Density Functional Theory for Reaction Energies: Test of Meta and Hybrid Meta Functionals, Range-Separated Functionals, and Other High-Performance Functionals

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Ⓢ *Supporting Information*

ABSTRACT: The present study compares the accuracy of 30 density functionals for four databases of reaction energies studied recently by Grimme and co-workers. For 20 of the density functionals, the calculations are new, and the calculations are compared to previous work for the other 10. We present the results in detail for 11 of the functionals and as mean unsigned errors for the others. The results presented in detail are for the seven most recent Minnesota functionals (M05-2X, M06-L, M06-HF, M06, M06-2X, M08-HX, and M08-SO), three range-separated functionals (HSE, LC-ωPBE, and ωB97X-D), and one dispersion-corrected global hybrid generalized gradient approximation (B97-D); the other functionals include five dispersion-corrected functionals and their uncorrected analogs, eight high-performing functionals on a recent catalytic-energies test, and the TPSSh functional because it is of special interest to compare its performance to that of M08-SO. Three of the four databases contain a total of 21 rearrangement reaction energies and 13 diverse dissociation or association energies, and the fourth contains three dissociation reaction energies of alkali metal clusters and three dissociation reaction energies of alkali-metal-cation−benzene complexes. The results are especially promising for the Minnesota hybrid meta-GGA functionals and the ωB97X-D, B2PLYP-D, and HSE functionals.

1. INTRODUCTION

Density functional theory (DFT) in the formulation of Kohn and Sham[1] is the most robust and popular electronic structure method in computational chemistry and physics. Although Kohn−Sham DFT is an exact many-body quantum mechanical theory for the ground-electronic-state properties of a given system, it depends on an unknown universal exchange−correlation (XC) functional that can only be approximated.[2] Many approximate functionals have been published in the literature.[3,4] Since the exact form of the universal XC functional is unknown, approximate functionals, no matter how they were developed, need to be carefully validated before their application to real chemical problems. To this end and also in order to design new density functionals, a large number of databases have been developed and used to test density functional theory for, for example, chemical reaction barrier heights,[5−14] thermochemistry,[9,12−22] noncovalent interactions,[9,13,14,23−30] transition metal chemistry,[4,9,31−35] spectroscopy,[9,13,36−41] and catalysis.[42,43] Goerigk and Grimme[14] recently compiled a quantum chemistry benchmark database for general main-group thermochemistry, kinetics, and noncovalent interactions, called GMTKN24, which includes 24 different subsets. Three subsets of GMTKN24 that are concerned with energies of reaction, namely SIE11 for 11 reactions that are very sensitive to self-interaction error, DC9 for nine reactions that had been shown to be very difficult for DFT, and DARC14 for Diels−Alder reactions, provide especially challenging problems for approximate density functionals. Here, we study these three

databases along with a database of alkali metal reaction energies taken from the more recent work of Grimme et al.[44] The details of these databases have been described in the original papers, and we give a brief introduction to each of the four databases in section 2.

The four databases contain 40 diverse benchmark reaction energies, and we calculate results for 20 density functionals of various types for comparison with this data. In addition, we compare to previous results for 10 other functionals for a total of 30 functionals to be compared. The first two functionals tested are range-separated functionals developed by Scuseria and co-workers, in particular the HSE[45−47] and LC-ωPBE[48] functionals. The next seven functionals tested are the seven most recent meta and hybrid meta functionals (terms that we explain below) that we developed in Minnesota over the past half dozen years,[9,13,20,36,50−52] in particular, M05-2X,[50] M06-L,[20] M06-HF,[36] M06,[9] M06-2X,[9] M08-HX,[13] and M08-SO.[13] The other two functionals for which we present detailed results are functionals with empirical dispersion corrections, namely, B97-D[53] and ωB97X-D.[54] The other functionals included in the present tests will be introduced in section 4.5.

The next two sections summarize the details of the four databases and computational methodology, and section 4 presents results and discusses them. Section 5 concludes the paper.

2. DATABASES

2.1. SIE11. SIE11 is a database of reaction energies for 11 systems that are especially sensitive to self-interaction error (which is discussed further below). This database includes the dissociation energies of five cationic reactions (e.g., $He_2^+ \rightarrow He^+ + He$) and six neutral reactions (e.g., $LiF_2 \rightarrow Li + F_2$). The reference data[14] were obtained by coupled cluster theory. All of the reference data are given in Table 2 along with the DFT results.

2.2. DC9. DC9 is a database of nine reaction energies that have been shown to be difficult for density functionals. We have already investigated two cases in our previous studies; in particular, the energy difference between hepta-1,2,3,5,6-hexaene and hepta-1,3,5-tryne (C_7H_4) is in our πIE3 database,[19] and the isomerization energy of the $(CH)_{12}$ isomers was included in our paper on medium-range correlation energy.[55] The reference data[14] for the DC9 database were obtained from experiments and various levels of theory, and they are listed in Table 3.

2.3. DARC14. DARC14 is a database of reaction energies for 14 typical Diels−Alder reactions; they are the reactions of butadiene, cyclopentadiene, cyclohexadiene, and furan with ethene, ethyne, maleic anhydride, and maleimide acting as dienophiles. This database was used by Johnson et al.[56] in a study of delocalization errors of density functionals. The reference data[14] are based on coupled cluster calculations, and they are tabulated in Table 4.

2.4. ALK6. ALK6 is a database of six dissociation energies for alkali metal complexes and clusters. There are three alkali-metal-cation−benzene complexes (BzM^+), which are of special interest because Grimme et al.[44] showed that they are significantly overbound by the second generation[53] of density functionals with empirical dispersion corrections. The other three data are dissociation energies of nonplanar alkali metal clusters with eight atoms that have large dispersion effects. Therefore, ALK6 is a challenging database for both empirically uncorrected and dispersion-corrected density functional methods. The reference data[44] are based on estimated coupled cluster energies, and they are given in Table 5.

3. COMPUTATIONAL METHODOLOGY

The methods tested here are based on the Kohn−Sham self-consistent-field (SCF) formulation[1] of DFT in which the electronic energy is approximated as the sum of the noninteracting kinetic energy calculated from the SCF orbitals, the classical Coulomb energy calculated from the total electron density ρ, and the XC energy calculated from an XC functional (usually just called the density functional). The density functional can depend on various quantities. For all functionals considered here, the density functional depends on the spin-labeled (α and β) electron densities, ρ_α and ρ_β (whose sum is ρ), and the reduced density gradients, s_α and s_β. Most of the density functionals considered here also depend on the SCF orbitals, which are functionals of ρ_α and ρ_β. We will at first consider two ways in which the XC energy can depend on the orbitals: dependence on the orbital-dependent kinetic energy densities, τ_α and τ_β, and dependence on the Hartree−Fock exchange integrals computed from the SCF orbitals. (A third kind of dependence, namely, nonlocal second-order perturbation terms, is considered in section 4.5.) Functionals depending on ρ_α, ρ_β, s_α, s_β, τ_α, and τ_β are called local; functionals including some Hartree−Fock exchange are called nonlocal or hybrid. The hybrid functionals considered in this article can be subdivided into global hybrids, in

Table 1. Density Functionals

name	year	ref	meta?	hybrid?	X	-D?
HSE	2003	45−47	no	range-separated	100/0a	no
LC-ωPBE	2006	48, 49	no	range-separated	0/100[a]	no
M05−2X	2006	50	yes	global	56	no
M06-L	2006	20	yes	no	0	no
M06-HF	2006	36	yes	global	100	no
M06	2008	9	yes	global	27	no
M06−2X	2008	9	yes	global	54	no
M08-HX	2008	13	yes	global	52.23	no
M08-SO	2008	13	yes	global	56.79	no
B97-D	2006	53	no	no	0	yes
ωB97X-D	2008	54	no	range-separated	22.2036/100[a]	yes

[a] The value before the slash is X for $r_{12} \rightarrow 0$, and the value after the slash is the value of X for $r_{12} \rightarrow \infty$.

which a fixed percentage X of Hartree−Fock exchange is added to some percentage (usually $100 - X$) of local exchange, and range-separated hybrids, in which X is not fixed but depends on the interelectronic separation r_{12} (note that X is defined here only in the limit of a uniform electron gas). A final distinction we need to make is that some density functionals are defined to include an empirical dispersion correction; that is, a post-SCF molecular-mechanics dispersion term is added to the result of the SCF calculation. (In density functionals without such a correction, dispersion-like contributions are present only when there is overlap of the interacting subsystems, and such effects, like other effects of dynamical electron correlation, are present in the correlation part of the density functional.) Density functionals including empirical dispersion terms have a suffix -D.

The present study compares results from several kinds of density functionals. The properties of those considered first are specified in Table 1 by using the distinctions explained in the previous paragraph. Functionals depending only on ρ_σ and s_σ (where $\sigma = \alpha, \beta$) are called generalized gradient approximations (GGAs), and functionals depending only on ρ_σ, s_σ, and τ_σ are called meta-GGAs or meta functionals. The table shows that the initial comparisons include a meta-GGA (M06-L), six global-hybrid meta-GGAs (the other M0x functionals), three range-separated functionals, and one GGA. Two of the range-separated functionals and the GGA contain empirical dispersion corrections. Furthermore, there is a difference in philosophy for the range-separated functions. In particular, HSE is a so-called screened functional with Hartree−Fock exchange at small r_{12} and local exchange at large r_{12}, whereas LC-ωPBE and ωB97X-D are so-called long-range-corrected functionals with Hartree−Fock exchange at large r_{12} and local exchange or mainly local exchange, respectively, at small r_{12}.

The M08-SO functional may also be singled out for special attention because it satisfies the second-order gradient expansion[57] (i.e., it is correct through second order in s_σ) in both exchange and correlation; the former is a constraint avoided in most constraint-based density functionals because, prior to M08-SO, it was not possible to make a functional that satisfied this constraint and was highly accurate for bond energies. The TPSS[58] and TPSSh[59] functionals (a meta-GGA and a global-hybrid meta-GGA, respectively) are also correct through second order in both exchange and correlation. Therefore, we have included both TPSS and TPSSh in our comparison. Because M08-SO and TPSSh are built from the same ingredients (they are both

Table 2. Performance of Density Functionals for the Reaction Energies of the SIE11 Database (kcal/mol)

reaction	reference	M08-HX	M06-HF	M08-SO	LC-ωPBE	M06-2X	M05-2X	ωB97X-D	M06	HSE	M06-L	B97-D
$He_2^+ \rightarrow He + He^+$	57.4	62.3	59.5	64.5	71.3	65.6	64.9	71.2	70.6	70.0	71.6	78.4
$(NH_3)_2^+ \rightarrow NH3 + NH3^+$	35.3	38.5	38.9	38.1	38.3	39.1	40.1	41.5	38.7	41.6	41.2	46.4
$(H_2O)_2^+ \rightarrow H_2O + H_2O^+$	37.3	43.7	39.6	44.8	44.5	44.3	43.9	47.3	46.2	48.4	51.2	55.0
$C_4H_{10}^+ \rightarrow C_2H_5 + C_2H_5^+$	35.3	37.1	39.8	36.2	35.3	37.9	39.5	38.8	38.9	38.7	39.4	41.2
$(CH_3)_2CO^+ \rightarrow CH_3 + CH_3CO^+$	22.6	24.3	25.8	25.6	27.0	25.9	27.9	28.7	24.4	29.8	26.2	25.9
$ClFCl \rightarrow ClClF$	−1.0	0.8	0.2	5.3	−0.1	4.6	2.5	5.4	7.3	10.8	19.1	16.9
$C_2H_4 \cdots F_2 \rightarrow C_2H_4 + F_2$	1.1	1.0	0.6	0.8	0.2	0.8	0.9	0.6	0.6	1.2	1.2	2.7
$C_6H_6 \cdots Li \rightarrow Li + C_6H_6$	9.5	8.0	8.5	8.2	8.2	8.5	11.2	3.6	5.2	5.2	5.8	12.6
$NH_3 \cdots ClF \rightarrow NH_3 + ClF$	10.5	10.3	11.0	9.8	9.8	10.4	11.4	11.2	11.9	13.9	13.5	14.4
$NaOMg \rightarrow MgO + Na$	69.6	79.5	84.1	78.0	82.3	83.2	82.9	79.6	77.3	74.2	83.0	71.6
$FLiF \rightarrow Li + F_2$	94.4	106.1	84.2	108.6	103.5	107.2	112.5	109.0	120.7	115.9	128.1	128.7
MSE		3.6	1.8	4.4	4.4	5.1	6.0	5.9	6.4	7.1	9.9	11.1
MUE		3.9	3.9	4.8	4.9	5.3	6.0	7.1	7.2	7.9	10.5	11.1

Table 3. Performance of Density Functionals for the Reaction Energies of the DC9 Database (kcal/mol)

reaction	reference	ωB97X-D	M08-SO	M08-HX	M06-2X	M05-2X	M06	M06-HF	HSE	LC-ωPBE	M06-L	B97-D
2-pyridone $\rightarrow$ 2-hydroxypyride	−1.0	0.4	−1.5	−1.0	−1.7	−1.7	0.5	−3.4	0.2	0.3	1.8	2.1
$(C_{20})_{case} \rightarrow (C_{20})_{bowl}$	−13.3	−18.7	−25.6	−29.1	−31.4	−31.0	−19.7	−45.0	−8.5	−6.4	−22.2	−29.4
hepta-1,2,3,5,6-hexaene $\rightarrow$ hepta-1,3,5-triyne	−14.3	−12.0	−13.1	−12.4	−13.5	−12.1	−11.7	−16.0	−6.6	−17.0	−5.8	−1.9
2 tetramethylethene $\rightarrow$ octamethylcyclobutane	−19.2	−18.8	−18.8	−17.3	−16.6	−16.1	−14.3	−20.7	−7.6	−16.6	−10.6	−10.8
$(CH)_{12} \rightarrow$ isomerization	−19.5	−23.7	−26.3	−24.9	−22.2	−20.9	−23.9	−19.4	−26.6	−51.4	−19.5	2.8
isomerization of carbo-[3]-oxocarbon	−26.9	−12.5	−7.5	−9.8	−10.5	−11.7	−6.0	−18.9	−4.9	1.3	−1.3	−16.5
$N_2CH_2 + C_3H_4 \rightarrow (CH_2)_3N_2$	−38.1	−38.3	−37.5	−37.6	−37.1	−39.0	−31.0	−43.2	−38.6	−45.8	−27.8	−24.1
$4Be \rightarrow Be_4$	−88.4	−91.4	−86.8	−86.5	−96.7	−94.0	−103.9	−71.7	−113.5	−98.2	−121.3	−98.5
$4S_2 \rightarrow S_8$	−101.0	−93.3	−98.4	−95.1	−99.9	−92.4	−105.7	−107.5	−96.2	−92.0	−95.1	−71.4
MSE		1.5	0.7	0.9	−0.9	0.3	0.7	−2.7	2.1	−0.5	2.2	8.2
MUE		4.3	5.0	5.6	5.7	6.2	7.5	8.2	9.4	11.1	11.5	14.0

global-hybrid meta-GGAs) and both are correct to second order in both exchange and correlation, the comparison of their performance will be especially interesting.

In the present study, we focus on testing against the four databases described in the previous section. None of these functionals has been tested against the four databases in previous studies except that the performance of B97-D for ALK6 has been given in a previous study.[44]

The geometries for the molecules in the various databases were taken from previous work where they were optimized at different levels of theory. Details are given in previous papers.[19,20,22]

All of the calculations in the present work employed the def2-QZVP basis set[60,61] with the *Gaussian 09* program[62] and a locally modified *Gaussian 03* program.[63]

4. RESULTS AND DISCUSSION

In this section, we will present the results for the four databases, and we will gauge the quality of the tested density functionals by mean unsigned errors (MUEs), which are the mean absolute deviations of calculated values from database reference values, and by mean signed errors (MSEs, same as mean deviations), which are used to detect systematic deviations.

4.1. Performance for Self-Interaction-Error Database. Most density functionals suffer from self-interaction error to at least some extent, although it is possible (e.g., by using kinetic energy density[18,64] or by making the Perdew−Zunger self-interaction correction)[65] to eliminate one-electron self-interaction error for

systems with an integer number of electrons. Recently, Cohen et al.[66] investigated self-interaction error by using simplified model systems, and they concluded that the error can be traced to the delocalization error (due to fractional charges, such as in the dissociated H_2^+ system) and static correlation error (due to fractional spins, such as in the dissociated H_2 system). Note, however, that approximate density functionals sometimes benefit in an indirect way from self-interaction error; for example, for transition metal systems with high multireference[67] character, local functionals having larger self-interaction errors often perform better than the Hartree−Fock theory, which has no self-interaction error, at least for physical systems, and hybrid functionals that have reduced self-interaction error. Handy and Cohen[68] concluded that local exchange functionals contain left−right correlation energies associated to some extent with the same properties that lead to self-interaction error. From a practical point of view, one can try to control these effects and hope to achieve useful accuracy for multireference systems. Tests against the SIE11 database provide a measure of whether such hopes are realized. The performance for the SIE11 database is given in Table 2.

The isomerization energy of ClFCl to ClClF is a difficult case, and—of the 11 functionals in Table 2—only LC-ωPBE predicts the correct sign of the reaction energy in this case.

The other 10 reactions are dissociation reactions. All tested functionals give large errors for the dissociation energies of NaOMg and FLiF. Furthermore, Table 2 shows that all tested

Table 4. Performance of Density Functionals for the Reaction Energies of DARC14 Database (kcal/mol)

reactions	reference	M08-SO	M05-2X	M06-HF	M08-HX	ωB97X-D	M06-2X	HSE	M06	LC-ωPBE	M06-L	B97-D
ethene + butadiene	−43.8	−46.1	−46.7	−45.4	−46.8	−47.5	−45.8	−47.6	−44.2	−55.3	−41.7	−33.8
ethyne + butadiene	−59.3	−61.7	−63.5	−60.7	−62.6	−64.4	−61.0	−66.6	−58.5	−71.3	−58.7	−51.1
ethene + cyclopentadiene	−30.0	−29.7	−29.1	−30.4	−29.5	−29.3	−28.1	−29.1	−27.2	−36.7	−23.7	−17.5
ethyne + cyclopentadiene	−33.1	−33.4	−33.1	−33.6	−33.0	−33.4	−30.9	−35.2	−29.0	−40.3	−28.1	−22.5
ethene + cyclohexadiene	−36.5	−37.8	−38.0	−38.9	−37.8	−37.3	−36.2	−36.8	−34.4	−44.7	−30.8	−25.7
ethyne + cyclohexadiene	−48.2	−49.3	−50.5	−51.0	−49.4	−49.3	−47.1	−51.1	−43.9	−56.2	−43.0	−38.1
furan + maleic anhydride (endoproduct)	−14.4	−12.3	−12.0	−14.6	−11.1	−11.3	−10.3	−8.9	−7.4	−17.7	−2.5	0.9
furan + maleic anhydride (exoproduct)	−16.2	−13.8	−13.9	−16.3	−12.8	−13.1	−12.2	−11.1	−9.6	−19.8	−4.1	−0.7
furan + maleimide (endoproduct)	−17.2	−14.9	−14.9	−17.4	−13.9	−14.2	−13.1	−11.7	−10.1	−20.1	−5.4	−2.1
furan + maleimide (exoproduct)	−19.2	−16.6	−17.0	−19.3	−15.8	−16.1	−15.2	−14.2	−12.5	−22.4	−7.2	−4.0
cyclopentadiene + maleic anhydride (endoproduct)	−31.6	−30.9	−31.0	−35.2	−30.5	−30.6	−29.4	−27.4	−26.6	−37.1	−21.5	−17.9
cyclopentadiene + maleic anhydride (exoproduct)	−32.1	−31.3	−31.4	−35.5	−30.9	−31.1	−29.9	−28.2	−27.2	−37.8	−22.2	−18.8
cyclopentadiene + maleimide (endoproduct)	−34.1	−33.1	−33.4	−37.6	−32.9	−33.1	−31.8	−29.9	−29.0	−39.2	−24.2	−20.7
cyclopentadiene + maleimide (exoproduct)	−34.4	−33.5	−33.8	−37.8	−33.3	−33.6	−32.3	−30.6	−29.5	−39.7	−24.7	−21.5
MSE		0.4	0.1	−1.7	0.7	0.4	1.9	1.5	4.3	−6.3	8.0	12.6
MUE[c]		1.5	1.7	1.7	2.0	2.0	2.4	3.9	4.4	6.3	8.0	12.6

functionals give positive MSEs, which means that they tend to overestimate the dissociation energies in the SIE11 database. The best performers in Table 2 are M08-HX and M06-HF, whereas the worst performers are M06-L and B97-D. The latter is not surprising because both M06-L and B97-D are local functionals (they have $X = 0$ in Table 1). As shown in Table 2, the two long-range corrected density functionals (LC-ωPBE and ωB97X-D), which both have full Hartree−Fock exchange at long-range, perform better than the screened HSE functional, which does not have Hartree−Fock exchange at long-range. And yet, despite having full Hartree−Fock exchange at long-range, ωB97X-D does not perform as well as five of the hybrid-meta GGAs, and LC-ωPBE does not perform as well as three of them.

4.2. Performance for the DC9 Database. The first case in DC9 is the energy of tautomerization of 2-pyridone to 2-hydroxypyridine, which has been shown[65] to be a difficult case for many popular density functionals, which cannot predict the correct sign of the tautomeric energy. Six of the density functionals in Table 3 predict the incorrect sign of this tautomeric energy. The long-range corrections (LC-ωPBE and ωB97X-D) and empirical dispersion corrections (as in ωB97X-D and B97-D) do not solve the problem. Only when the functionals have a high-percentage of Hartree−Fock exchange, as in M05-2X, M06−-2X, M06-HF, M08-HX, and M08-SO, can they predict the correct sign of the tautomerization energy of 2-pyridone. This is in agreement with the finding of Piacenza and Grimme[69] that only BHandHLYP (which has 50% HF exchange) gives the correct sign, whereas B3LYP ($X = 20$), PBE ($X = 0$), and BP86 ($X = 0$) predict the wrong sign.

The second system in Table 3 is the isomerization energy of C_{20}, and it is a difficult case for our M0x functionals, and most of the M0x functionals give large errors for this case. HSE and ωB97X-D give the best results for this reaction.

The third case is one of the cases in our πIE3 database,[19] and the fourth case is the reaction energy of the pericyclic addition reaction of two tetramethylethene molecules to form a octamethylcyclobutane molecule. Most of the functionals in Table 3 predict both of these reaction energies within 5 kcal/mol with the exceptions being the two local functionals (M06-L and B97-D) and the screened HSE functional, which is local at large r_{12}.

The fifth datum in Table 3 is the isomerization energy of $(CH)_{12}$ isomers, which have been shown by Schreiner et al.[70] and us[55] to be a difficult case for many popular density functionals. In the tests of Table 3, only LC-ωPBE and B97-D give large errors for this case.

The sixth case of DC9 is a very challenging isomerization of carbo-[3]-oxocabon from a monocyclic isomer, which is the ring carbo-mer of the neutral oxidized form of dihydroxycyclopropenone, to a tetracyclic isomer, which is the trioxo derivative of tricyclopropabenzene. This isomerization was first reported by Lepetit et al.[71] Most of the tested functionals give large errors for this case, and the best performer is M06-HF, which gives an error of 8 kcal/mol.

The seventh datum of DC9 is the reaction energy for the 1,3-dipolar cycloaddition between ethylene and diazomethane, and this is a less demanding case for the tested functionals. Only the local M06-L and B97-D give large errors for this case.

The eighth and ninth cases in Table 3 are polycondensation reactions, first of four Be atoms to form Be_4 and then of four S_2 molecules to form an S_8 molecule. For Be_4, the M08-HX and M08-SO density functionals give the best agreement with the reference data, whereas M06-L overestimates the exothermicity by a large margin. For S_8, the M06-2X density functional gives the best prediction, and B97-D severely underestimates the association energy.

Overall, ωB97X-D and M08-SO give the best performance for the DC9 database, whereas M06-L and B97-D are the worst performers.

4.3. Performance for Diels−Alder Reaction Energies. Johnson et al.[56] employed the DARC14 database to illustrate the delocalization errors in DFT. They concluded that the DFT errors arise primarily from the overstabilization of the conjugated reactants relative to the unconjugated products. They also showed that M05-2X (among the 12 functionals tested in their paper) gives the best performance for Diels−Alder reactions. This is consistent with the results in Table 3, where M08-SO (which was not included in their analysis) and M05-2X give the best performance. The slight difference between our MUE for M05-2X and that of Johnson et al.[56] is due to the different basis sets employed.

Table 5. Performance of Density Functionals for the Reaction Energies of the ALK6 database (kcal/mol)

	reference	M06-2X	LC-ωPBE	M05-2X	ωB97X-D	HSE	M08-SO	M08-HX	M06	M06-HF	B97-D	M06-L
$C_6H_6\cdots Li^+ \rightarrow C_6H_6 + Li^+$	38.4	41.2	41.3	42.7	38.5	40.3	42.1	43.5	36.1	49.1	47.7	34.6
$C_6H_6\cdots Na^+ \rightarrow C_6H_6 + Na^+$	25.0	26.3	25.4	27.3	25.2	25.2	27.1	27.9	22.4	31.7	32.1	21.8
$C_6H_6\cdots K^+ \rightarrow C_6H_6 + K^+$	19.2	19.7	17.6	20.0	18.7	17.8	20.1	20.5	16.7	22.7	21.3	16.6
$Li_8 \rightarrow 4\ Li_2$	83.2	83.0	84.6	83.3	78.3	90.8	86.6	80.8	78.5	77.1	81.1	88.3
$Na_8 \rightarrow 4\ Na_2$	54.6	54.6	52.1	51.9	51.5	53.8	54.4	51.5	57.2	49.3	45.2	70.0
$K_8 \rightarrow 4\ K_2$	47.1	49.0	45.8	46.5	43.4	45.3	51.6	48.7	53.8	44.7	32.6	65.8
MSE		1.1	−0.1	0.7	−2.0	1.0	2.4	0.9	−0.5	1.2	−1.3	4.9
MUE		1.1	1.7	1.8	2.1	2.3	2.5	2.8	3.6	5.8	7.4	8.1

Table 6. Additional Density Functionals for Which Calculations Are Reported Here

name	year	ref	meta?	hybrid?	X	-D?
B3PW91	1993	72	no	global	20	no
B98	1998	73	no	global	21.98	no
VS98	1998	74	yes	no	0	no
PBE0	1999	75, 76	no	global	25	no
τ-HCTHh	2002	77	yes	global	15	no
TPSSh	2003	59	yes	global	10	no
TPSS1KCIS	2005	58, 78	yes	global	13	no
B97−3	2005	79	no	global	26.93	no
M05	2005	18	yes	global	28	no

Table 7. Previously Tested Density Functionals Included in the Present Comparisons

name	year	ref	meta?	hybrid?	X	-D?
BLYP	1988	80, 81	no	no	20	no
B3LYP	1994	82	no	global	21.98	no
PBE	1996	83	no	no	0	no
TPSS	2003	58	yes	no	25	no
B2PLYP	2006	84	no	global	53(27)[a]	no
BLYP-D	1988	53	no	no	20	yes
B3LYP-D	1994	53	no	global	21.98	yes
PBE-D	1996	53	NO	no	0	yes
TPSS-D	2003	53	yes	no	25	yes
B2PLYP-D	2006	53	no	global	53(27)[a]	yes

[a] The value in parentheses is the fraction of local correlation energy that is replaced by a nonlocal second-order perturbation energy term.

4.4. Performance for the ALK6 Database. Grimme et al.[44] have shown that some density functionals with empirical dispersion corrections significantly overbind alkali-metal-cation−benzene complexes, as seen in the large error of B97-D for the $C_6H_6\cdots Li^+$ complex (Table 5). Table 5 shows that M06-HF also severely overbinds these complexes, and M06-L strongly overestimates the dissociation energies of the alkali metal clusters: $M_8 \rightarrow M_2$ (M = Na, K). Among the tested functionals, M06-2X, LC-ωPBE, and M05-2X give good performance for both kinds of data, and they have small MUEs (less than 2 kcal/mol) for the ALK6 database. The ωB97X-D density functional also gives a small MUE of 2.1 kcal/mol, which is less than the MUEs of the other dispersion-corrected methods.

4.5. Overall Performance. To keep the discussion to a reasonable length while still illustrating in detail the variation in results that can be obtained with various density functionals, we singled out 11 density functionals for detailed discussion in sections 4.1−4.4. But we have also made calculations for nine other density functionals, and in this section, we compare the mean errors for these functionals to those for the functionals already discussed and to those for 10 density functionals tested by Georigk and Grimme.[14] This affords a comparison of 30 density functionals for the four reaction energy databases.

The nine additional density functionals[18,59,72−79] for which we carried out calculations are characterized in Table 6, which has the same format as Table 1. Eight of these functionals were selected because, along with M06, M05, and M06-L, they had the best performance (out of 34 density functionals tested) for the recent tests[43] of density functionals against a broad catalytic energies database. (Functionals with more than 28% nonlocal exchange at all or small interelectronic separations were not included in those tests.)

Finally, our comparisons include 10 of the density functionals studied by Grimme and co-workers.[14,44,53] These consist of four standard density functionals, BLYP,[80,81] B3LYP,[82] PBE,[83] TPSS,[58] and B2PLYP,[84] plus each of these functionals with an empirical dispersion correction. The dispersion term in these functionals, like that in B97-D, is Grimme's second generation version[53] (sometimes[44] called D2), but an important difference from B97-D is that the parameters of B97-D were optimized in the presence of dispersion, but in the five dispersion-corrected density functionals in Table 7, the parameters were not reoptimized when dispersion was added.

B2PLYP deserves a special note because it is considered here to illustrate the effect of a third way to include a dependence on the SCF orbitals. In particular, B2PLYP includes a post-SCF term that depends on the unoccupied orbitals; it has the form of a second-order perturbation approximation to the dynamical correlation energy, although the first-order term, which does not vanish unless Hartree−Fock orbitals are used,[85] is not included (note that the Hartree−Fock SCF orbitals and the Kohn−Sham orbitals are both functionals of the same exact density). Functionals that include nonlocal correlation terms as well as nonlocal Hartree−Fock exchange are called doubly hybrid. For practical work, it is important to note that the doubly hybrid B2PLYP and B2PLYP-D methods have higher cost, steeper dependence of cost on system size, and greater basis set dependence than the other density functionals considered in Table 8.

The mean unsigned errors and average mean unsigned errors of all 30 density functionals of Tables 1, 6, and 7 are given in Table 8.

For perspective, we review the effects of empirical dispersion corrections for the performance of the approximate density functionals by first considering the comparison of the MUEs of B3LYP to those of B3LYP-D. From Table 8, we can see that

Table 8. Mean Unsigned Errors for all Four Databases (kcal/mol)

method	DARC14	SIE11	DC9	ALK6	AMUE[a]
M08-SO	1.5	4.8	5.0	2.5	3.4
M08-HX	2.0	3.9	5.6	2.8	3.6
M06−2X	2.4	5.3	2.7	1.1	3.7
ωB97X-D	2.0	7.1	4.3	2.1	3.9
M05−2X	1.7	6.0	6.2	1.8	3.9
B2PLYP-D[b]	3.7	4.6	5.5	4.4	4.5
M06-HF	1.7	3.9	8.2	5.8	4.9
M06	4.4	7.2	7.5	3.6	5.7
HSE	3.9	7.9	9.4	2.3	5.9
LC-ωPBE	6.3	4.9	11.1	1.7	6.0
PBE0	3.6	7.7	10.3	2.3	6.0
B2PLYP[b]	7.8	4.7	7.7	4.2	6.1
M05	5.4	6.9	10.4	1.8	6.1
B3PW91	6.9	7.9	9.7	3.2	6.9
B97−3	8.7	7.3	9.2	3.9	7.3
B98	8.3	8.3	8.4	4.1	7.3
τ-HCTHh	7.8	9.4	8.9	3.3	7.3
TPSSh	8.2	9.2	10.4	2.1	7.5
TPSS-D[b]	3.7	11.6	8.7	7.2	7.8
PBE-D[b]	2.8	12.6	9.9	6.8	8.0
TPSS1KCIS	9.8	8.6	11.8	2.8	8.2
PBE[b]	6.8	12.6	10.8	2.8	8.2
B3LYP-D[b]	7.6	8.1	9.9	8.2	8.5
TPSS[b]	11.1	10.7	12.3	2.3	9.1
M06-L	8.0	10.5	11.5	8.1	9.6
B97-D	12.6	11.1	14.0	7.4	11.3
B3LYP[b]	15.4	7.6	15.1	9.1	11.8
BLYP-D[b]	14.0	12.2	14.5	9.0	12.4
VS98	6.8	9.3	16.6	24.2	14.2
BLYP[b]	22.9	11.7	20.3	10.8	16.4

[a] Average of MUEs for the DARC14, SIE11, DC9, and ALK6 databases. [b] Results for these functionals are taken from previous studies,[14,44] and all DFT-D methods are the DFT-D2 versions of Grimme et al.[44,53]

empirical dispersion corrections improve the performance of B3LYP for the DARC14 and DC9 databases by a large margin but slightly deteriorate the performance for the SIE11 and ALK6 databases. This trend can also be seen in the other four pairs of functionals involving the methods of Table 7. Although the empirical dispersion correction does not improve upon the SIE11 and ALK6 databases, and although the empirical dispersion correction can lead to unphysical results in some cases, adding a molecular mechanics term does show some improvement in the performance of density functionals that are not accurate for medium-range correlation energy.

Next, consider the results for the functionals of Table 6 for the individual databases in Table 8. The best performance for the reaction energies sensitive to self-interaction error is obtained with M05 and PBE0, with MUEs of 6.9 and 7.7 kcal/mol, as compared to 3.9 kcal/mol for M08-HX and M06-HF. However, PBE0 and M05 have MUEs of 10.3 and 10.4 kcal/mol for the DC difficult cases database. For DC9, the best performance of the Table 6 density functionals is obtained by B98 with an MUE of 8.4 kcal/mol, in comparison to 4.3 and 5.0 kcal/mol for the

ωB97X-D and M08-SO density functionals, respectively. For the Diels−Alder reactions, PBE0 and M05 do the best of the functionals in Table 6, with MUES of 3.6 and 4.4 kcal/mol, as compared to 1.5−1.7 kcal/mol for M08-SO, M05-2X, and M06-HF, whereas B98 has an MUE of 8.3 kcal/mol; in fact, the MUE of B98 is remarkably constant at 8.3−8.4 kcal/mol for SIE11, DC9, and DARC14.

For the ALK6 reaction energy database, M05 and PBE0 are again the best of the functionals in Table 6, with MUEs of 1.8 and 2.3 kcal/mol, as compared to 1.1−1.8 kcal/mol for M06-2X, LC-ωPBE, and M05-2X.

The AMUEs in Table 8 are averages over all four reaction energy databases, and they show that M08-SO, M08-HX, and M06-2X give the best overall performance for the reaction energies considered in this article, with average mean unsigned errors of 3.7 kcal/mol or less. The comparison of the two global-hybrid meta GGAs that satisfy second-order constraints (as discussed above) shows an AMUE of 3.4 kcal/mol for M08-SO and 7.5 kcal/mol for TPSSh.

Casting a wider net and looking at the top nine entries in Table 8 (as in Tables 2−5, the density functionals are listed in Table 8 in order of increasing mean unsigned errors), we see that six Minnesota hybrid meta functionals plus ωB97X-D, B2PLYP-D, and HSE give the best performance, with average mean unsigned errors of 5.9 kcal/mol or less.

5. CONCLUSIONS

It is important to validate practical density functional approximations in order to ascertain the reliability of their predictive capabilities in many areas of chemistry. Here, we have performed benchmark calculations aimed at testing the M0x functionals against some recently developed databases of reaction energies that are challenging for popular density functionals and are outside the fitting data of the M0x functionals and most or all other functionals. We placed a special emphasis on comparing the recent Minnesota meta and hybrid meta functionals, range-separated functionals, functionals with empirical dispersion corrections, functionals that performed well on a recent test for energetic quantities relevant to catalysis, and global-hybrid meta-GGA functionals accurate to second order in the gradient expansion.

The examination of these reaction energies has allowed us to identify some especially problematic cases: (1) In the database of reaction energies sensitive to self-interaction error, the energy of isomerization of ClFCl to ClClF is a challenging case. Only LC-ωPBE predicts the correct sign for it. (2) M08-HX performs the best for the SIE11 database, but it gives large errors for the dissociation energies in NaOMg and FLiF. (3) In the DC9 database, the isomerization energy of $(C_{20})_{cage}$ to $(C_{20})_{bowl}$ and the isomerization energy of carbo-[3]-oxocarbon from monocycle to tetracycle are difficult cases for the M0x functionals. (4) In the alkali metal database, M06-HF severely overbinds alkali-metal-cation−benzene complexes, and M06-L strongly overestimates the dissociation energies of the alkali metal clusters: $M_8 \rightarrow M_2$ (M = Na, K). (5) Empirical dispersion corrections improve the performance of approximate density functionals for the DARC14 and DC9 databases by a large margin but slightly deteriorate the performance for the SIE11 and ALK6 databases.

The final average mean unsigned error (AMUE) provides an overall assessment, averaged over the four databases. M08-SO, M08-HX, M06-2X, ωB97X-D, and M05-2X give the overall smallest AMUEs.

The generally good success of the most recent hybrid meta density functionals, especially M06-2X, M06-HX, and M08-SO, is very encouraging, as is the success of the range-separated and dispersion-corrected ωB97X-D density functional. The hybrid meta functionals were developed by a combination of satisfying constraints such as the uniform electron gas limit and the second-order gradient expansion and by fitting parameters to experimental and high-quality theoretical reference data, and they have previously been shown to perform well in many cases outside their training set, including several cases where popular older functionals fail. The ωB97X-D functional, also optimized by a parameter-fitting strategy, achieves almost as good performance in the present tests by a different route, namely, range separation and empirical dispersion rather than employing kinetic energy density.

■ ASSOCIATED CONTENT

ⓢ Supporting Information. Full results for the density functionals of Table 6. This material is available free of charge via the Internet at http://pubs.acs.org.

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