

Performance of meta-GGA Functionals on General Main Group Thermochemistry, Kinetics, and Noncovalent Interactions

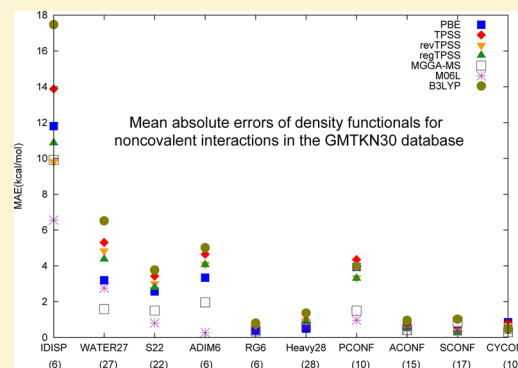
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S Supporting Information

ABSTRACT: Among the computationally efficient semilocal density functionals for the exchange–correlation energy, meta-generalized-gradient approximations (meta-GGAs) are potentially the most accurate. Here, we assess the performance of three new meta-GGAs (revised Tao–Perdew–Staroverov–Scuseria or revTPSS, regularized revTPSS or regTPSS, and meta-GGA made simple or MGGA_MS), within and beyond their “comfort zones,” on Grimme’s big test set of main-group molecular energetics (thermochemistry, kinetics, and noncovalent interactions). We compare them against the standard Perdew–Burke–Ernzerhof (PBE) GGA, TPSS, and Minnesota M06L meta-GGAs, and Becke–3–Lee–Yang–Parr (B3LYP) hybrid of GGA with exact exchange. The overall performance of these three new meta-GGA functionals is similar. However, dramatic differences occur for different test sets. For example, M06L and MGGA_MS perform best for the test sets that contain noncovalent interactions. For the 14 Diels–Alder reaction energies in the “difficult” DARC subset, the mean absolute error ranges from 3 kcal mol^{−1} (MGGA_MS) to 15 kcal mol^{−1} (B3LYP), while for some other reaction subsets the order of accuracy is reversed; more generally, the tested new semilocal functionals outperform the standard B3LYP for ring reactions. Some overall improvement is found from long-range dispersion corrections for revTPSS and regTPSS but not for MGGA_MS. Formal and universality criteria for the functionals are also discussed.



I. INTRODUCTION

Kohn–Sham (KS) density functional theory (DFT)^{1,2} is one of the most widely used electronic structure theories for atoms, molecules, and solids in areas of physics, chemistry, and molecular biology. It simplifies a many-body wave function problem to an auxiliary noninteracting one-electron problem, delivering in principle the exact ground-state electron density and energy.¹ The performance of a KS-DFT calculation depends on the quality of the approximation to its exchange–correlation energy. Semilocal approximations^{3–7} employ only local and semilocal information and so are efficient for large molecules or unit cells. They can be reasonably accurate for the near-equilibrium and compressed ground-state properties of “ordinary” matter, where neither strong correlation nor long-range van der Waals interaction is important. They can also serve as a base for the computationally more-expensive fully nonlocal approximations needed to describe strongly correlated systems⁸ and soft matter.⁹

All semilocal functionals are computationally efficient. Among them, meta-generalized gradient approximations (meta-GGAs) are of special interest because they can achieve high simultaneous accuracy for atoms, molecules, solids, and surfaces at equilibrium. Meta-GGA^{6,7,10,11} is the highest rung at the semilocal level of Jacob’s ladder of DFT,¹² which includes the kinetic energy density as an input in addition to the

electron density and its density gradient. The local density approximation (LDA)^{1,3–5,13} only depends on the electron density, while the generalized gradient approximations (GGA)^{4,14–18} add the local electron density gradient. The inclusion of the kinetic energy density enables meta-GGAs to distinguish single-orbital regions from orbital overlap regions, allowing one to predict accurate properties for molecules, surfaces, and solids.¹⁹ This was highlighted in the study of the CO molecule adsorbed on transition-metal surfaces,¹⁹ where the revised Tao–Perdew–Staroverov–Scuseria (revTPSS) meta-GGA,⁷ unlike other tested LDA and GGAs, predicts at the same time the accurate adsorption energy of the molecule to the surface and the lattice constant and surface energy of the metal substrate.

With the help of the kinetic energy density, the revTPSS⁷ was constructed to recover the total energies of two paradigm densities—the uniform electron gas for condensed matter physics and the hydrogen atom for quantum chemistry. Moreover, revTPSS restores the second-order gradient expansion of a slowly varying density for exchange over a wide range of densities as the PBEsol¹⁵ GGA does and thus improves the lattice constants of solids over its predecessor

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TPSS.⁶ The regularized revTPSS (denoted as regTPSS)²⁰ was designed to remove the order-of-limits anomaly^{20,21} in the revTPSS exchange functional. The regTPSS gives atomization energies and lattice constants with an accuracy similar to that of revTPSS. The recently proposed meta-GGA made simple (MGGA_MS) results from the study of the effect of the dependence of the meta-GGA¹¹ on kinetic energy density. The MGGA_MS simplifies the construction of the exchange functional as an interpolation between the single-orbital regime (e.g., the hydrogen atom) and the slowly varying density regime. For the correlation part of regTPSS and MGGA_MS, a variant of the PBE correlation^{11,20} is used. In terms of atomization energies, surface energies, and lattice constants, the overall performance of MGGA_MS is comparable to that of revTPSS. An interesting feature of MGGA_MS for users is that it yields excellent binding energies for the W6 water clusters²²—better than revTPSS, TPSS, and even PBE¹¹—and thus clearly demonstrates its excellent performance for hydrogen bonds. In this study, we will further show that MGGA_MS gives a quite good description for the noncovalent bonds with a systematic improvement over PBE, TPSS, revTPSS, and regTPSS.

Within the comfort zones, i.e., for “ordinary matter”, these newly developed meta-GGAs provide very accurate ground-state properties for molecules, surfaces, and solids.^{6,7,11,20} However, it is known that approximate DFT functionals might perform well for a specific property (e.g., for the frequently used enthalpies of formation) and fail badly for other properties (e.g., for reaction barriers). For this study, we chose the GMTKN30 database^{23,24} (1218 single point energies and 841 relative energy values) to identify further comfort zones of these new meta-GGAs. We also present new results that are outside of these comfort zones. Notice that these functionals were constructed by using exact constraints, and no fitting to large molecular test sets was included in the design procedure.

GMTKN30 is a large main-group molecular energy test set composed of 30 smaller test sets and covers a large cross section of chemically relevant properties and, thus, can give a comprehensive main-group molecular evaluation and assessment for a tested functional. Moreover, since all the popular density functionals have been tested by using GMTKN30, these results can be used to compare with those of the new meta-GGAs results. The GMTKN30 database involves decomposition energies, atomization energies, adiabatic ionization potentials, electron affinities, proton affinities, self-interaction-error related energies, reaction energy barrier heights, reaction energies, radical stabilization energies, isomerization energies, difficult systems for semilocal approximations, intramolecular dispersion energies, intermolecular noncovalent interaction energies, and conformational energies. The detailed description of the database can be found in refs 23 and 24. The reference geometries and energies are available from the GMTKN30 Web site.²⁵ The reference energies are obtained from high-level calculations like W1, W4, CCSD(T)/CBS, and/or from experiments.

The computational details are explained in section II. In section III, we show results and discussions, where details of mean absolute errors of different functionals from the reference data for each individual subset are given and discussed. We also assess in section III the performances of different functionals with and without long-range dispersion corrections through the pairwise potential approach.

II. COMPUTATION DETAILS

We used the Gaussian 03 code²⁶ with new subroutines for revTPSS and MGGA_MS, which were implemented by us self-consistently. For nonself-consistent regTPSS calculations, we used the self-consistent (SCF) revTPSS electron densities. Earlier results show that even LSDA electron densities can be successfully used for tests of the performance of various functionals, so it is expected that revTPSS electron densities give an excellent starting point for regTPSS calculations.

The basis set convergence was tested for the MB08_165, DARC, and WATER27 subsets. In Table 1, comparisons

Table 1. The Mean Absolute Errors (kcal mol^{−1}) of the Basis Sets Compared to the Basis-Set Limit for Three Smaller Test Sets Using the revTPSS Functional

subset	aug-cc-pVDZ	6311+G(3df,2p)	aug-cc-pVTZ
MB08-165	1.8	1.2	0.3
DARC	4.7	1.0	0.1
WATER27	3.4	3.6	0.9

between results from aug-cc-pVDZ, 6-311+G(3df,2p), aug-cc-pVTZ, and aug-cc-pVQZ basis sets show that the aug-cc-pVTZ basis set gives reasonable results with considerable efficiency. This latter TZ basis set is used for most of our calculations. Our results are in agreement with the conclusion in the literature²⁷ that the Kohn–Sham limit of semilocal functionals is almost reached with the (aug-)def2-TZVPP basis set; thus the expensive QZ basis sets are not necessary to test these functionals. We used “fine grid” (a pruned grid with 75 radial shells and 302 angular points per shell) for all calculations.

To account for scalar relativistic effects, Heavy28 and RG6 energies were calculated using the ECP-121G effective core potentials. The alkaline and alkaline-cation-benzene complexes were calculated using the 6-311++G basis set.

We have tested the functionals without but also with long-range dispersion corrections. Since geometries were fixed for all calculations, we extracted the D3 dispersion energy corrections from the published TPSS-D3 results²⁵ and used these corrections to correct the new meta-GGA results. The results of LSDA, PBE, M06L, and B3LYP are from the GMTKN30 Web site.²⁵

III. RESULTS AND DISCUSSION

1. The Mean Absolute Errors. The mean absolute errors (MAEs) of the three new meta-GGA functionals—revTPSS, regTPSS, and MGGA-MS—for the 30 subsets of the GMTKN30 test set are compared with those of TPSS, PBE,¹⁴ M06L,¹⁰ and B3LYP.^{28,29} The latter two functionals are popular in molecular electronic structure calculations, and this comparison is helpful for us to assess the overall performance of the new meta-GGAs. For the discussion, we group the 30 subsets into three groups as suggested in the ref 27. The first group (or section) contains eight subsets related to miscellaneous basic properties like decomposition energies, atomization energies, ionization potentials, electron affinities, proton affinities, self-interaction error related energies, and reaction energy barrier heights. This group or section was called basic properties in ref 27. The second group contains 12 subsets related to chemical reaction energies like isomerizations, Diels–Alder reactions, ozonolyses, and reactions involving alkaline metals. The third group (the remaining 10 subsets) is related to noncovalent interactions and contains

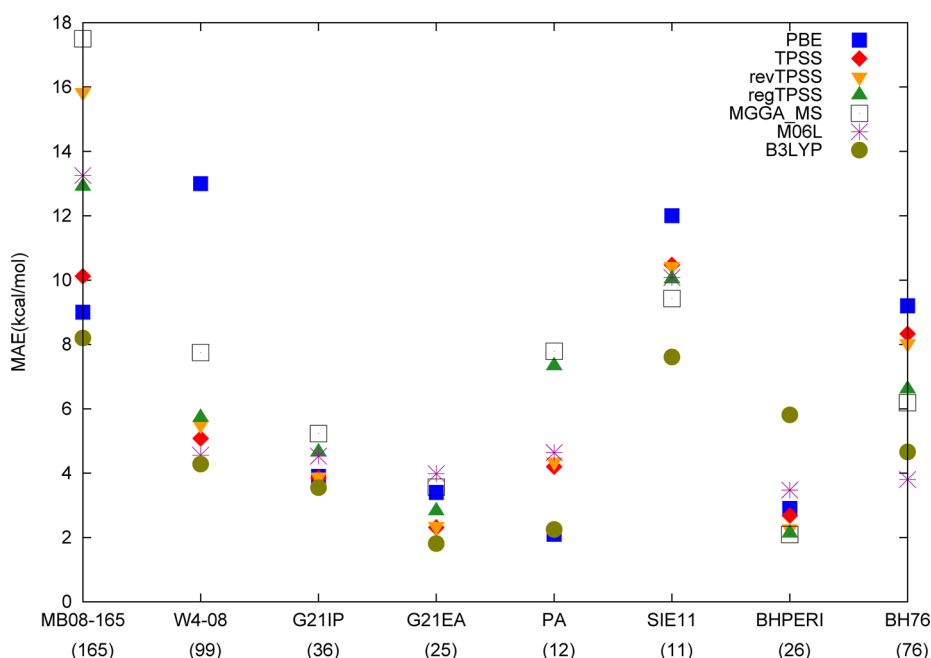


Figure 1. MAEs of PBE, TPSS, revTPSS, regTPSS, MGGA_MS, M06L, and B3LYP for the eight subsets of the miscellaneous properties group in the GMTKN30 database. A number under the name of a subset in a bracket indicates the number of entries of the subset.

water clusters, conformational space energies, and systems with inter- and intramolecular London-dispersion interactions.

a. Miscellaneous Properties. Figure 1 shows the MAEs of different functionals for eight subsets of the GMTKN30 test set related to miscellaneous basic properties, which are related to miscellaneous basic properties. The “mindless benchmarking” or MB08-165 subset refers to the decomposition energies of 165 “artificial”, nonconventional, random-structure molecules into hydrides and diatomic homonuclear molecules. Figure 1 shows that the MB08-165 subset is a difficult test for the present semilocal functionals, and the largest errors occur here in the first group of the subsets. This can be attributed to the stretched structures where the nonlocality of the electron hole is poorly described by the semilocal functionals. Inclusion of the exact exchange remedies the problem to some degree (notice the slightly improved performance of PBE0 and TPSSH functionals for these test sets in ref 27). Consequently, the hybrid B3LYP gives the smallest MAE (8.2 kcal mol⁻¹) followed by PBE (MAE = 9.0 kcal mol⁻¹). The calculated MAEs for TPSS, revTPSS, regTPSS, MGGA_MS, and M06L are 10.1, 15.8, 12.9, 17.5, and 13.3 kcal mol⁻¹, respectively. Notice from ref 27 that M06L does not converge for one of the decomposition energies, so its MAE cannot be evaluated correctly. Like M05,³⁰ M06L has an oscillating enhancement factor that can cause a convergence problem,³¹ and no known convergence-improving technique can remedy this problem. The new meta-GGAs have no such problem. TPSS performs best among the tested meta-GGA functionals. An optimized TPSS (oTPSS)²⁷ (not shown in Figure 1) gives an MAE only 6.5 kcal mol⁻¹, and this shows that meta-GGA might give superior results over the more expensive hybrid functionals. oTPSS is an optimized functional that has the same form as TPSS. Seven TPSS parameters (not including the gradient coefficients for exchange) were fitted in a standard least-squares procedure.²⁴ Lifting all physical constraints has a great influence on all seven parameter values. (For details, see Table 5 of ref 24.) oTPSS gives the best meta-GGA results for this test.

However such optimization to molecular test sets might lead to poor results in solid state applications. The accuracy of the heavily parametrized M06L (fitted to 350 energies) is worse than that of TPSS and regTPSS, but it is better than that of MGGA_MS and revTPSS. Although both regTPSS and MGGA_MS are free of the order-of-limits anomaly^{11,20} present in TPSS and revTPSS, their construction differences lead to different results for the MB08-165 subset.

The W4-08 subset contains the atomization energies of 99 small molecules. As B3LYP^{28,29} was parametrized to reproduce atomization energies and enthalpies of formation of small molecules, it is not surprising that it gives the best results with MAE (4.3 kcal mol⁻¹). For meta-GGAs, in this study the empirically fitted M06L delivers the best results, followed by TPSS, revTPSS, regTPSS, and then MGGA_MS. Literature data²⁷ show that oTPSS shows the best meta-GGA performance (MAE = 3.2 kcal mol⁻¹). For this subset, regTPSS gives only slightly (by 0.2 kcal mol⁻¹) increased MAE compared to its parent revTPSS functional. For this subset, PBE gives poor results and the largest MAE (13 kcal mol⁻¹). As described earlier,³² the PBE gives quite unbalanced molecular and heavy atomic energies, and this error is corrected by TPSS and by all the new meta-GGAs efficiently. One important factor might be the one-electron self-correlation error freedom of the TPSS that gives improved atomization energies for molecules that contain H atoms. This will be discussed later (see discussions of PA and SIE11 subsets).

The next three subsets are G21IP, G21EA, and PA, which represent the adiabatic ionization potentials, adiabatic electron affinities, and adiabatic proton affinities, containing 36, 25, and 12 energies, respectively. The results in Figure 1 show that all of the tested functionals give reasonable results for these three subsets. B3LYP shows the smallest MAE for the G21IP and the G21EA subsets and has an MAE comparable to that of PBE for the PA subset. At the basis-set limit, some negative ions are bound only when at least a fraction of exact exchange is included in the effective potential.³³ The overall performances

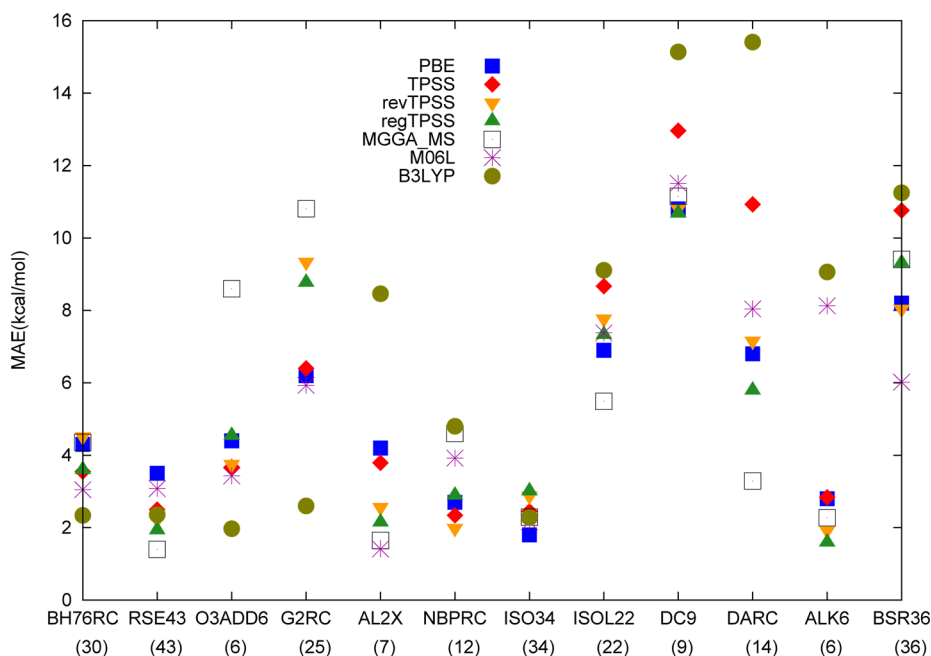


Figure 2. MAEs of PBE, TPSS, revTPSS, regTPSS, MGGA_MS, M06L, and B3LYP for the reaction group in the GMTKN30 database. A number under the name of a subset in a bracket indicates the number of entries of the subset.

of TPSS and revTPSS for these three subsets are better than regTPSS, MGGA_MS, and M06L. Notice that oTPSS shows a worse performance than TPSS for the G21IP and the G21EA subsets. For the PA subset, PBE works better than the meta-GGAs, and regTPSS and MGGA_MS give large errors (cf. MAE = 7.3 and 7.8 kcal mol⁻¹, respectively). For correct proton affinity results, the accuracy of the total energy for the hydrogen atom is particularly important. PBE and TPSS give excellent total energy for the hydrogen atom, and this is reflected in the good results. Although regTPSS and MGGA_MS recover the exact exchange energy of the hydrogen atom, these functionals have the one-electron self-correlation error that makes the total energy of one-electron regions slightly less accurate.

The SIE11 subset includes 11 self-interaction related problems. The semilocal functionals are spoiled by one- and many-electron self-interaction error as described in the literature.^{34,35} Figure 1 shows that all studied functionals perform relatively poorly for this test set. The worst result is given by PBE (cf. Figure 1, MAE = 12 kcal mol⁻¹). The meta-GGA functionals improve over PBE noticeably (cf. MAEs close to 10 kcal mol⁻¹). Among the semilocal functionals, MGGA_MS gives the smallest MAE = 9.4 kcal mol⁻¹. The B3LYP hybrid functional performs best (cf. MAE = 7.6 kcal mol⁻¹), as this functional contains 25% exact exchange that decreases the electron self-interaction error for exchange, and the LYP functional is one-electron self-correlation error free. But notice that the self-correlation error was reintroduced by the mixture of LSDA correlation into the correlation part of the functional. However, the overall balance of decrease and increase of the self-interaction errors helps B3LYP to decrease this error. Despite its optimization of the parameters, oTPSS gives only a negligible improvement over TPSS, as the many-electron self-interaction error cannot be corrected at the level of semilocal approximation.

The subsets BHPERI (26 barrier heights of pericyclic reactions) and BH76 (76 barrier heights of hydrogen transfer, heavy atom transfer, nucleophilic substitution, unimolecular,

and association reactions) test the performance for stretched-bond transition states. For the stretched bonds, the correct description of electron hole delocalization is particularly difficult for the semilocal functionals. However, beside the similarities of the two tests, important differences exist. BHPERI is the only subset in this miscellaneous group of subsets that also tests the noncovalent interactions classified in the third group. The 25% exact exchange helps B3LYP to describe better the electron hole delocalization effect and to give improved results for the BH76 test set. However, this is not sufficient for BHPERI where the noncovalent interactions of the crowded ring structures are incorrectly described by the strongly repulsive B88 exchange functional. (Further proof of this is that the D3 noncovalent correction helps to bring down the large B3LYP error from almost 6 kcal mol⁻¹ to 2.8 kcal mol⁻¹). Thus, the uncorrected B3LYP shows the poorest performance for BHPERI. For BH76, where the noncovalent interactions are unimportant, B3LYP shows the second best performance after M06L. The good performance of the M06L is expected, as BH76 was in the training set of the parametrization of M06L, and M06L describes some part of the noncovalent interactions correctly. MGGA_MS and regTPSS are better than TPSS and revTPSS with noticeable improvement on MAEs as shown in Figure 1. Notice that oTPSS without long-range dispersion correction fails seriously for BHPERI (MAE = 4.6 kcal mol⁻¹) and gives considerably worse results than TPSS, while oTPSS-D3 performs well (MAE = 2.1 kcal mol⁻¹),²⁷ suggesting that the noncovalent interactions might be important for these energies. At this point, it is interesting to note that revTPSS and regTPSS restore the second-order gradient expansion of a slowly varying density for exchange over a wide range of densities like PBEsol, but PBEsol shows a poor performance for BHPERI (MAE = 6.9 kcal mol⁻¹), and this error is largely corrected by the more flexible revTPSS and regTPSS, showing the advantage of the meta-GGA formalism. Notice also that revPBE, which performs

well for molecular test sets, fails for this test set ($\text{MAE} = 4.2 \text{ kcal mol}^{-1}$).

b. Reaction Energies. Figure 2 shows the MAEs of the studied functionals for 12 subsets in the GMTKN30 test set related to reaction energies. The first BH76RC subset includes the energies of 30 chemical reactions related to the previous BH76 subset. For the BH76RC subset, M06L gives the smallest MAE among the tested meta-GGAs, followed by TPSS, *regTPSS*, PBE, MGGA_MS, and *revTPSS*. There are only small differences between the semilocal functionals for this test set, and inclusion of the exact exchange is needed to improve the results (see improved B3LYP results). As published PBE with 25, 32,³⁶ and 38%²⁷ of exact exchange gives also very much improved results for this subset ($\text{MAE} = 2.5 \pm 0.1 \text{ kcal mol}^{-1}$). The optimized *oTPSS* gives marginal improvements.²⁷

The RSE43 subset studies the stabilization energies of 43 radicals. As shown in Figure 2, the meta-GGA functionals work better for this subset than PBE, which actually gives the largest MAE. As expected, the inclusion of 25, 32, or 38% of exact exchange helps to bring down the MAE of the PBE hybrid to $1.5 \pm 0.3 \text{ kcal mol}^{-1}$. TPSS and M06L give similar MAEs of $3.0 \text{ kcal mol}^{-1}$ and $3.1 \text{ kcal mol}^{-1}$, respectively. MGGA_MS gives the best meta-GGA results ($\text{MAE} = 2.0 \text{ kcal mol}^{-1}$), followed by B3LYP, *regTPSS*, *revTPSS*, TPSS, M06L, and PBE.

The O3ADD6 subset is specifically designed for studying the reaction and association energies and barrier heights for the addition of ozone (O_3) to C_2H_4 and C_2H_2 molecules, and the G2RC subset describes 25 reaction energies for molecules selected from the G2/97 test set. Figure 2 shows that the best overall performance ($\text{MAE} = 2.0 \text{ kcal mol}^{-1}$ for O3ADD6 and $2.6 \text{ kcal mol}^{-1}$ for G2RC) is achieved by B3LYP. Notice that B3LYP was optimized using the G2/97 test set. The meta-GGAs give an MAE around 4 kcal mol^{-1} for the O3ADD6 with small differences, and M06L gives marginally better results than *revTPSS*. It is interesting that MGGA_MS behaves very differently from the other meta-GGAs and gives a very large error for O3ADD6 and particularly for G2RC ($\text{MAE} > 10 \text{ kcal mol}^{-1}$). MGGA_MS gives a larger error when single bonds are produced in a reaction. These poor MGGA_MS results might be attributed to an excessive enhancement function for small s and α regions. For the G2RC subset M06L, PBE and TPSS perform about the same, and these functionals perform somewhat better than *revTPSS* and *regTPSS*. Notice that the empirical *oTPSS* gives a considerably better result ($\text{MAE} = 3.5 \text{ kcal mol}^{-1}$) only slightly worse than B3LYP.

The AL2X subset contains dimerization energies of AlX_3 molecules, where $X = \text{H}, \text{CH}_3, \text{F}, \text{Cl},$ and Br and the NBPRC subset contains oligomerization and H_2 fragmentation energies of NH_3 or BH_3 molecules and H_2 activation reactions with PH_3 or BH_3 molecules. For these reactions, the correct description of noncovalent interactions again might give improved results. Figure 2 shows that B3LYP misses most of the noncovalent interaction energy, and it performs particularly poorly for the AL2X and also gives the worst results for NBPRC reactions. All tested meta-GGA functionals are more suitable than B3LYP or PBE for calculating the AL2X subset, and M06L and MGGA_MS give only slightly better results than *revTPSS* or *regTPSS*. For NBPRC, *revTPSS* gives the best results with $\text{MAE} = 2.0 \text{ kcal mol}^{-1}$, and M06L and MGGA_MS show considerably poorer performance (MAEs around 4 kcal mol^{-1}).

The next two subsets test the description of the isomerization energies. ISO34 contains isomerization energies of small and medium-sized organic molecules, and ISOL22 contains

isomerization energies of large-sized organic molecules. The fundamental difference between the two test sets is that for large-sized molecules the correct description of the intramolecular noncovalent interactions is important. For ISO34, the B3LYP MAE of $2.3 \text{ kcal mol}^{-1}$ is comparable to those of TPSS ($2.5 \text{ kcal mol}^{-1}$), *revTPSS* ($2.9 \text{ kcal mol}^{-1}$), MGGA_MS ($2.3 \text{ kcal mol}^{-1}$), and M06L ($2.2 \text{ kcal mol}^{-1}$). PBE gives the best results for the ISO34 subset with an MAE of $1.8 \text{ kcal mol}^{-1}$. MGGA_MS gives the best results for ISOL22.

ISOL22 apparently requires the correct description of intramolecular noncovalent interactions. Notice that *oTPSS* gives very poor results for the ISOL22 reactions ($\text{MAE} = 9.1 \text{ kcal mol}^{-1}$), and D3 correction helps to decrease this error to $6.8 \text{ kcal mol}^{-1}$. This shows clearly that noncovalent corrections might improve the meta-GGA results for ISOL22. MGGA_MS gives the best meta-GGA results for ISOL22 ($\text{MAE} = 5.5 \text{ kcal mol}^{-1}$).

The DC9 subset deals with nine difficult cases for density functional calculations. Figure 2 shows that B3LYP gives the largest MAE of $15.1 \text{ kcal mol}^{-1}$. All the new meta-GGAs perform better than TPSS, although even those relatively good results are quite poor (MAEs around 10 kcal mol^{-1}). For the DC9 subset, the inclusion of the noncovalent corrections might improve the result, as illustrated by the very poor *oTPSS* results ($\text{MAE} = 16.3 \text{ kcal mol}^{-1}$) that are improved somewhat by D3 corrections ($\text{MAE} = 12.8 \text{ kcal mol}^{-1}$). The best new meta-GGAs for this are *regTPSS* and *revTPSS*.

The DARC subset includes 14 Diels–Alder reactions. For several of these reactions, the ring structures provide some degree of intramolecular noncovalent interactions that are poorly described by B3LYP. Consequently, B3LYP performs rather poorly for the DARC subset with an MAE of $15.4 \text{ kcal mol}^{-1}$ (as it performs poorly for all subsets where noncovalent interactions play any role, e.g., DC9, ISOL22, AL2X, etc.). PBE gives better results for the DARC subset than TPSS ($10.9 \text{ kcal mol}^{-1}$), M06L ($8.0 \text{ kcal mol}^{-1}$), and *revTPSS* ($7.2 \text{ kcal mol}^{-1}$) but is worse than *regTPSS* ($5.8 \text{ kcal mol}^{-1}$). The smallest MAE is obtained by MGGA_MS ($3.3 \text{ kcal mol}^{-1}$) as it includes some intramolecular interactions. The new meta-GGA functionals largely outperform the earlier meta-GGAs for the DARC.

The ALK6 subset contains chemical reactions of alkaline and alkaline-cation-benzene complexes. Figure 2 shows that the performances of M06L ($\text{MAE} = 8.1 \text{ kcal mol}^{-1}$) and B3LYP ($\text{MAE} = 9.1 \text{ kcal mol}^{-1}$) are particularly poor for this subset. The new *revTPSS* and *regTPSS* give reasonably good performance ($\text{MAE} < 2 \text{ kcal mol}^{-1}$), and they are slightly better than TPSS and MGGA_MS.

The BSR36 subset contains 36 bond separation reactions of saturated hydrocarbons. B3LYP again gives the largest MAE ($11.3 \text{ kcal mol}^{-1}$), as it does for ALK6, DARC, and DC9 subsets. At the meta-GGA level, M06L performs the best, while TPSS is the worst. *revTPSS* gives the best results among TPSS, *revTPSS*, *regTPSS*, and MGGA_MS. The calculated MAEs of *regTPSS* and MGGA_MS are similar to each other. For this subset, the long-range dispersion corrections are very large for TPSS-type functionals (about $5.5 \text{ kcal mol}^{-1}$ improvement for MAE).

c. Noncovalent Interactions. The weak dispersion interactions and hydrogen bonds are considered in the following six subsets: IDISP, WATER27, S22, ADIM6, RG6, and HEAVY28. In the WATER27 subset, hydrogen bonds between water molecules are dominant for the binding energies. The IDISP, ADIM6, and RG6 subsets require the correct description of the

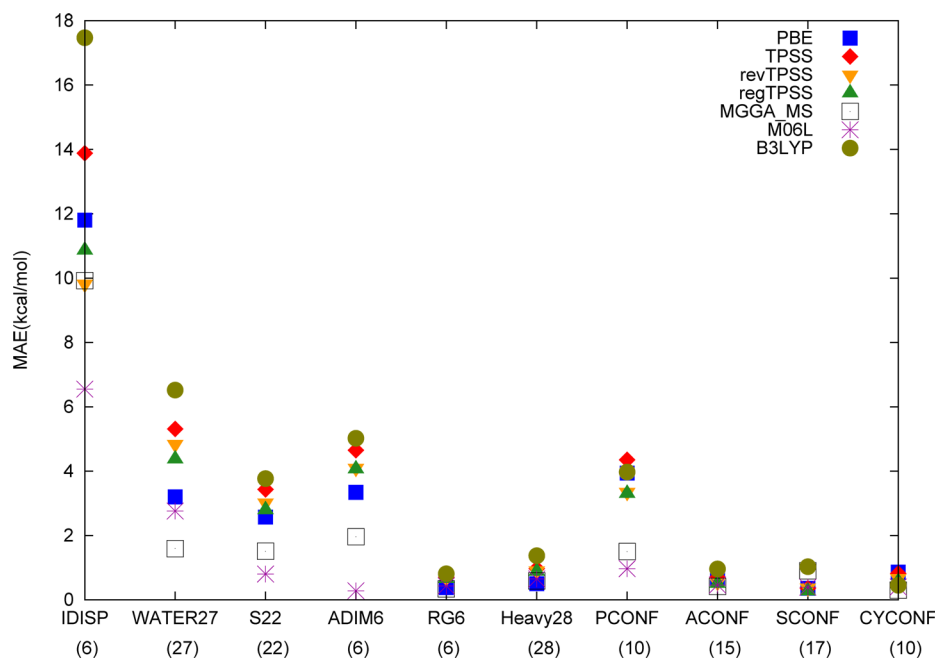


Figure 3. MAEs of PBE, TPSS, revTPSS, regTPSS, MGGA_MS, M06L, and B3LYP for the noncovalent interaction group in the GMTKN30 database. A number under the name of a subset in a bracket indicates the number of entries of the subset.

Table 2. The MAE or WTMAE of the Discussed Functionals for the MB08-165 Subset, the Miscellaneous Properties Group, the Reaction Energies, the Noncovalent Bonds, and the Total Test Set^a

	LSDA	PBE	TPSS	revTPSS	regTPSS	MGGA_MS	M06L	B3LYP
MB08-165 ^b	20.3	9.0	10.1	15.8	12.9	17.5	13.3	8.2
misc. properties(7) ^c	22.5	8.3	5.5	5.5	5.3	5.9	4.3	4.4
misc. properties(8) ^d	21.7	8.5	7.2	9.4	8.1	10.2	7.7	5.8
reaction energies (12) ^e	6.9	5.5	6.5	5.6	5.6	5.5	5.0	7.1
noncovalent bonds(10) ^f	4.9	2.9	3.7	3.0	2.9	1.9	1.3	4.2
total(29) ^g	10.5	5.4	5.2	4.7	4.6	4.3	3.5	5.3
total (30) ^h	11.9	5.9	5.9	6.3	5.8	6.2	4.9	5.8

^aUnit is in kcal mol⁻¹. The values in the parentheses are the number of subsets. ^bThe MAE of the MB08-165. ^cThe WTMAE of the miscellaneous properties subgroup that excludes the MB08-165 subset. ^dThe WTMAE of the miscellaneous properties subgroup that includes the MB08-165 subset. ^eThe WTMAE of the reaction energies subgroup. ^fThe WTMAE of the noncovalent bonds subgroup. ^gThe WTMAE of the total GMTKN database that includes the MB08-165 subset. ^hThe WTMAE of the total GMTKN database that excludes the MB08-165 subset.

van der Waals interactions between molecules or atoms. Due to its long-range feature, the van der Waals interaction is believed to be difficult for a semilocal functional. However, results from the semilocal M06L, which was heavily fitted to a large number of training sets including noncovalent systems, suggest that a meta-GGA can capture medium-range exchange and correlation energies dominating noncovalent complexes.¹⁰ Therefore, as expected, M06L delivers the best overall performance for the six subsets, while B3LYP is the worst among the tested functionals. But M06L is unable to bind the Kr₂ and Xe₂ dimers in RG6 and the PbH₄-water and (TeH₂)₂ complexes in HEAVY28 as observed earlier.²⁷ This together with a failure of M06L for MB08-165 requires caution when M06L is used for new problems. In this respect, the new meta-GGAs are more robust, and we observed no similar problems. Although the nonempirical MGGA_MS is inferior to M06L, it still yields quite good results for these subsets and systematically improves over the other semilocal functionals, among which TPSS captures the least noncovalent interactions. revTPSS and regTPSS show comparable overall performances, which are slightly worse than that of PBE. But notice that for WATER27, where hydrogen bonds dominate binding energies, MGGA_MS

yields the smallest MAE, which is consistent with the finding for the W6 set of ref 11. This confirms that MGGA_MS describes the hydrogen bond excellently. Moreover, the quite good results for the other subsets from MGGA_MS also corroborate the findings from the semilocal M06L that equilibrium structures of noncovalent complexes are dominated by medium-range exchange and correlation energies, which a meta-GGA is able to describe at least partly. Without long-range dispersion correction, no TPSS-type meta-GGA can perform reasonably for IDISP, Water27, S22, and ADIM6.

The last four subsets are PCONF, ACONF, SCONF, and CYCONF. These four subsets are related to the relative energies of different conformers of molecules. The transformation between different conformers is usually associated with the change of chemical bonds. The results of MAEs are given in Figure 3. For PCONF, the noncovalent energy contributions are particularly large; consequently, M06L performs the best (1.0 kcal mol⁻¹), followed by MGGA_MS (1.5 kcal mol⁻¹), regTPSS (3.3 kcal mol⁻¹), revTPSS (3.4 kcal mol⁻¹), PBE (3.9 kcal mol⁻¹), B3LYP (4.0 kcal mol⁻¹), and TPSS (4.4 kcal mol⁻¹). For the other three subsets, the overall performances of the tested functionals are close to each other.

Table 3. The WTMAE of the Discussed Functionals for Different Test Sets with D3 Correction in kcal mol^{-1a}

	PBE	TPSS	revTPSS	regTPSS	MGGA_MS	M06L	B3LYP
misc. properties(7) ^b	8.6	5.8	6.0	5.8	6.4	4.3	4.1
misc. properties(8) ^c	8.8	7.2	9.4	8.0	10.3	7.6	5.0
reaction energies	4.3	4.6	4.0	4.2	4.8	4.9	4.7
noncovalent bonds	1.6	1.2	1.2	1.2	2.2	1.2	1.1
total (29) ^b	4.5	3.8	3.6	3.6	4.3	3.4	3.3
total (30) ^c	5.2	4.6	5.2	4.7	6.1	4.8	3.7

^aThe D3 corrections for revTPSS, regTPSS, and MGGA_MS are those designed for TPSS and are not optimal for other functionals, especially MGGA_MS. ^bThe subset MB08-165 is excluded. ^cThe subset MB08-165 is included.

B3LYP is the least accurate, and the meta-GGAs give somewhat worse result than PBE.

2. Weighted Total Mean Absolute Error. We use the weighted total mean absolute error (WTMAE) defined by Goerigk and Grimme²⁷ as $((\sum_i W_i \text{MAE}_i)/(\sum_i W_i))$, where W_i and MAE_i are the weight and MAE for subset i (see the definition of W_i from ref 27). To keep the analysis consistent with previous work, we use this definition of weight for each subset. However, because the MB08-165 subset consists of “artificial” reactions which have a large weight, an assessment of density functionals based on this subset might not be indicative for “real” chemical reactions. So we shall report the WTMAE without as well as with the MB08-165 subset. While the exact density functional should describe MB08-165, the meta-GGAs may fail there because of the high level of strain in the artificial complexes. Table 2 shows the MAE of the MB08-165 subset, the WTMAEs of the miscellaneous properties, the total GMTKN30 database with and without the MB08-165 subset, and the WTMAEs of the reaction energies and the noncovalent bonds. Considering miscellaneous properties and the total test set, if we exclude the MB08-165 subset, there is a little change for PBE, but for meta-GGAs, particularly for revTPSS, regTPSS, and MGGA_MS, the change is considerable. The large weight of the performance for the “artificial” MB08-165 (37.6% of the eight miscellaneous properties’ subsets and 14.4% of the total 30 weights) hides considerably the reasonable performance of meta-GGAs for “real” chemical reactions. So we exclude the MB08-165 subset for later discussion.

The LSDA¹ in the SPW92 parametrization⁵ is included in Table 2, using the data from refs 25 and 27. LSDA works the worst for the total 29 subsets. It especially delivers a much larger WTMAE for miscellaneous properties, and its overbinding yields a bad performance for noncovalent interactions, which cannot be corrected by long-range dispersion. M06L delivers the best performance for these three groups separately or together in terms of WTMAE. B3LYP works well for miscellaneous properties but yields the largest WTMAE for the reaction energies and noncovalent interactions except SVWN. While the three new meta-GGAs (revTPSS, regTPSS, and MGGA_MS) have similar performance on miscellaneous properties and reaction energies, MGGA_MS outperforms the other two for the noncovalent interactions. For the 29 subsets, B3LYP, PBE, and TPSS have larger WTMAEs than those of the three new meta-GGAs.

3. Results with the Dispersion Correction. As we know, the long-range correlation interaction decays exponentially for semilocal functionals³⁷ arising only from the density overlap region, while the true van der Waals interaction decays as of R^{-6} for objects separated by a large distance R . Therefore, semilocal density functionals cannot capture long-range correlation energy for van der Waals interactions.³⁸ The

DFT-D approach is a very quick, simple way to compensate for the missing dispersion energy,³⁹ which treats the dispersion energy as a post hoc correction to a semilocal functional.

One possible formula for the long-range dispersion interactions that decays as R^{-6} is

$$E_{\text{disp}} = -\frac{1}{2} \sum_{A \neq B} \sum_{n=6,8} S_n \frac{C_n^{\text{AB}}}{R_{\text{AB}}^n} f_{\text{damp},n}(R_{\text{AB}})$$

where C_n^{AB} is the averaged n th-order van der Waals coefficient for the pair of atoms A and B and R_{AB} is the separation between the two atoms. S_n is a scaling factor for the n th-order dispersion energy. In the DFT-D3 version, S_6 is equal to unity and S_8 is adjusted specifically for a given functional.²⁷ $f_{\text{damp},n}(R_{\text{AB}})$ is a damping function that is used to remove the energy singularity for small R and the double counting of the correlation at intermediate range. The damping function involves a functional-dependent parameter $S_{r,n}$, which is a scaling factor for the cutoff radius. This cutoff radius usually refers to the van der Waals radius,⁴⁰ but in DFT-D3, it is derived from the average atomic radius.³⁹ For DFT-D3, $S_{r,8}$ is equal to unity and $S_{r,6}$ is dependent on the specific functional.²⁷ Decreasing S_n or increasing $S_{r,n}$ can reduce the dispersion energy. For the three new meta-GGAs, their optimized damping functions are not known yet. We used the TPSS-D3 dispersion energy to correct these new functionals as described in the section II.

Table 3 shows that the inclusion of the TPSS-D3 dispersion energy largely improves WTMAEs of regTPSS and revTPSS for the noncovalent interactions to the same level of TPSS-D3, but deteriorates MGGA_MS slightly. This suggests that TPSS, revTPSS, and regTPSS miss a large portion of noncovalent interactions, but MGGA_MS behaves very differently (it is more overbinding than regTPSS or revTPSS). The addition of long-range dispersion binding to an already correct or overbinding result naturally worsens the result as it increases the overbinding. The inclusion of the TPSS-D3 dispersion energy causes double counting of the part of noncovalent interactions captured by MGGA_MS and thus deteriorates its performance with increasing the noncovalent WTMAE from 1.9 kcal mol⁻¹ to 2.2 kcal mol⁻¹. If we correct MGGA_MS by using the M06L-D3 dispersion energy correction—which has a smaller dispersion energy correction with $S_{r,6} = 1.581$ and $S_8 = 0$ with practically no correction for the MAE—the WTMAE for the noncovalent reactions is improved from 1.9 kcal mol⁻¹ to 1.6 kcal mol⁻¹. The inclusion of the dispersion corrections also improves the performances of all the tested functionals for the reaction energies but deteriorates those for the miscellaneous basic properties (e.g., reaction barrier heights). Otherwise, B3LYP-D3 yields the smallest WTMAE for the total 29 subsets. revTPSS-D3 and regTPSS-D3 also give quite good results for the total 29 subsets with the WTMAEs only 0.3 kcal mol⁻¹

larger than that of M06L. revTPSS-D3 even gives the smallest WTMAE for the reaction energies among all tested functionals. As it does not use a properly fitted D3 correction, some improvement is possible, mostly for the worsened miscellaneous energies.

IV. SUMMARY

We have tested the nonempirical semilocal meta-GGAs, i.e., TPSS, revTPSS, regTPSS, and MGGA_MS, on the GMTKN30 molecular database for a variety of properties, some of which (for example, barrier heights and noncovalent interactions) are difficult for semilocal functionals. For comparison, we also included results of PBE, M06L, and B3LYP from the literature.²⁷ While revTPSS and regTPSS are comparable to each other overall, MGGA_MS, when compared to them, is slightly worse for miscellaneous properties, comparable for reaction energy, and systematically better for noncovalent interactions. For miscellaneous properties, these three meta-GGAs perform in general much better than PBE and not as well as M06L and B3LYP. For kinetic properties, B3LYP surprisingly delivers the worst overall performance, and TPSS performs the second worst, while the other functionals perform better with accuracies similar to each other. For noncovalent interactions, B3LYP is again the worst one, and M06L performs the best. MGGA_MS is the second best one, which shows large improvement on noncovalent interactions (stronger binding) over PBE, TPSS, revTPSS, and regTPSS. The latter functionals are at the same accuracy level and can be significantly improved by the inclusion of the dispersion correction for this category. The quite good performances of MGGA_MS and M06L, compared to those of the other semilocal functionals without long-range dispersion corrections, suggest that equilibrium structures of noncovalent complexes are dominated by medium-range van der Waals interactions which then can be described at least partly by semilocal meta-GGAs.

The density functionals tested here for main-group chemical energetics achieve a similar overall accuracy. So what are the take-home lessons for users and developers?

The first is that no density functional yet comes close to the desired chemical accuracy (mean absolute error of 1 kcal mol⁻¹), but all of those tested achieve a useful accuracy. Moreover, the tested semilocal functionals (PBE GGA and the meta-GGAs) are more computationally efficient for large molecules than is the hybrid functional B3LYP.

The second is that for some individual data subsets there is a wide range of mean absolute errors among these functionals. A dramatic example is the DARC subset of 14 Diels–Alder reaction energies, where the mean absolute error is 3 kcal mol⁻¹ for MGGA_MS but 15 kcal mol⁻¹ for B3LYP. This suggests that, for a specific application, the user can sometimes choose a functional that is expected to work best.

The Diels–Alder reactions (DARC) and the dimerization of aluminum complexes (AL2X) involve the formation of rings and the reaction energies are influenced by noncovalent interactions. They have been discussed as difficult cases for approximate functionals.⁴¹ For both, B3LYP is the worst performer and MGGA-MS is the best or nearly the best. But this order of performance is reversed in the reaction subsets BH76RC, O3ADD6, and G2RC. More generally, the standard B3LYP is outperformed by the tested semilocal functionals for data sets dominated by ring structures (DARC, AL2X, BHPERI, DC9). But notice that B3LYP has the worst MAD of all hybrids.²⁷ Interestingly, the originally suggested B3PW91-

D3 is one of the best functionals. Among the conventional hybrids PW6B95-D3 gives the best results for GMTKN30, and it is somewhat outperformed by the nonconventional, heavily fitted M06-2X-D3 dispersion corrected meta-GGA hybrid (but naturally the same convergence problems hold for M06L and M06-2X³¹). The new meta-GGAs perform better than the older ones for several subsets. revTPSS is the best or very close to be the best for 15 subsets, namely G21IP, G21EA, BHPERI, NBPRC, ISOL22, DC9, BSR36, ALK6, BSR36, IDISP, S22, RG6, PCONF, ACONF, and SCONF. For BHPERI, ALK6, and SCONF, revTPSS is marginally beaten by regTPSS. MGGA_MS is the best or almost the best for seven subsets: SIE11, BHPERI, RS43, AL2X, ISOL22, WATER27, and CYCONF. There is a very delicate question of what to do when the D3 correction worsens the results of functionals that were constructed on the basis of the exact constraints. For example, in the BHPERI and BH76 subgroups the barrier height is typically underestimated. Adding D3 shifts the results in the wrong direction for many functionals (oTPSS, TPSS). Worsening the results this way might be consistent but hard to accept.

The third is that, if one seeks an overall-best functional, then one must identify or develop candidates beyond the current meta-GGAs and B3LYP hybrid studied here, or look for criteria beyond main-group chemical energetics. Indeed, some of the hybrid functionals studied in ref 27, with dispersion corrections, do perform somewhat better overall than the functionals in our Table 3. And there may be much room for further improvement of meta-GGA and hybrid meta-GGA functionals. Savin and collaborators^{42,43} have proposed that currently the selection of a functional is largely a personal choice, like the selection of a spouse. They have also shown how different statistical measures on the same data set can lead to different conclusions about the relative performance of approximate functionals.

A formal criterion is the extent to which the approximation was constructed from exact constraints on the density functional for the exchange-correlation energy (as in PBE, TPSS, revTPSS, regTPSS, and MGGA_MS) and not from fitting to experimental (as in M06L and B3LYP) or calculated high-level reference data.

A “universality” criterion would be the applicability of the functional for non-main-group chemistry as well as for solids, solid surfaces, and molecules on surfaces, where revTPSS has shown promise,¹⁹ as have (at least for bulk solids) highly empirical functionals⁴⁴ fitted to solid state as well as chemical data.

While this article reports only error statistics, the individual energy differences and their errors are available as Supporting Information.

■ ASSOCIATED CONTENT

Supporting Information

All reaction energies with and without D3 correction from the three new meta-GGA functionals—revTPSS, regTPSS, and MGGA_MS—for the GMTKN30. The energy difference between calculated results and reference values. The mean (ME), mean absolute (MAE), and root-mean-square (RMSE) errors for each subset. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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