2	-4.4	-0.3	-3.2	-2.5	-5.6

Database	System	CASPT2	CASSCF	tM06-L	tPBE	tPBE0	tτHCTH	MC23
	NH_2CHO	0.7	-17.6	1.8	4.0	-1.4	2.7	-4.5
	He	-0.6	-12.7	12.4	-2.8	-5.3	9.9	10.3
	acetone	1.3	11.5	5.8	1.5	4.0	3.2	6.1
	propynal	1.9	3.8	5.6	2.2	2.6	4.4	4.2
	pyrimidine	-1.4	10.4	5.0	-1.3	1.6	1.5	3.5
	cyanoformaldehyde	3.3	6.5	6.5	2.7	3.6	4.8	5.3
	butadiene	-0.4	-2.6	4.8	2.6	1.3	3.8	2.0
	cyclopropenone	4.4	9.5	7.4	2.3	4.1	5.3	6.8
	pyrrole	1.1	-5.0	5.8	4.3	2.0	4.5	3.0
	CH_2	2.5	1.2	-5.0	-1.8	-1.0	-6.2	-1.9
	NH_2	2.8	-0.3	-6.9	-4.0	-3.1	-7.3	-3.6
	SiH_2	1.2	2.6	-3.5	-0.6	0.2	-3.2	-1.6
	PH_2	0.8	0.1	-5.8	-2.3	-1.7	-4.9	-3.0
	Be_2CO ^{3}6–^{1}6	-11.6	-13.7	-10.3	-8.0	-9.4	-3.4	-8.8
	Be_2CO ^{5}6–^{1}6	-11.6	-13.6	-10.3	-8.0	-9.4	-3.3	-8.8
	Be_2CO ^{3}5–^{1}5	-13.8	-10.9	-8.0	-8.2	-8.9	-4.8	-8.8
MR-MGM-BE3	CaO	-21.4	-1.3	-0.1	-3.0	-2.6	9.5	1.8
	BeO	-13.6	4.9	-8.5	-9.2	-5.7	-3.2	2.5
	MgS	-8.4	-17.3	-3.4	-8.5	-10.7	-3.6	-7.2
MR-MGN-BE4	CN	-8.8	-34.8	-8.9	-3.9	-11.6	-5.4	-5.4
	Cl_2–O	-3.0	-21.7	3.0	6.1	-0.8	8.7	1.8
	SO	-5.7	-40.1	-2.9	1.8	-8.7	4.6	-2.6
	NO	-7.6	-28.5	-5.5	4.0	-4.1	10.6	-0.2

Database	System	CASPT2	CASSCF	tM06-L	tPBE	tPBE0	tτHCTH	MC23
NC-CE5	H_2O–H_2O	0.1	-1.4	-0.5	-0.5	-0.7	-1.1	0.1
	C_2H_4–F_2	1.8	-1.5	-0.6	-0.8	-1.0	-1.3	-0.1
	parallel-displaced CO_2–CO_2	0.3	-2.3	-0.7	-1.3	-1.6	-2.0	-0.1
	sandwich C_6H_6–C_6H_6	1.6	-3.7	-0.2	-3.2	-3.4	-3.9	-0.2
	parallel-displaced C_6H_6–C_6H_6	1.9	-4.8	-0.1	-3.8	-4.1	-5.0	0.0
NG-IP4	He	-7.4	-16.4	5.0	-0.1	-4.2	11.2	1.3
	Ne	-5.9	-18.1	-1.8	1.2	-3.6	10.2	1.5
	Ar	0.1	-16.1	4.7	1.0	-3.3	6.9	1.0
	Kr	-0.9	-12.5	1.1	3.2	-0.8	9.4	3.9
NGD-CE5	He_2	-0.02	-0.03	0.00	0.02	0.01	0.06	0.00
	Ne_2	-0.01	-0.11	0.07	-0.04	-0.06	0.02	0.01
	Ar_2	-0.03	-0.54	-0.19	-0.28	-0.34	-0.28	0.00
	He_2	-0.03	-0.07	0.02	0.01	-0.01	0.05	-0.01
	He_2	-0.04	-0.11	-0.03	0.00	-0.03	0.06	-0.01
PA8	NH_3	2.7	-2.3	2.8	0.5	-0.2	4.0	-0.1
	H_2O	-4.0	1.0	2.5	0.0	0.2	3.4	-0.3
	C_2H_2	-1.1	0.5	6.8	2.2	1.7	5.8	1.7
	SiH_4	0.1	0.2	-2.5	1.3	1.0	3.2	-0.1
	PH_3	-0.7	5.7	-1.9	-3.4	-1.1	1.6	-1.6
	H_2S	-0.3	2.8	-0.4	-1.3	-0.2	2.4	-1.1
	HCl	-1.7	-0.2	1.5	1.0	0.7	3.3	0.3
	H_2	-1.1	-3.8	-5.4	0.0	-1.0	2.4	-0.5
PB-BE4	BN	-4.5	-22.3	-5.5	1.6	-4.4	-4.2	-0.6

Database	System	CASPT2	CASSCF	tM06-L	tPBE	tPBE0	tτHCTH	MC23
	SiO	-7.2	-13.2	-9.9	-10.3	-11.0	-4.2	-2.2
	AlCl	-2.7	-14.0	5.3	-2.3	-5.2	-0.7	1.2
	H–P–H	0.2	-13.2	1.2	-0.3	-3.5	1.9	0.4
PC-ED5	N_2	-4.2	-3.9	-2.3	3.2	1.4	12.3	5.1
	F_2	-3.9	-21.8	10.5	10.4	2.3	12.5	3.4
	Li_2	-10.0	-13.8	-5.1	-4.6	-6.9	-6.6	-2.7
	KH	-7.3	-11.0	13.0	-3.2	-5.2	8.3	-3.1
	ClF	-1.9	-6.9	2.8	1.9	-0.3	4.8	1.0
PERI-BH4	C_4H_6 (cyclobutene)	-0.7	1.0	6.7	1.1	1.1	2.1	1.6
	C_6H_8 (*cis*-1,3,5-hexatriene)	-1.3	14.8	2.3	-1.2	2.8	0.3	1.7
	C_8H_8 (*ortho*-xylylene)	-2.3	11.0	2.1	-2.3	1.0	-1.4	1.1
	C_5H_6 (1,3-cyclopentadiene)	-2.9	15.3	-3.3	-7.4	-1.8	-5.9	-0.7
PX-BH3	$4NH_3$	-2.8	21.1	1.5	-7.8	-0.6	-3.2	1.1
	$4H_2O$	-3.8	19.3	2.3	-8.0	-1.2	-5.2	-0.6
	4HF	-3.0	12.6	3.6	-6.0	-1.3	-5.2	-1.0
SIE4x4	H_2^+ at 1.0 r_e	-0.9	-0.9	3.1	3.4	2.3	5.6	0.9
	H_2^+ at 1.25 r_e	-1.8	-1.8	5.8	6.5	4.5	8.1	2.4
	H_2^+ at 1.5 r_e	-3.0	-3.0	8.1	9.8	6.6	10.9	4.0
	H_2^+ at 1.75 r_e	-4.0	-4.0	10.2	13.4	9.1	14.3	5.8
	He_2^+ at 1.0 r_e	-1.7	-3.9	9.6	14.5	9.9	15.3	10.9
	He_2^+ at 1.25 r_e	-0.8	-2.2	16.1	22.8	16.5	22.7	17.6
	He_2^+ at 1.5 r_e	-0.2	-1.2	23.1	31.3	23.2	31.0	24.1
	He_2^+ at 1.75 r_e	0.2	-0.8	29.7	39.2	29.2	39.4	29.7

Database	System	CASPT2	CASSCF	tM06-L	tPBE	tPBE0	tτHCTH	MC23
	$(NH_3)_2^+$ at 1.0 r_e	11.1	-4.5	13.2	17.6	12.1	17.8	10.6
	$(NH_3)_2^+$ at 1.25 r_e	11.1	-1.7	17.8	22.1	16.1	21.9	13.7
	$(NH_3)_2^+$ at 1.5 r_e	3.7	2.6	2.9	3.6	3.4	2.8	4.5
	$(NH_3)_2^+$ at 1.75 r_e	5.9	5.1	3.6	5.4	5.4	4.5	5.2
	$(H_2O)_2^+$ at 1.0 r_e	0.9	-24.6	14.9	18.3	7.6	18.2	5.6
	$(H_2O)_2^+$ at 1.25 r_e	1.3	-23.0	21.4	25.5	13.3	24.7	10.3
	$(H_2O)_2^+$ at 1.5 r_e	-4.4	-19.5	2.2	3.8	-2.0	3.4	-3.1
	$(H_2O)_2^+$ at 1.75 r_e	-2.3	-15.6	2.4	3.1	-1.6	2.9	-2.6
ΣTMD-BE4	Cr_2	-4.7	-33.5	-24.8	-11.3	-16.9	-0.6	0.3
	Cu_2	-3.7	-16.5	-1.8	-3.9	-7.0	-4.7	-1.1
	Ag_2	-1.0	-11.4	0.2	-1.8	-4.2	-2.1	1.3
	AgCu	-1.8	-15.6	-1.0	-3.0	-6.1	-3.4	-0.3
ΣTML-BE17	$TiCl_2$–Cl	3.8	6.4	-9.8	-21.2	-14.3	-20.7	-4.9
	VCl–Cl	-0.3	-16.2	-6.5	-10.9	-12.2	-8.5	-0.7
	CrCl	-4.4	-30.3	-2.9	-9.8	-14.9	-2.1	-0.6
	$CrO_3 \rightarrow Cr + 3O$	-8.8	-39.2	-11.7	-3.3	-12.3	0.0	-2.0
	MnCl–Cl	-9.7	-25.6	-10.7	-15.9	-18.3	-7.8	-6.8
	MnCl	1.9	-5.3	15.4	6.4	3.5	-1.4	-2.7
	CuH	-8.1	-26.8	-3.9	-9.0	-13.4	-6.3	-7.0
	ZnH	-3.7	-3.8	-4.4	-3.5	-3.6	-1.7	-8.2
	ZnO	-6.8	-37.7	-10.3	-7.0	-14.7	-5.0	-17.4
	ZnCl–Cl	1.3	-19.8	9.6	2.8	-2.9	6.3	4.3
	Cu–H_2O^+	-6.0	-9.0	-6.2	-4.7	-5.8	-10.7	-2.5

Database	System	CASPT2	CASSCF	tM06-L	tPBE	tPBE0	tτHCTH	MC23
	$Cr–CH_3$	-5.1	-19.4	-2.6	2.6	-2.9	-3.5	5.2
	CrH	0.5	-15.8	-0.5	0.2	-3.8	4.0	7.6
	CrN	-13.4	-33.1	-26.0	-9.7	-15.6	-4.8	-0.2
	MnH	1.0	4.0	13.1	9.3	8.0	3.3	-1.0
	$Mn–CH_3^+$	-6.2	-24.7	-13.2	-8.4	-12.5	-2.2	-4.2
	AgH	-6.2	-23.1	-1.1	-4.0	-8.8	-0.9	-3.8
TM-SS6	CoC_2H_4	2.9	-10.2	-10.4	7.2	2.8	5.1	1.5
	$Fe(H_2O)_6^{2+}$	-14.4	-6.6	22.8	21.0	14.1	8.2	14.4
	$Fe(H_2O)_6^{3+}$	-17.6	-30.6	0.6	15.3	3.8	4.4	3.8
	$FeO(NH_3)_5$	-18.3	-27.7	-7.5	0.7	-6.4	-11.2	-2.7
	Fe^{3+}	8.8	14.7	15.7	-9.2	-3.2	-2.9	-3.5
	Mn^{2+}	8.0	15.0	16.1	-5.0	0.0	-0.6	-2.1

Table S20. Signed error (in kcal/mol) of all KS-DFT functionals tested in this work for each system (non-meta functionals)

Database	System	PBE	PBE0	B1LYP	B3LYP	BLYP	HCTH
HTBH29	V_f H + HCl → H_2 + Cl	-5.17	-2.77	-5.94	-6.53	-8.25	-4.23
	V_r H + HCl → H_2 + Cl	-8.55	-5.01	-1.88	-3.02	-4.86	-4.05
	V_r OH + H_2 → H_2O + H	-8.29	-4.63	-8.20	-8.69	-11.68	-6.56
	V_r CH_3 + H_2 → CH_4 + H	-5.96	-3.35	-5.05	-5.75	-7.65	-4.77
	V_f OH + CH_4 → H_2O + CH_3	-11.37	-4.07	-1.89	-3.88	-8.58	-7.64
	V_r OH + CH_4 → H_2O + CH_3	-11.36	-6.26	-5.34	-6.41	-9.80	-6.96
	V_f H + H_2 → H_2 + H	-5.87	-3.91	-4.80	-5.34	-6.68	-2.72
	V_f OH + NH_3 → H_2O + NH_2	-14.49	-4.69	-2.74	-5.18	-11.86	-9.99
	V_r OH + NH_3 → H_2O + NH_2	-14.28	-5.99	-4.32	-6.29	-11.92	-9.34
	V_f OH + C_2H_6 → H_2O + C_2H_5	-11.53	-3.69	-1.56	-3.62	-8.71	-7.86
	V_r OH + C_2H_6 → H_2O + C_2H_5	-9.94	-4.96	-4.21	-5.17	-8.50	-5.27
	V_f F + H_2 → HF + H	-13.54	-5.54	-4.93	-6.73	-12.26	-10.12
	V_r F + H_2 → HF + H	-9.70	-6.41	-11.05	-11.13	-14.18	-8.34
	V_r O + CH_4 → OH + CH_3	-8.91	-4.32	-2.82	-4.00	-6.83	-7.27
	V_f H + PH_3 → H_2 + PH_2	-4.63	-2.47	-3.33	-3.98	-5.53	-2.84
	V_r H + PH_3 → H_2 + PH_2	-4.73	-2.55	0.57	-0.05	-1.17	1.31
	V_f H + HO → H_2 + O	-7.32	-3.89	-6.26	-6.98	-9.55	-7.70
	V_r H + HO → H_2 + O	-13.70	-6.46	-4.36	-6.17	-10.96	-6.67
	V_f H + H_2S → H_2 + HS	-4.43	-2.13	-3.20	-3.86	-5.51	-2.10
	V_r H + H_2S → H_2 + HS	-6.87	-3.96	0.38	-0.56	-2.06	-0.57
	V_r O + HCl → OH + Cl	-16.51	-6.30	-3.17	-5.34	-13.09	-13.86
	V_f CH_3 + NH_2 → CH_4 + NH	-7.54	-3.10	-0.91	-2.17	-4.81	-5.50

Database	System	PBE	PBE0	B1LYP	B3LYP	BLYP	HCTH
	V_r $CH_3 + NH_2 \rightarrow CH_4 + NH$	-11.26	-5.36	-3.25	-4.79	-8.61	-5.81
	V_f $C_2H_5 + NH_2 \rightarrow C_2H_6 + NH$	-4.95	-0.83	1.51	0.33	-2.03	-2.54
	V_r $C_2H_5 + NH_2 \rightarrow C_2H_6 + NH$	-10.25	-4.01	-1.63	-3.27	-7.26	-4.77
	V_f $NH_2 + C_2H_6 \rightarrow NH_3 + C_2H_5$	-8.86	-2.96	0.13	-1.60	-5.14	-4.87
	V_r $NH_2 + C_2H_6 \rightarrow NH_3 + C_2H_5$	-7.47	-2.92	-0.94	-2.05	-4.87	-2.93
	V_f $NH_2 + CH_4 \rightarrow NH_3 + CH_3$	-10.01	-4.45	-1.50	-3.15	-6.49	-5.97
	V_r $NH_2 + CH_4 \rightarrow NH_3 + CH_3$	-10.09	-5.23	-3.26	-4.47	-7.56	-5.85
MC-BE3	LiO^-	4.76	0.31	-0.74	-0.42	4.75	4.48
	CuCl	-4.88	-7.22	-12.97	-11.19	-11.06	-9.35
	FeCl	3.46	6.06	-4.69	-2.52	-4.94	-5.35
MR-MGN-BE8	SiO (multiplicity = 1)	2.44	-10.84	-10.81	-5.89	1.47	-7.05
	CO	8.66	-4.70	-10.43	-4.85	1.66	-1.97
	ClO	15.31	1.30	-4.42	0.20	8.62	5.75
	$O_3 \rightarrow O_2 + O$	14.20	-9.31	-14.72	-8.98	7.57	0.99
	N_2	14.46	-3.66	-5.50	0.57	11.19	-9.01
	O_2	22.37	3.27	-3.89	2.55	14.06	13.33
	B_2	11.87	6.17	-5.62	-3.04	0.65	10.32
	C_2	7.03	-10.12	-21.12	-16.34	-1.54	-2.62
NHTBH4	V_f $H + FH \rightarrow HF + H$	-14.59	-7.93	-9.54	-10.84	-15.81	-7.59
	V_f $H + ClH \rightarrow HCl + H$	-8.01	-4.31	-4.39	-5.36	-7.94	-3.56
	V_r $H + FCH_3 \rightarrow HF + CH_3$	-16.84	-8.00	-7.79	-9.35	-15.75	-8.26
	V_f $H + F_2 \rightarrow HF + F$	-11.45	-6.07	-8.30	-9.15	-13.36	-7.77

Database	System	PBE	PBE0	B1LYP	B3LYP	BLYP	HCTH
SR-MGM-BE2	NaO	2.50	-4.85	-3.70	-1.07	3.25	4.65
	ZnCl	-2.14	-0.34	-8.63	-7.71	-10.40	-6.42
SR-MGN-BE17	CH_3–CH_3	-0.54	-2.10	-7.54	-5.66	-6.93	-4.67
	CH_3O–CH_3	-3.04	-4.82	-9.93	-7.80	-9.15	-7.27
	Et–H	-4.26	-4.35	-4.08	-2.78	-4.31	-4.55
	Et–CH_3	-2.80	-3.78	-9.29	-7.58	-9.35	-7.56
	Et–OCH_3	-9.07	-10.14	-15.22	-13.28	-15.26	-13.82
	Et–OH	-0.85	-4.59	-9.71	-7.15	-7.02	-5.18
	CH ($^2\Pi$)	0.16	-1.41	-0.55	0.82	0.93	-2.29
	NH	4.58	1.35	2.54	4.09	5.54	-2.09
	OH	1.34	-2.78	-2.72	-0.37	1.08	-2.57
	HCl	-1.73	-3.17	-4.95	-3.15	-3.79	-1.78
	Si_2 (multiplicity = 3)	3.54	-0.69	-5.58	-3.48	-1.84	0.45
	P_2	4.00	-6.04	-5.37	-1.64	4.05	-10.28
	S_2	10.88	2.64	-4.48	-1.01	2.97	2.71
	Cl_2	5.74	-0.35	-7.22	-4.40	-1.86	-0.70
	SC	7.70	-3.79	-10.08	-5.56	0.41	-1.93
	H_2	-4.94	-5.24	-0.72	0.54	-0.23	-1.43
	SH	0.58	-0.65	-0.75	0.73	0.26	-1.40
CH-BE5	C_2H–H	-3.36	-3.55	-2.15	-0.87	-2.49	-5.30
	C_2H_3–H	-5.58	-4.45	-3.46	-2.29	-4.96	-5.56
	$C_2H_4 \rightarrow C_2H_2 + H_2$	3.14	6.25	0.98	1.04	-2.68	-0.10
	C^+–H	-0.13	-1.35	-1.31	0.08	-0.19	-0.37

Database	System	PBE	PBE0	B1LYP	B3LYP	BLYP	HCTH
	tert-butyl–H	-6.76	-5.97	-5.59	-4.55	-6.77	-7.65
DAC-DE5	$Al_2H_6 \rightarrow 2AlH_3$	-0.34	-0.10	-6.05	-5.45	-7.10	-7.05
	$Al_2F_6 \rightarrow 2AlF_3$	-7.01	-3.15	-6.06	-6.40	-11.20	-13.35
	$Al_2Cl_6 \rightarrow 2AlCl_3$	-5.86	-4.00	-11.22	-10.81	-14.26	-14.25
	$Al_2HMe_5 \rightarrow AlHMe_2 + AlMe_3$	-4.50	-3.35	-11.47	-10.88	-13.82	-12.70
	$Al_2Me_6 \rightarrow 2AlMe_3$	-6.00	-4.46	-14.81	-14.12	-17.84	-16.10
G2-BE5	Be_2	7.07	5.09	0.79	1.61	3.14	4.77
	Mg_2	1.44	1.00	-1.31	-0.97	-1.10	0.08
	Ca_2	2.68	1.60	-1.97	-1.36	-1.09	0.71
	Sr_2	1.61	0.99	-2.39	-1.88	-1.96	-0.35
	Ba_2	1.82	0.83	-2.97	-2.33	-2.14	-0.06
HP-BE6	$H_3Ge–GeH_3$	-3.39	-3.01	-6.77	-5.84	-7.88	-9.06
	$Me_3Pb–PbMe_3$	-9.30	-6.82	-12.74	-12.13	-15.91	-15.57
	$Me_2As–AsMe_2$	-4.92	-5.68	-11.72	-10.37	-11.96	-13.45
	HS–SH	1.23	-2.01	-9.45	-7.23	-7.00	-4.63
	Br_2	-2.82	-7.89	-13.92	-11.51	-9.40	-10.83
	MeTe–TeMe	0.45	-3.22	-8.15	-6.42	-5.08	-7.88
IP10	Cl_2	-8.58	-4.49	-6.26	-3.23	-10.31	-4.27
	SH	0.55	-0.01	-1.32	2.68	-0.78	1.73
	PH_2	3.91	4.60	-0.55	2.84	-1.31	7.60
	O_2	3.13	6.90	7.44	10.10	3.75	10.54
	Zn	0.27	-6.87	-3.78	0.72	2.64	2.26
	OH	4.49	0.65	1.23	6.05	4.97	4.50

Database	System	PBE	PBE0	B1LYP	B3LYP	BLYP	HCTH
	Mo	9.56	3.51	-0.99	4.15	5.04	5.19
	Cu	10.02	1.03	2.68	7.32	11.24	5.52
	Cr	11.58	3.93	0.99	6.07	8.55	4.89
	Cl	1.03	0.61	-0.97	3.18	-0.53	3.00
IsoE6	C_3H_4	4.59	3.42	3.50	3.70	4.58	4.37
	C_6NH_7	7.28	5.88	12.77	12.56	14.00	11.68
	$C_{14}H_{20}O$	-1.80	-1.36	-4.91	-4.60	-5.28	-3.40
	$C_{14}H_{12}F_2$	0.44	0.73	-0.25	-0.21	-0.43	0.65
	$C_{12}N_2H_{12}$	-2.88	-2.43	-3.73	-3.64	-4.19	-2.67
	$C_{12}H_{20}$	-4.24	-3.12	-3.71	-3.82	-5.20	-5.93
Lix-AE3	Li_2	-2.38	-2.75	-2.26	-2.06	-2.18	1.84
	Li_4	-2.71	-3.19	-3.83	-3.45	-3.71	0.89
	Li_5	-2.01	-2.65	-4.15	-3.66	-3.92	1.16
MG-SS26	NH	-22.93	-22.14	-23.70	-23.39	-24.41	-15.50
	OH^+	-32.48	-31.40	-32.80	-32.54	-33.81	-22.12
	NF	-23.42	-22.16	-22.78	-22.71	-23.91	-16.21
	O_2	-13.89	-11.90	-12.13	-12.38	-14.16	-7.76
	H_2CC	4.88	6.87	1.26	0.97	0.01	9.22
	C_2H_5CHS	3.86	6.66	5.63	4.69	3.06	6.00
	C_4H_3CHO	2.15	-0.55	-0.30	0.44	2.14	1.60
	$C_4H_3NH_2$	1.88	-0.69	-0.56	0.16	1.78	1.49
	$Me_2C{=}CH_2$	4.15	7.08	5.16	4.06	2.61	6.15
	CH_3CHO	7.49	9.25	8.12	7.24	6.55	7.86

Database	System	PBE	PBE0	B1LYP	B3LYP	BLYP	HCTH
	NH_2CHO	4.95	8.04	7.45	6.15	4.70	4.76
	He	4.80	5.09	17.61	18.46	18.09	12.91
	acetone	-7.28	-8.43	-7.65	-6.84	-6.79	-8.16
	propynal	-7.17	-9.64	-8.14	-7.09	-5.94	-7.63
	pyrimidine	-12.62	-4.53	-3.08	-4.39	-11.34	-12.60
	cyanoformaldehyde	-8.98	-10.13	-8.69	-7.75	-7.59	-9.70
	butadiene	-4.08	-4.81	-3.57	-3.06	-3.15	-5.79
	cyclopropenone	-8.41	-6.34	-5.40	-5.27	-7.55	-7.01
	pyrrole	-1.48	-3.52	-3.47	-2.54	-1.71	-2.89
	CH_2	0.17	1.25	-2.41	-2.23	-3.36	3.39
	NH_2	-8.02	-6.42	-9.10	-9.02	-10.59	-1.39
	SiH_2	4.82	6.00	0.56	0.40	-0.40	7.16
	PH_2	4.28	5.54	0.57	0.22	-0.63	8.36
	Be_2CO ^{3}6–^{1}6	-0.49	-1.81	2.66	1.96	3.70	-8.42
	Be_2CO ^{5}6–^{1}6	-0.43	-1.75	2.75	2.05	3.90	-8.25
	Be_2CO ^{3}5–^{1}5	0.75	-0.28	1.68	1.44	2.48	-4.15
MR-MGM-BE3	CaO	20.60	-0.63	-5.99	1.25	15.30	15.09
	BeO	11.10	-3.99	-4.65	0.44	9.72	2.08
	MgS	-1.43	-7.77	-12.63	-9.79	-6.44	-7.57
MR-MGN-BE4	CN	15.29	-3.47	-8.72	-2.78	9.10	-0.83
	Cl_2–O	11.19	-1.83	-5.75	-1.51	6.17	1.66
	SO	13.79	0.00	-5.40	-0.47	7.35	4.20
	NO	18.62	-0.17	-4.53	1.66	12.93	1.07

Database	System	PBE	PBE0	B1LYP	B3LYP	BLYP	HCTH
NC-CE5	H_2O–H_2O	0.15	0.05	-0.40	-0.34	-0.74	-0.76
	C_2H_4–F_2	1.83	0.18	-0.05	0.19	1.36	1.78
	parallel-displaced CO_2–CO_2	-0.85	-0.97	-1.36	-1.37	-1.70	-0.98
	sandwich C_6H_6–C_6H_6	-2.56	-3.04	-4.18	-4.04	-4.30	-2.32
	parallel-displaced C_6H_6–C_6H_6	-3.11	-3.45	-4.85	-4.70	-5.18	-3.57
NG-IP4	He	-2.77	-3.19	4.00	8.09	5.15	7.88
	Ne	2.19	-2.58	-2.32	3.36	2.39	11.05
	Ar	-0.94	-0.73	-3.24	0.98	-3.47	4.65
	Kr	1.40	2.48	-0.02	3.92	-1.04	4.61
NGD-CE5	He_2	0.04	0.02	-0.05	-0.05	-0.08	0.15
	Ne_2	0.05	0.00	-0.11	-0.12	-0.20	0.30
	Ar_2	-0.19	-0.24	-0.53	-0.51	-0.69	0.18
	He_2	0.08	0.03	-0.06	-0.07	-0.10	0.28
	He_2	0.08	0.02	-0.11	-0.11	-0.15	0.32
PA8	NH_3	-0.86	1.21	-0.51	-0.51	-2.20	1.66
	H_2O	-0.86	1.04	-0.87	-0.81	-2.41	0.99
	C_2H_2	2.41	4.23	2.02	1.96	0.57	5.39
	SiH_4	0.40	-0.02	0.65	0.76	1.50	4.19
	PH_3	-2.74	-0.26	0.37	0.04	-1.70	1.52
	H_2S	0.80	1.50	1.07	1.13	0.74	3.64
	HCl	1.66	1.53	0.37	0.62	0.85	3.68
	H_2	-0.05	0.23	-2.02	-1.73	-2.03	1.80
PB-BE4	BN	13.98	3.79	0.22	3.83	9.66	0.08

Database	System	PBE	PBE0	B1LYP	B3LYP	BLYP	HCTH
	SiO	1.88	-11.52	-11.48	-6.55	0.92	-7.66
	AlCl	-3.64	-5.53	-9.06	-7.31	-7.83	-7.03
	H–P–H	0.47	-0.24	1.37	2.49	1.93	-1.62
PC-ED5	N_2	13.46	3.66	0.76	5.42	8.57	-4.20
	F_2	12.97	-4.66	-7.56	-2.16	9.33	6.87
	Li_2	-3.92	-4.46	-3.51	-3.21	-3.54	-1.71
	KH	-5.23	-3.80	-4.65	-4.13	-6.46	-3.98
	ClF	-1.99	4.80	1.16	0.45	-5.71	0.05
PERI-BH4	C_4H_6 (cyclobutene)	-2.83	1.92	-1.34	-1.86	-6.13	-1.18
	C_6H_8 (*cis*-1,3,5-hexatriene)	-5.44	-2.45	1.42	0.37	-1.55	-1.05
	C_8H_8 (*ortho*-xylylene)	-4.98	-2.22	0.98	0.09	-1.94	-2.98
	C_5H_6 (1,3-cyclopentadiene)	-5.71	-4.10	-0.63	-1.33	-2.24	-5.47
PX-BH3	$4NH_3$	-12.39	-6.57	-1.11	-3.04	-6.65	-2.46
	$4H_2O$	-12.23	-6.99	-2.12	-4.01	-7.14	-4.02
	4HF	-9.84	-5.89	-3.01	-4.38	-6.71	-4.27
SIE4x4	H_2^+ at 1.0 r_e	3.78	2.71	2.47	2.64	3.74	5.94
	H_2^+ at 1.25 r_e	7.27	4.93	4.99	5.37	7.53	8.90
	H_2^+ at 1.5 r_e	10.97	7.18	7.66	8.23	11.63	12.21
	H_2^+ at 1.75 r_e	15.10	9.83	10.71	11.47	16.15	16.17
	He_2^+ at 1.0 r_e	19.08	12.66	17.67	19.12	24.02	19.77
	He_2^+ at 1.25 r_e	28.52	18.67	24.22	26.24	33.95	29.92
	He_2^+ at 1.5 r_e	38.01	25.12	30.84	33.41	43.61	40.27
	He_2^+ at 1.75 r_e	46.51	31.19	36.84	39.90	52.10	49.42

Database	System	PBE	PBE0	B1LYP	B3LYP	BLYP	HCTH
	$(NH_3)_2^+$ at 1.0 r_e	11.73	6.14	5.02	6.60	9.99	8.63
	$(NH_3)_2^+$ at 1.25 r_e	18.40	9.78	10.09	12.01	18.12	16.64
	$(NH_3)_2^+$ at 1.5 r_e	24.68	13.64	14.45	16.77	24.95	23.99
	$(NH_3)_2^+$ at 1.75 r_e	30.01	17.24	18.20	20.85	30.51	29.73
	$(H_2O)_2^+$ at 1.0 r_e	17.81	8.85	8.00	10.22	16.26	14.43
	$(H_2O)_2^+$ at 1.25 r_e	26.61	13.76	14.05	16.80	26.25	24.73
	$(H_2O)_2^+$ at 1.5 r_e	33.86	18.42	18.93	22.15	33.83	33.08
	$(H_2O)_2^+$ at 1.75 r_e	39.25	22.15	22.68	26.25	39.36	38.76
ΣTMD-BE4	Cr_2	-1.82	-29.72	-24.60	-19.64	4.16	3.23
	Cu_2	0.47	-3.45	-4.03	-3.03	-0.65	-2.25
	Ag_2	1.22	-1.52	-2.24	-1.46	0.10	0.78
	AgCu	0.77	-2.57	-3.52	-2.54	-0.66	-1.13
ΣTML-BE17	$TiCl_2$–Cl	8.94	-0.86	-5.94	-2.69	3.16	4.49
	VCl–Cl	16.00	12.40	4.13	6.72	7.70	10.10
	CrCl	-1.10	-4.66	-5.58	-4.30	-2.63	5.34
	$CrO_3 \rightarrow Cr + 3O$	12.45	-20.39	-21.18	-12.80	10.55	2.12
	MnCl–Cl	0.41	-4.44	-6.63	-4.79	-2.50	0.09
	MnCl	10.34	6.53	-5.55	-2.98	-1.23	-3.11
	CuH	-5.26	-10.13	-8.79	-6.97	-4.12	-6.76
	ZnH	0.66	2.30	0.45	0.96	-0.86	-0.13
	ZnO	2.32	-8.82	-13.63	-11.20	-1.19	-7.46
	ZnCl–Cl	0.21	-0.30	-6.26	-4.75	-6.59	-4.41
	Cu–H_2O^+	5.97	1.73	0.77	1.86	4.20	-2.67

Database	System	PBE	PBE0	B1LYP	B3LYP	BLYP	HCTH
	$Cr–CH_3$	14.77	3.94	3.34	5.93	13.27	13.67
	CrH	5.19	1.40	6.67	7.62	10.09	18.21
	CrN	17.95	-18.81	-15.42	-7.44	21.00	0.99
	MnH	13.71	11.91	6.03	7.80	8.33	7.35
	$Mn–CH_3^+$	9.81	-1.44	-2.31	0.54	8.35	16.83
	AgH	1.89	-2.07	-1.26	0.47	2.57	2.16
TM-SS6	CoC_2H_4	17.88	14.81	15.07	15.82	18.01	15.27
	$Fe(H_2O)_6^{2+}$	23.83	14.68	21.90	22.39	31.58	3.20
	$Fe(H_2O)_6^{3+}$	21.40	10.22	13.56	15.90	24.56	5.77
	$FeO(NH_3)_5$	10.49	-0.85	-0.59	2.29	9.82	-4.18
	Fe^{3+}	-32.21	-26.54	-30.33	-30.89	-36.28	-10.97
	Mn^{2+}	-25.25	-20.65	-25.46	-25.70	-30.25	-9.70

Table S21. Signed error (in kcal/mol) of all KS-DFT functionals tested in this work for each system (meta-GGAs)

Database	System	τHCTH	M06-L	M06	MN15-L	MN15	CF22D
HTBH29	V_f H + HCl → H_2 + Cl	-3.68	-2.24	-2.86	1.21	-0.11	-0.28
	V_r H + HCl → H_2 + Cl	-4.55	-6.52	-3.38	0.87	-0.66	-0.65
	V_r OH + H_2 → H_2O + H	-5.39	-6.59	-3.15	-2.85	-1.32	-2.47
	V_r CH_3 + H_2 → CH_4 + H	-3.13	-1.14	-1.42	-2.20	0.10	-0.89
	V_f OH + CH_4 → H_2O + CH_3	-6.58	-2.39	-0.69	1.31	-0.31	-0.88
	V_r OH + CH_4 → H_2O + CH_3	-8.57	-8.87	-3.08	-0.89	-1.76	-2.16
	V_f H + H_2 → H_2 + H	-0.70	-2.83	-0.91	-1.91	0.39	-0.47
	V_f OH + NH_3 → H_2O + NH_2	-8.01	-5.36	-2.32	-0.50	-0.52	-0.74
	V_r OH + NH_3 → H_2O + NH_2	-8.71	-7.03	-2.69	-0.91	-1.92	-2.07
	V_f OH + C_2H_6 → H_2O + C_2H_5	-6.34	-3.01	-0.61	1.17	0.02	-0.70
	V_r OH + C_2H_6 → H_2O + C_2H_5	-6.94	-7.46	-1.64	-0.29	-0.55	-1.43
	V_f F + H_2 → HF + H	-7.71	-6.96	-4.74	0.05	-2.75	-2.88
	V_r F + H_2 → HF + H	-7.35	-9.54	-5.11	-4.81	-3.05	-5.07
	V_r O + CH_4 → OH + CH_3	-7.49	-5.54	-2.00	0.01	-0.17	-0.18
	V_f H + PH_3 → H_2 + PH_2	-0.53	0.20	0.38	0.25	0.93	0.80
	V_r H + PH_3 → H_2 + PH_2	-0.24	-3.44	-0.10	2.88	1.49	1.31
	V_f H + HO → H_2 + O	-4.74	-4.18	-2.39	-3.36	-0.90	-1.44
	V_r H + HO → H_2 + O	-6.10	-5.50	-2.04	0.00	-1.42	-1.77
	V_f H + H_2S → H_2 + HS	-0.48	0.54	0.64	0.58	1.14	1.12
	V_r H + H_2S → H_2 + HS	-1.06	-3.45	0.17	1.33	0.44	0.48
	V_r O + HCl → OH + Cl	-10.00	-10.30	-4.93	-5.30	-1.53	-1.69
	V_f CH_3 + NH_2 → CH_4 + NH	-5.91	-3.89	-2.31	0.91	0.89	0.27

Database	System	τHCTH	M06-L	M06	MN15-L	MN15	CF22D
	V_r $CH_3 + NH_2 \rightarrow CH_4 + NH$	-6.73	-4.03	-2.33	-0.91	-2.03	-1.22
	V_f $C_2H_5 + NH_2 \rightarrow C_2H_6 + NH$	-3.18	-0.96	0.39	2.60	3.15	2.13
	V_r $C_2H_5 + NH_2 \rightarrow C_2H_6 + NH$	-5.38	-3.14	-0.98	0.04	-0.65	0.10
	V_f $NH_2 + C_2H_6 \rightarrow NH_3 + C_2H_5$	-4.73	-0.69	0.22	1.89	0.54	0.04
	V_r $NH_2 + C_2H_6 \rightarrow NH_3 + C_2H_5$	-4.63	-3.47	-0.45	0.85	1.37	0.64
	V_f $NH_2 + CH_4 \rightarrow NH_3 + CH_3$	-6.15	-1.66	-1.27	0.88	-0.91	-1.29
	V_r $NH_2 + CH_4 \rightarrow NH_3 + CH_3$	-7.33	-6.38	-3.19	-0.80	-0.86	-1.14
MC-BE3	LiO^-	-0.13	18.37	-5.29	-0.46	-2.88	-4.66
	CuCl	-2.95	0.51	-6.59	-2.09	-4.42	-4.76
	FeCl	-4.14	2.24	-10.47	5.72	0.59	0.48
MR-MGN-BE8	SiO (multiplicity = 1)	-3.37	-4.65	-2.03	-5.59	0.94	-0.36
	CO	-1.58	-2.17	-1.44	0.77	-0.28	0.69
	ClO	3.95	1.75	-0.58	0.96	1.14	0.83
	$O_3 \rightarrow O_2 + O$	-5.16	-6.21	-9.39	-2.03	-5.24	-6.99
	N_2	-3.02	-4.74	-7.91	0.14	-1.58	-1.75
	O_2	7.40	3.04	-1.01	-0.87	0.95	1.97
	B_2	-0.09	11.07	-2.46	1.06	-4.36	-0.82
	C_2	-7.98	2.79	-6.17	-10.44	-13.06	-16.12
NHTBH4	V_f $H + FH \rightarrow HF + H$	-4.32	-1.25	-0.73	-3.04	-4.61	-5.01
	V_f $H + ClH \rightarrow HCl + H$	-1.74	-0.07	-0.51	-0.39	0.77	0.68
	V_r $H + FCH_3 \rightarrow HF + CH_3$	-9.07	-7.54	-3.08	-4.12	-5.46	-5.13
	V_f $H + F_2 \rightarrow HF + F$	-4.72	-5.41	-4.41	-4.40	-3.08	-3.40
SR-MGM-BE2	NaO	3.02	7.16	3.91	-1.38	1.50	0.05

Database	System	τHCTH	M06-L	M06	MN15-L	MN15	CF22D
	ZnCl	-5.21	-2.14	-10.77	1.40	-2.29	-1.93
SR-MGN-BE17	CH_3–CH_3	-0.97	-0.30	-0.22	-3.94	-0.13	-0.27
	CH_3O–CH_3	-3.66	-5.63	-1.15	-2.88	1.00	-0.55
	Et–H	-3.60	-3.42	-2.18	-3.19	-1.85	-1.11
	Et–CH_3	-3.21	-3.24	-2.02	-4.56	-1.18	-0.78
	Et–OCH_3	-9.65	-11.92	-6.65	-7.44	-3.83	-4.85
	Et–OH	-2.88	-6.02	-1.98	-3.76	0.14	-0.80
	CH ($^2\Pi$)	-1.45	-1.37	-0.74	1.33	-2.62	-0.79
	NH	0.06	-1.86	-2.06	0.96	-2.12	-1.11
	OH	-2.71	-4.81	-2.68	-3.02	-1.08	-0.10
	HCl	-3.26	-1.91	-1.88	0.61	-1.11	-0.13
	Si_2 (multiplicity = 3)	1.26	6.62	5.79	2.73	1.63	2.76
	P_2	-1.96	-1.40	3.16	-3.93	-2.34	-3.14
	S_2	3.28	6.18	2.24	2.25	0.53	1.57
	Cl_2	0.75	1.76	1.64	2.15	0.61	0.48
	SC	-1.57	1.15	-1.85	3.16	0.54	1.10
	H_2	-3.97	-6.03	-2.24	0.44	-1.50	-0.34
	SH	-0.93	-0.68	-0.12	1.03	1.20	1.93
CH-BE5	C_2H–H	-1.61	-7.77	-4.64	-3.48	-2.44	0.64
	C_2H_3–H	-3.91	-6.13	-3.75	-4.68	-1.41	-1.54
	$C_2H_4 \rightarrow C_2H_2 + H_2$	3.31	3.63	0.70	-0.85	0.39	0.80
	C^+–H	-1.52	-1.15	-0.50	1.02	0.13	0.70
	tert-butyl–H	-5.76	-6.98	-4.16	-4.19	-2.66	-1.30

Database	System	τHCTH	M06-L	M06	MN15-L	MN15	CF22D
DAC-DE5	$Al_2H_6 \rightarrow 2AlH_3$	-2.52	0.20	-3.10	1.75	3.24	-1.06
	$Al_2F_6 \rightarrow 2AlF_3$	-5.37	-0.38	-2.62	1.21	2.39	1.26
	$Al_2Cl_6 \rightarrow 2AlCl_3$	-6.67	-2.22	-4.31	-0.56	1.41	-0.87
	$Al_2HMe_5 \rightarrow AlHMe_2 + AlMe_3$	-6.74	-1.13	-3.19	1.20	1.44	-1.92
	$Al_2Me_6 \rightarrow 2AlMe_3$	-8.90	-1.05	-1.95	1.95	1.37	-1.45
G2-BE5	Be_2	3.33	6.34	1.83	0.35	-0.98	3.40
	Mg_2	0.83	0.40	0.97	-0.43	0.57	-0.05
	Ca_2	1.38	1.20	1.47	-0.82	-0.87	-1.22
	Sr_2	0.71	0.37	0.73	-1.29	-1.04	-1.10
	Ba_2	0.63	0.52	0.63	-1.41	-1.70	-1.47
HP-BE6	$H_3Ge–GeH_3$	-0.34	1.28	1.98	-7.48	-3.69	-0.90
	$Me_3Pb–PbMe_3$	-6.21	-7.99	-3.64	-14.27	-7.93	-4.23
	$Me_2As–AsMe_2$	-5.63	-3.53	-1.56	-5.28	-6.16	-3.00
	HS–SH	-2.30	0.25	-0.14	-0.26	-0.82	-0.48
	Br_2	-6.83	-10.12	-10.53	-11.98	-12.82	-9.82
	MeTe–TeMe	-1.34	-0.62	-0.44	-9.06	-8.18	-3.59
IP10	Cl_2	-2.94	-7.36	-4.34	-1.64	0.37	-1.12
	SH	2.32	-1.41	-0.77	-1.20	2.74	-0.20
	PH_2	4.35	1.43	-2.80	4.46	3.16	-1.18
	O_2	9.93	1.84	4.84	2.06	5.50	2.98
	Zn	3.66	-3.85	5.90	-5.35	-2.25	-3.25
	OH	3.74	-3.96	-0.05	-2.62	4.91	3.32
	Mo	1.83	-2.03	-4.52	7.58	2.33	3.55

Database	System	τHCTH	M06-L	M06	MN15-L	MN15	CF22D
	Cu	1.30	1.10	6.33	-1.42	-0.98	-1.02
	Cr	-0.04	1.52	-0.12	-1.06	-5.00	-0.76
	Cl	3.02	-1.58	-1.04	0.06	2.96	1.11
IsoE6	C_3H_4	3.98	2.16	0.73	4.13	2.35	2.35
	C_6NH_7	8.54	9.49	5.61	1.96	0.64	3.18
	$C_{14}H_{20}O$	-2.81	-4.99	-3.15	-3.00	-2.48	-1.35
	$C_{14}H_{12}F_2$	0.20	-1.43	-0.90	-0.34	-0.83	-0.57
	$C_{12}N_2H_{12}$	-3.06	-2.16	-2.40	-0.83	-3.60	-2.48
	$C_{12}H_{20}$	-3.70	-2.87	0.12	-1.36	-1.47	-0.54
Lix-AE3	Li_2	-1.39	0.36	0.05	-0.16	-0.40	1.67
	Li_4	-2.45	-0.52	-1.08	-1.64	-2.16	1.11
	Li_5	-2.86	-0.24	-1.58	-1.24	-1.74	-0.16
MG-SS26	NH	-19.44	-21.04	-16.33	-16.45	-21.42	-17.90
	OH^+	-27.49	-27.23	-21.91	-22.42	-29.80	-28.16
	NF	-19.33	-19.18	-16.00	-14.45	-17.95	-16.15
	O_2	-10.07	-8.46	-6.33	-3.88	-9.97	-8.56
	H_2CC	1.37	9.07	2.54	1.10	1.33	-1.60
	C_2H_5CHS	4.47	4.15	3.60	-0.28	2.03	0.40
	C_4H_3CHO	0.71	1.19	0.42	0.52	-1.07	-0.25
	$C_4H_3NH_2$	0.47	1.39	0.46	0.68	-1.43	-0.35
	$Me_2C{=}CH_2$	3.36	5.72	6.00	1.16	0.71	-0.44
	CH_3CHO	7.22	6.61	4.79	0.98	3.83	1.92
	NH_2CHO	5.19	3.78	4.29	-2.45	4.48	2.04

Database	System	τHCTH	M06-L	M06	MN15-L	MN15	CF22D
	He	13.88	15.55	15.16	27.55	28.54	21.79
	acetone	-7.15	-6.52	-4.56	-0.56	-3.31	-0.49
	propynal	-7.05	-7.23	-5.45	-2.24	-4.29	-2.76
	pyrimidine	-6.35	-9.37	-3.85	0.26	2.49	5.22
	cyanoformaldehyde	-7.88	-8.84	-5.91	-3.34	-4.19	-2.69
	butadiene	-3.18	-4.88	-3.80	-0.07	1.09	2.08
	cyclopropenone	-5.43	-5.18	-3.32	2.54	-0.72	0.76
	pyrrole	-1.67	-1.08	-3.16	2.66	0.09	1.84
	CH_2	-1.09	-2.37	-1.12	-1.33	-2.53	0.55
	NH_2	-5.72	-7.00	-3.12	-5.83	-10.14	-7.16
	SiH_2	1.14	1.50	-3.56	6.17	2.76	-0.54
	PH_2	2.22	1.51	-3.74	8.42	2.70	-0.58
	Be_2CO ^{3}6–^{1}6	-2.85	-4.39	-5.63	-2.63	-6.38	-6.97
	Be_2CO ^{5}6–^{1}6	-2.74	-4.34	-5.34	-2.49	-6.29	-6.89
	Be_2CO ^{3}5–^{1}5	-1.03	-3.96	-4.74	-2.21	-1.28	-2.32
MR-MGM-BE3	CaO	9.56	10.31	-0.75	-5.50	-6.36	-6.39
	BeO	1.29	3.12	0.51	-4.86	1.34	1.67
	MgS	-4.47	-2.79	-4.21	-3.18	-5.72	-8.64
MR-MGN-BE4	CN	-2.23	2.98	-3.52	-2.22	-6.58	-8.03
	Cl_2–O	0.92	-2.55	-3.09	-0.27	1.67	1.19
	SO	3.34	1.09	-1.58	0.51	0.56	0.61
	NO	1.75	-2.12	-4.12	-0.49	0.08	-0.12
NC-CE5	H_2O–H_2O	-0.29	-0.18	-0.15	-0.67	0.05	0.02

Database	System	τHCTH	M06-L	M06	MN15-L	MN15	CF22D
	C_2H_4–F_2	0.39	0.93	-0.04	1.07	0.04	0.21
	parallel-displaced CO_2–CO_2	-1.25	-0.55	-0.86	0.12	-0.23	-0.16
	sandwich C_6H_6–C_6H_6	-2.91	-0.10	-0.81	1.80	0.16	-0.10
	parallel-displaced C_6H_6–C_6H_6	-3.44	-0.15	-0.75	2.32	0.51	0.02
NG-IP4	He	5.01	0.90	3.56	9.86	6.77	3.30
	Ne	3.80	-8.36	2.31	-3.48	2.20	-2.78
	Ar	2.20	0.68	0.14	3.73	1.21	0.23
	Kr	5.05	-4.45	-2.47	1.18	-0.01	2.51
NGD-CE5	He_2	0.013	0.016	0.107	0.006	0.010	0.039
	Ne_2	-0.048	0.078	0.042	-0.008	-0.018	0.045
	Ar_2	-0.349	-0.159	-0.273	0.029	0.081	-0.052
	He_2	0.009	0.004	0.053	-0.001	0.005	0.049
	He_2	0.000	0.012	0.078	0.013	0.036	0.066
PA8	NH_3	1.73	1.87	-0.63	-1.96	-1.00	-2.43
	H_2O	1.53	2.81	1.48	0.16	1.30	-0.90
	C_2H_2	4.50	6.24	3.74	4.43	2.82	2.18
	SiH_4	2.05	-0.97	-0.37	-5.39	-1.85	0.14
	PH_3	0.92	0.32	-1.93	-1.86	-1.65	0.23
	H_2S	2.51	3.40	1.10	-1.10	-0.89	0.08
	HCl	2.50	3.12	1.10	-0.90	-0.11	-0.18
	H_2	0.47	-0.35	3.65	1.44	0.08	1.28
PB-BE4	BN	1.63	7.88	1.33	4.61	5.05	1.44
	SiO	-4.03	-5.31	-2.74	-6.24	0.21	-1.05

Database	System	τHCTH	M06-L	M06	MN15-L	MN15	CF22D
	AlCl	-2.84	0.48	0.14	-0.72	2.36	0.21
	H–P–H	0.11	0.26	1.81	1.69	0.81	1.14
PC-ED5	N_2	0.86	0.81	0.20	5.68	3.97	4.25
	F_2	2.44	-2.30	-5.47	-0.15	-0.38	-1.69
	Li_2	1.15	-1.40	0.71	-3.62	-1.66	2.95
	KH	1.56	5.28	3.39	-2.66	0.84	-0.51
	ClF	1.45	0.61	3.80	4.43	6.06	4.07
PERI-BH4	C_4H_6 (cyclobutene)	-1.02	2.75	1.68	3.25	1.71	1.40
	C_6H_8 (*cis*-1,3,5-hexatriene)	-2.60	-1.35	-0.40	1.07	-0.16	0.04
	C_8H_8 (*ortho*-xylylene)	-2.15	-0.44	0.67	-0.36	-0.40	0.25
	C_5H_6 (1,3-cyclopentadiene)	-2.72	-3.53	-2.76	-4.52	-3.27	-2.38
PX-BH3	$4NH_3$	-6.88	-1.25	-0.31	4.82	0.50	-1.38
	$4H_2O$	-7.29	-0.90	-2.48	6.92	-1.83	-0.24
	4HF	-6.90	0.53	0.84	5.96	-2.45	-1.14
SIE4x4	H_2^+ at 1.0 r_e	4.59	3.94	2.18	1.87	-3.14	0.41
	H_2^+ at 1.25 r_e	7.06	6.77	5.44	4.09	1.50	3.33
	H_2^+ at 1.5 r_e	9.75	9.28	8.62	6.20	6.39	6.09
	H_2^+ at 1.75 r_e	12.99	12.14	12.25	9.40	10.95	9.61
	He_2^+ at 1.0 r_e	14.98	15.00	13.71	-0.59	8.51	8.25
	He_2^+ at 1.25 r_e	22.61	21.89	20.60	7.99	16.25	15.96
	He_2^+ at 1.5 r_e	30.33	29.54	27.45	17.01	23.64	23.01
	He_2^+ at 1.75 r_e	37.47	37.05	33.94	24.86	29.80	28.57
	$(NH_3)_2^+$ at 1.0 r_e	8.82	5.19	2.69	-0.96	3.78	3.71

Database	System	τHCTH	M06-L	M06	MN15-L	MN15	CF22D
	$(NH_3)_2^+$ at 1.25 r_e	13.92	12.03	7.86	6.68	7.88	7.49
	$(NH_3)_2^+$ at 1.5 r_e	18.68	17.65	12.41	12.97	11.35	10.30
	$(NH_3)_2^+$ at 1.75 r_e	22.92	22.44	16.07	17.81	14.03	12.64
	$(H_2O)_2^+$ at 1.0 r_e	12.39	11.69	6.79	5.24	5.96	6.15
	$(H_2O)_2^+$ at 1.25 r_e	18.84	19.90	13.44	13.88	10.56	10.18
	$(H_2O)_2^+$ at 1.5 r_e	24.55	26.15	18.31	20.34	14.22	13.16
	$(H_2O)_2^+$ at 1.75 r_e	29.05	31.08	22.00	25.15	16.84	15.59
ΣTMD-BE4	Cr_2	-3.09	-5.30	-15.90	-17.30	-17.12	-26.42
	Cu_2	2.05	1.89	-0.23	-0.69	-1.22	-1.61
	Ag_2	3.68	1.85	1.61	1.35	1.32	0.60
	AgCu	2.94	1.67	0.32	0.33	0.32	-0.32
ΣTML-BE17	$TiCl_2$–Cl	6.62	12.90	8.99	8.69	-0.33	-0.26
	VCl–Cl	7.83	15.94	7.80	15.67	12.24	15.11
	CrCl	2.63	7.46	-0.17	5.88	3.86	0.74
	$CrO_3 \rightarrow Cr + 3O$	-3.12	-0.71	-15.08	-10.00	-15.26	-20.59
	MnCl–Cl	5.50	10.25	5.11	2.55	3.52	-1.27
	MnCl	-7.87	2.00	-10.25	4.66	2.60	2.69
	CuH	-4.05	-3.96	-7.26	-4.95	-7.71	-6.79
	ZnH	-1.42	-1.63	-6.49	3.65	0.67	1.32
	ZnO	-9.87	-8.99	-20.78	-11.43	-10.27	-9.78
	ZnCl–Cl	2.18	6.54	2.28	3.00	2.97	1.83
	Cu–H_2O^+	2.11	6.58	3.62	0.48	3.04	1.92
	Cr–CH_3	11.82	14.95	4.60	3.23	2.82	3.95

Database	System	τHCTH	M06-L	M06	MN15-L	MN15	CF22D
	CrH	10.26	10.98	4.14	10.43	8.18	6.17
	CrN	-1.11	0.35	-16.48	-7.35	-9.41	-18.38
	MnH	-0.43	5.56	-6.01	8.32	7.17	7.69
	$Mn–CH_3^+$	10.74	8.90	0.87	0.25	4.42	-0.46
	AgH	3.90	0.54	-0.59	2.15	2.03	1.77
TM-SS6	CoC_2H_4	16.42	11.63	17.35	7.65	29.02	24.76
	$Fe(H_2O)_6^{2+}$	13.69	14.50	-4.05	-14.22	27.36	18.13
	$Fe(H_2O)_6^{3+}$	12.91	3.33	-1.36	-14.24	19.92	15.88
	$FeO(NH_3)_5$	2.70	-1.62	-9.46	-16.70	0.41	-0.03
	Fe^{3+}	-25.70	-12.76	-0.93	29.49	-19.57	-19.09
	Mn^{2+}	-21.23	-12.01	-1.07	21.40	-14.57	-13.75

S11. Sample Input Files

S11.1. Sample Input File for CASSCF Calculations

The following *OpenMolcas* input file performs a CASSCF calculation of the F_2 molecule at the equilibrium bond distance (1.41193 Å). The coordinates of the F_2 molecule are stored in a file named "`F2_eq.xyz`". One needs to put the basis set file "`JUN-CC-PVTZ`" in the basis library under the *OpenMolcas* installation directory. Both files are available in the Zenodo repository,[113] as indicated in the Data Availability section of the paper. At the end of the calculation, the RunFile and JobIph files are saved to the current working directory. These two files are necessary for further post-CASSCF calculations.

```
&GATEWAY
COOR = F2_eq.xyz
BASI = jun-cc-pVTZ
GROU = C1
RICD

&SEWARD
Grid Input
Grid = Ultrafine
End of Grid Input

&RASSCF
INAC = 4
RAS2 = 6
NACT = 10 0 0
CIRO = 1 1 1
SPIN = 1
CHAR = 0

>> COPY $Project.JobIph $CurrDir/$Project.JobIph
>> COPY $Project.RunFile $CurrDir/$Project.RunFile
```

S11.2. Sample Input File for CASPT2 Calculations

The following *OpenMolcas* input file performs a CASPT2 calculation of the F_2 molecule at the equilibrium bond distance using the CASSCF reference wave function from the RunFile and JobIph files generated by the previous input file.

```
&GATEWAY
COOR = F2_eq.xyz
BASI = jun-cc-pVTZ
GROU = C1
RICD

&SEWARD
Grid Input
Grid = Ultrafine
End of Grid Input

>>> COPY $CurrDir/$Project.JobIph $Project.JobIph
>>> COPY $CurrDir/$Project.RunFile $Project.RunFile

&CASPT2
IPEA=0.25
IMAG=0.25
```

S11.3. Sample Input File for MC-PDFT Calculations

The following *OpenMolcas* input file performs several MC-PDFT calculations of the F_2 molecule at equilibrium bond distance using the CASSCF reference wave function from the RunFile and JobIph files generated by the previous input file.

```
&GATEWAY
COOR = F2_eq.xyz
BASI = jun-cc-pVTZ
GROU = C1
RICD

&SEWARD
Grid Input
Grid = Ultrafine
End of Grid Input

>>> COPY $CurrDir/$Project.JobIph $Project.JobIph
>>> COPY $CurrDir/$Project.RunFile $Project.RunFile

&MCPDFT
 KSDFT=t:MGGA_X_tau_HCTH

&MCPDFT
 KSDFT=t:GGA_C_tau_HCTH

&MCPDFT
 KSDFT=t:M06L

&MCPDFT
 KSDFT=t:PBE
```

From the last two `&MCPDFT` sections, one can directly obtain the energy of tM06-L and tPBE. By adding the classical energy, the tτ-HCTH exchange energy from the first `&MCPDFT` section, and the tτ-HCTH correlation energy from the second `&MCPDFT` section, one can obtain the total energy of tτ-HCTH. One can combine 0.75 times the tPBE energy with 0.25 times the wave function energy to obtain the tPBE0 energy.

S11.4. Sample Input File for MC23 Calculations

The following *OpenMolcas* input file performs an MC-PDFT calculation using the MC23 functional of the F_2 molecule at the equilibrium bond distance using the CASSCF reference wave function from the RunFile and JobIph files generated by the previous input file.

```
&GATEWAY
COOR = F2_eq.xyz
BASI = jun-cc-pVTZ
GROU = C1
RICD

&SEWARD
Grid Input
Grid = Ultrafine
End of Grid Input

>>> COPY $CurrDir/$Project.JobIph $Project.JobIph
>>> COPY $CurrDir/$Project.RunFile $Project.RunFile
>>> COPY /path_to_param_files/rtM06-L.expm EXPM

&MCPDFT
 KSDF = t:M06L
 EXPM = EXPM
 LAMB = 0.2952
```

This calculation requires a parameter file of the optimized functional parameters. Replace "`/path_to_param_files/rtM06-L.expm`" with the actual location of your parameter file. The content of the parameter file is given below. Note that the parameter file should contain only four lines, where the third and fourth lines correspond to the parameters of the exchange and correlation part of the functional, respectively.

```
2

18 27

3.352197e+00 6.332929e-01 -9.469553e-01 2.030835e-01 2.503819e+00
8.085354e-01 -3.619144e+00 -5.572321e-01 -4.506606e+00 9.614774e-01
6.977048e+00 -1.309337e+00 -2.426371e+00 -7.896540e-03 1.364510e-02 -
1.714252e-06 -4.698672e-05 0.0

0.06 0.0031 0.00515088 0.00304966 2.427648e+00 3.707473e+00 -
7.943377e+00 -2.521466e+00 2.658691e+00 2.932276e+00 -8.832841e-01 -
1.895247e+00 -2.899644e+00 -5.068570e-01 -2.712838e+00 9.416102e-02 -
3.485860e-03 -5.811240e-04 6.668814e-04 0.0 2.669169e-01 -7.563289e-02
7.036292e-02 3.493904e-04 6.360837e-04 0.0 1e-10
```

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