Supporting Information for:

Screened-exchange density functionals with broad accuracy for chemistry and solid-state physics

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This supporting information consists of a total of 16 pages, and it is organized as follows:

- Section I presents the databases that compose BC345.
- Section II presents details of the calculation and results.
- References

I. Databases

A brief introduction to the databases and their subsets used in this work are presented below with the corresponding references.

Primary Databases. 22 databases from previous work have been used in the current training function, namely:

- MGAE109/11:[1,2] 109 main group atomization energies, for which we used the MG3S basis set.[3]
- SRMBE12:[4] 12 single-reference metal bond energies, for which we used the def2-TZVP basis set.[5,6]
- MRBE10:[4] 10 multi-reference bond energies, for which we used the def2-TZVP basis set.[5,6]
- IsoL6:[7] 6 isomerization energies of large organic molecules, for which we used the MG3SXP basis set.[8]
- IP21: Our previous ionization potential database (IP13/03[1,3,9,10]) was recently updated[11] by adding seven IPs of transition metal atoms and one IP of a transition metal containing molecule (FeC[12]). Calculations on molecules involve separately optimized geometries from neutral and cations. The MG3S basis set[3] is used for the main group atoms and molecules, the cc-pVTZ-DK basis set of Peterson et al.[13] was used for the seven metal atoms, while for the calculations of the IP of FeC we used the SDD+2fg[14] basis for Fe and the def2-QZVPP basis[15] for C. The scalar relativistic effects are included in the calculations of the seven transition metal atomic IPs by using the Douglas-Kroll-Hess

(DKH) second-order scalar relativistic Hamiltonian,[16-18] while they are included in the calculations of FeC within the SDD relativistic effective core potential.[14]

- EA13/03:[1,3,9,10] 13 electron affinities, for which we used the MG3S basis set.[3]
- PA8:[19] 8 proton affinities, for which we used the MG3S basis set.[3]
- ABDE4/05[1,20,21] and ABDEL8:[21,22] 4 and 8 alkyl bond dissociation reaction energies, for which we used the MG3S basis set.[3]
- HC7/11:[22] 7 hydrocarbons, for which we used the 6-311+G(2df,2p) basis set.[23]
- πTC13:[10,19,20] 13 π system thermochemistry, for which we used the MG3S basis set.[3]
- HTBH38/08[1,24,25] and NHTBH38/08:[1,24,25] 38 hydrogen-transfer and 38 non-hydrogen-transfer barrier heights, for which we used the MG3S basis set.[3]
- NCCE31/05:[9,26-28] 31 noncovalent complexation energies, for which we used the MG3S basis set.[3]
- DC9/12:[29,30] 9 difficult cases, for which we used the MG3S basis set.[3]
- AE17:[29,31] The absolute energy of the first 17 atoms. We used the cc-pwCV5Z basis set[32] for H, He, and atoms from Be to Ne and from Al to Ar, while we used the cc-pCVQZ basis set[33] for Li, Be, Na and Mg atoms.
- SSLC18:[34,35] 18 equilibrium lattice constants of solids, for which we used the m-6-311G* basis set.[36]
- DG6:[30] 6 geometries of diatomic molecules, for which we used the 6-311+G(2df,2p) basis set.[23]
- SLC34:[37] 34 semiconductors lattice constants, for which we used the m-6-311G* basis set.[36]
- SBG31:[37] 31 semiconductors band gaps, for which we used the m-6-311G* basis set.[36]
- SSCE8:[35] 8 solid-state cohesive energies, for which we used the m-6-311G* basis set.[36]
- MGBL20:[30] 20 main group bond length, for which we used the 6-311+G(2df,2p) basis set.[23]

Subsets. Some of the primary databases described above are composed of subdatabases, each one representing a particular class of compound or a class of properties (e.g., proton affinities of Schiff basis or barrier heights of nucleophilic substitutions). The performance on these subsets may be of interest to specialists who are considering the subsets that already have a presence in the literature. The subsets are:

AE6:[38] six atomization energies (from MGAE109/11).

SB1AE97:[4] small-B1 atomization energies (from MGAE109/11).

LB1AE12:[4] large-B1 atomization energies (from MGAE109/11).

TMBE15:[37] 15 transition metals bond energies (from SRMBE13 and MRBE10).

MBE18:[37] 18 metals bond energies (from SRMBE13 and MRBE10).

IP13/03:[1,3,9,10] 13 ionization potentials of main group atoms and molecules (from IP21).

IPM8:[11] 8 ionization potentials of metal atoms and metal containing molecule (from IP21).

πIE3/06:[19,39] three π systems isomerization energies (from πTC13).

PA-CP5/06:[19] five proton affinities of conjugated polyenes (from πTC13).

PA-SB5/06:[19] five proton affinities of Schiff basis (from πTC13).

HATBH12/08:[25] 12 barrier heights of heavy-atom transfer (from NHTBH38/08).

NSBH16/08:[25] 16 barrier heights of nucleophilic substitution (from NHTBH38/08).

UABH10/08:[25] ten barrier heights of unimolecular and association reactions (from NHTBH38/08).

DBH24/08:[40] 24 diverse barrier heights (from HTBH38/08 and NHTBH38/08)

HB6/04:[26] six hydrogen bonding complexes (from NCCE31/05).

CT7/04:[26] seven charge-transfer complexes (from NCCE31/05).

DI6/04:[26] six dipole interaction complexes (from NCCE31/05).

WI7/05:[9,26] seven weak interactions complexation energies (from NCCE31/05).

PPS5/05:[9,26-28] five π-π stackings energies (from NCCE31/05).

Performances of N12-SX and MN12-SX and all other considered functionals for the subsets are reported in the next section of this supporting information.

II. Details of the Calculations and Results

For the calculation of the mean unsigned error per bond (MUE_{PB}) of the atomization energies databases we used the following formula:

$$\mathrm{MUE_{PB}} = \frac{1}{n_{\mathrm{bond}}} \sum_{i=1}^{n_{\mathrm{molec}}} \frac{\left| AE_i - AE_i^{\mathrm{Ref}} \right|}{n_{\mathrm{molec}}} \qquad \text{(S1)}$$

where n_{molec} is the total number of molecules in the database, AE_i and AE_i^{Ref} are respectively the calculated and the reference atomization energy for molecule i, and n_{bond} is the average number of bonds per molecule in the database, namely:

$$\begin{aligned} n_{\mathrm{bond}} &= 4.71 \text{ for MGAE109/11,} \\ n_{\mathrm{bond}} &= 5.10 \text{ for SB1AE97,} \\ n_{\mathrm{bond}} &= 1.33 \text{ for LB1AE12,} \\ n_{\mathrm{bond}} &= 4.67 \text{ for AE6,} \\ n_{\mathrm{bond}} &= 9.22 \text{ for DC9/12.} \end{aligned} \qquad \text{(S2)}$$

The global mean unsigned error for BC345 is calculated from the databases as:

$$\begin{aligned}\mathrm{MUE(BC345)} = 1/n_{\mathrm{tot}}\{&109*\mathrm{MUE_{PB}(MGAE109/11)} + 13*\mathrm{MUE(SRMBE13)} + \\ &10*\mathrm{MUE(MRBE10)} + 6*\mathrm{MUE(IsoL6/11)} + \\ &21*\mathrm{MUE(IP21)} + 13*\mathrm{MUE(EA13/03)} + 8*\mathrm{MUE(PA8/06)} + \\ &4*\mathrm{MUE(ABDE4/05)} + 8*\mathrm{MUE(ABDEL8)} + 7*\mathrm{MUE(HC7/11)} + \\ &13*\mathrm{MUE(\pi TC13)} + 38*\mathrm{MUE(HTBH38/08)} + 38*\mathrm{MUE(NHTBH38/08)} + \\ &31*\mathrm{MUE(NCCE31/05)} + 9*\mathrm{MUE_{PB}(DC9/12)} + 17*\mathrm{MUE(AE17)}\} \qquad \text{(S3)}\end{aligned}$$

where n_{tot} is the total number of elements in the database (which is n_{tot}=345). The mean unsigned error for BC328xAE are calculated using the same formula, and excluding MUE(AE17) (with n_{tot}=328).

The weights used for the calculation of the training function (eq 11 in the main text) are reported in Table S1 for N12-SX and in Table S2 for MN12-SX.

Table S1. Weights (h_1 to h_{16} in [cal/mol]$^{-1}$, h_{17} and h_{18} in Å^{-1}) used in the training function of the N12-SX functional.

h_1	h_2	h_3	h_4	h_5	h_6	h_7	h_8	h_9
60	2	2	2	4	2	1	10	2
h_{10}	h_{11}	h_{12}	h_{13}	h_{14}	h_{15}	h_{16}	h_{17}	h_{18}
1	5	10	30	100	1	2	30	30

Table S2. Weights (h_1 to h_{16} in [cal/mol]$^{-1}$, h_{17} and h_{18} in Å^{-1}) used in the training function of the MN12-SX functional.

h_1	h_2	h_3	h_4	h_5	h_6	h_7	h_8	h_9
120	3	3	2	5	4	1	20	4
h_{10}	h_{11}	h_{12}	h_{13}	h_{14}	h_{15}	h_{16}	h_{17}	h_{18}
1	5	20	60	100	1	2	6	4

Detailed performances of N12-SX for BC345 and its subsets are presented in Table S3, while those of MN12-SX are presented in Table S4; results for the significant subsets are reported for all considered functionals in Table S5.

Table S3. Mean Unsigned Errors, Mean Signed Errors, Largest Absolute Error, and Smallest Absolute Error (all in kcal/mol) of the N12-SX Functional for Subsets of BC345.

N12-SX	MUE	MSE	Largest |ε|	Smallest |ε|
MGAE109/11	0.76	-0.02	15.30	0.06
SRMBE13	3.22	2.75	9.63	0.30
MRBE10	8.47	-7.33	33.26	0.66
IsoL6/11	1.78	-0.67	3.86	0.12
IP21	4.06	0.72	12.64	0.36
EA13/03	2.99	-2.97	7.28	0.15
PA8/06	1.97	1.97	4.46	0.55
ABDE4	3.73	-2.57	6.78	0.76
ABDEL8	6.08	-6.08	18.28	1.19
HC7/11	11.05	5.81	23.24	4.45
πTC13	7.64	7.64	14.12	3.43
HTBH38/08	3.71	-3.60	6.79	0.15
NHTBH38/08	2.83	-1.60	9.84	0.07
NCCE31/05	0.74	-0.05	2.96	0.02
DC9/12	1.19	0.58	38.74	0.36
AE17	10.22	-5.98	25.78	0.24

Table S4. Mean Unsigned Errors, Mean Signed Errors, Largest Absolute Error, and Smallest Absolute Error (all in kcal/mol) of the MN12-SX Functional for Subsets of BC345.

MN12-SX	MUE	MSE	Largest |ε|	Smallest |ε|
MGAE109/11	0.52	-0.08	10.98	0.03
SRMBE13	4.03	3.32	12.73	0.12
MRBE10	10.49	-7.41	40.92	0.26
IsoL6/11	1.21	-0.81	2.55	0.13
IP21	5.11	1.49	15.80	0.27
EA13/03	1.62	-0.16	5.11	0.67
PA8/06	1.16	-0.58	2.30	0.18
ABDE4	3.42	-1.13	5.44	1.27
ABDEL8	4.03	-4.03	16.55	0.24
HC7/11	2.21	-0.25	4.18	0.48
πTC13	3.57	3.32	8.18	0.54
HTBH38/08	0.95	-0.04	3.93	0.03
NHTBH38/08	1.35	-0.61	5.47	0.07
NCCE31/05	0.30	-0.07	1.28	0.00
DC9/12	1.20	0.69	32.28	0.65
AE17	4.52	-2.12	25.87	0.60

Table S5. Mean Unsigned Errors of the N12-SX and MN12-SX Functionals Compared to Those of Other Functionals for Subsets of the BC345 Database

	HSE	SOGGA11-X	M11	N12	MN12-L	N12-SX	MN12-SX
AE6/11[a]	0.94	0.72	0.40	0.91	0.65	0.79	0.56
SB1AE97[a]	0.82	0.65	0.45	1.12	0.63	0.68	0.47
LB1AE12[a]	2.81	3.28	2.58	6.03	2.72	3.43	2.22
TMBE15	14.99	22.17	26.76	5.47	5.26	4.76	6.88
MBE18	12.81	18.79	22.49	5.12	4.79	4.19	6.23
IP13/03	3.23	3.20	3.64	3.14	2.71	3.06	3.17
IPM8	5.27	4.48	13.01	4.04	4.73	5.67	8.27
πIE3/06	5.91	3.86	1.36	9.14	7.50	6.03	5.75
PA-CP5/06	5.89	7.28	1.23	7.63	4.14	7.46	1.99
PA-SB5/06	6.70	6.21	3.78	9.28	5.19	9.44	2.98
HATBH12/08	6.69	1.86	1.56	12.02	3.88	3.65	1.93
NSBH16/08	2.55	0.54	1.11	5.66	1.41	2.21	0.96
UABH10/08	2.05	1.33	1.20	2.59	1.59	2.83	1.29
DBH24/08	3.77	1.29	1.26	6.43	1.87	3.13	1.25
HB6/04	0.48	0.24	0.37	0.49	0.73	0.60	0.44
CT7/04	1.31	0.21	0.30	1.87	0.70	0.96	0.40
DI6/04	0.34	0.54	0.33	0.85	0.42	0.36	0.34
WI7/05	0.13	0.42	0.09	0.42	0.18	0.25	0.13
PPS5/05	1.65	2.07	0.22	3.25	0.27	1.75	0.19

[a]Errors for AE6, SB1AE97, and LB1AE12, are reported on a per bond basis using eqs S1 and S2, so they are effectively mean unsigned errors in bond dissociation energies.

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