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

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Abstract. Thirty-four density functional approximations are tested against two diverse databases, one with 18 bond energies and one with 24 barriers. These two databases are chosen to include bond energies and barrier heights which are relevant to catalysis, and in particular the bond energy database includes metal-metal bonds, metal-ligand bonds, alkyl bond dissociation energies, and atomization energies of small main group molecules. The RPBE and revPBE functionals, widely used for catalysis, do improve the performance of PBE against the two diverse databases, but give worse results than B3LYP. Our results show that the Minnesota functionals, M05, M06, and M06-L give the best performance for the two diverse databases, which suggests that they deserve more attention for applications to catalysis. We also obtain notably good performance with the τ-HCTHhyb, ωB97X-D, and MOHLYP functionals.

1. INTRODUCTION

All widely used density functional approximations (usually called density functionals) have parameters or involve an experience-based choice of constraints, and their accuracy is best determined by validation studies. We have performed a large number of such studies, as have other workers; a review limited to transition metal chemistry cites over 40 recent such studies in that subfield alone.[1] In order to facilitate validation studies, we have developed a number of "representative" databases, where such a database represents a subset of a larger database that has been shown statistically to yield similar mean signed errors (MSEs), mean unsigned errors (MUEs), and root mean squared errors (RMSEs) as are obtained with a larger, more diverse database.[2] Examples of such representative databases are AE6, consisting of six main-group atomization energies representative of a larger set of 109,[2] TMAE4, consisting of four transition metal dimer atomization energies representative of a larger set of 9,[3] MLBE4, consisting of four metal-ligand bond energies representative of a larger set of 21,[4] and DBH24, consisting of 24 diverse barrier heights representative of a larger set of 82 chemical reaction barrier heights.[5]

Some tests of density functionals against the representative databases have already been reported.[2-6] We originally tested 42 density functionals against TMAE4[3] and later added 9 more to the list.[6] The original tests with the MLBE4 database included 57 density functionals,[4] and a later study added 9 more to the list.[6] In the original article reporting the DBH24 database, it was tested against 67 density functionals. In these tests, however, two density functionals that have been popular for catalysis applications, in particular revPBE[7] and RPBE,[8] were not included. The RPBE article has been cited more than 1000 times so only a few representative references are selected for citation here.[9–25] Representative references for the revPBE functional may also be consulted,[9,14,22,26–28] and we note that when they have been applied to the same problem, these two functionals usually give similar results.[1,9,14,22] In the present article,

we have tested these two functionals (and 32 others—see section 2) against the AE6, TMAE4, MLBE4, and DBH24 databases, plus one additional database explained next, and we present the results. The additional database added to the ones already mentioned is the ABDE4 database that contains four alkyl bond dissociation energies. The reason for adding this is that it has been shown that the performance of many density functionals degrades when the molecule becomes larger[6,29–41] so it is important to test the performance of functionals not just for the smallest homologs. The ABDE4 database contains four alkyl bond dissociation energies, two for methyl groups and two for isopropyl groups, with two nonpolar bonds and two polar bonds, and although it was not obtained as a statistically representative database, we have found, following the work of Izgorodina et al.,[29] that it provides a qualitatively representative test of the errors one encounters on going to large molecules.[36,42] Combining this database with AE6, TMAE4, and MLBE4 yields a new database of 18 diverse bond energies that we call DBE18. Our test of density functionals will include both DBE18 and DBH24. To put the results in context we also present tests against these databases of several other functionals that are also often used for catalysis and some newer functionals, not yet popular for catalysis applications—but perhaps they should be.

The purpose of the present article is to provide a systematic test of density functionals that might be considered for catalysis against representative databases of main-group and transition-metal bond energies and barrier heights to ascertain which functionals have good overall performance and what is the typical error to be expected in applications. We test 34 functionals, 7 from our own group and 27 from other groups.

II. FUNCTIONALS STUDIED

The functionals[4,7,8,36,42–72] for which we present tests in this article are listed in chronological order of their development in Table I, which also gives their year of origin and two of their characteristics, in particular X, which is the percentage of Hartree-Fock

exchange energy (as calculated with self-consistently optimized Kohn-Sham orbitals obtained with the same value of X), and—in the last column—whether or not the functional depends on up-spin kinetic energy density and down-spin kinetic energy density. All functionals in the table depend on the reduced gradients of the spin densities as well as the spin densities themselves. Functionals that include neither kinetic energy density nor Hartree-Fock exchange are called GGAs. Those functionals including kinetic energy density are called meta-GGAs, those including Hartee-Fock exchange are called hybrid GGAs, and those including both are called hybrid meta-GGAs. It is worthwhile to express the reasons for inclusion of some of these functionals in the present study, and the rest of this section provides that background.

BP86, a combination of Becke's 1988 exchange functional and Perdew's 1986 correlation functional, although old, still retains a loyal user group in the organometallic community.[73] The original version of BP86 used Becke's 1988 exchange functional,[44] and the correlation functional is composed of Perdew's 1986 local spin density approximation and approximation to the gradient contribution.[43] A newer version, called BVP86 in the *Gaussian* program[74,75] and called Becke-Perdew in the *ADF* program,[76] uses Becke's 1988 exchange functional,[44] Vosko et al.'s functional V for local spin density part of the correlation functional,[45] and Perdew's 1986 approximation for the gradient contribution to correlation.[43]

The LYP correlation functional is a simplification of the Colle-Salvetti correlation energy formula[77] with second order gradient expansion. It contains four parameters which were determined by fitting the correlation energy of helium atom. Unlike other GGA correlation functionals, the LYP functional does not reduce to the correct limit for a uniform electron gas. When combined with Becke's 1988 exchange functional, the resulting BLYP functional is a very widely used GGA functional in the chemistry community. The B3LYP functional, which is the most widely used functional in the chemistry community, was constructed by including 20% of the Hartree-Fock exchange

and adjusting the gradient contribution to both the exchange and correlation.[48,49] Note that the version of B3LYP used here employs Vosko et al.'s functional III[45] for the local spin density part of the correlation functional, as in the originally defined version of the functional,[49] whereas some other programs employ Vosko et al.'s functional V, so B3V5LYP[50] is also tested and compared with B3LYP in the present study.

The PW91 functional, based on B88 exchange, was developed to satisfy several constraints. However, it is very complicated. The PBE functional was developed by using a simpler ansatz for the exchange part; the parameters in the PBE functional were obtained by forcing the functional to satisfy chosen constraints. The PW91 and PBE functionals are widely used in the physics and surface science communities.

The revPBE and RPBE functionals are discussed in the introduction, and they represent attempts to improve the PBE functional. The revPBE functional was constructed by optimizing one parameter of the PBE functional against the exchange energy of noble gas atoms from He to Ar.[7] It improves the atomization energies and chemisorption energies over the PBE functional. The RPBE functional[8] gives nearly the same chemisorption energies as the revPBE function, without any fitting of parameters.

PBE0 (also called PBE1, PBE1PBE, and PBEh, but not to be confused with the functional called PBEh in *Gaussian09*[75]) represents an empirical attempt to improve the PBE functional for molecules by including 25% Hartree-Fock exchange. PBEsol, in contrast, was constructed to restore the correct second order expansion for the exchange energy and was designed for solids. PBEsol improves the equilibrium properties of solids and their surfaces over PBE, but it is not designed to be broadly accurate.

PBEhole (called PBEh in *Gaussian09*) is a functional in which a GGA hole model replaces the PBE exchange functional, retaining PBE correlation. PBEhole was constructed by modeling the exchange hole to reproduce and rationalize the exchange energy of the PBE functional.

WC06[65] (which was designed with solids as a target application) was an attempt to make PBE valid through fourth. It does not accomplish this,[78] but it has had some empirical success for lattice constants, crystal structures, and metal surface energies.[65]

Finally, SOGGA was a recent attempt to illustrate some fundamental issues in DFT, namely the effect of a tight Lieb-Oxford bound and the second-order term in the gradient expansion; although not designed as a broadly accurate functional, it has had some empirical success.[69,79]

We include two representatives from a long line (B97, B98, HCTH, B97-1, B97-2, B97-3) of closely related hybrid GGAs developed by Becke, Handy, and Tozer and their coworkers,[52,63,80–83] namely B98[52] and B97-3[63] because they have the best average performance for bond energies and barrier heights.

Functionals discussed so far are GGAs and hybrid GGAs. In an effort related to the B97/HCTH series just discussed, a meta-GGA called τ-HCTH and two hybrid meta-GGAs called τ-HCTHhyb and BMK, were developed by Boese, Handy, and Martin[58,62] (Boese and Handy[58] also discuss an earlier meta-GGA developed by Becke in 1998,[84] which they label B98, which can be confusing because the label B98 has subsequently become associated in the literature with the 1998 hybrid GGA of Schmider and Becke,[53] and it is in that sense that we use B98 above and in our other papers). Note that τ-HCTHhyb is obtained by introducing 15% Hartree-Fock exchange into τ-HCTH and re-optimizing the other parameters.[57] The BMK functional was developed with the aim of obtaining good results for barrier heights; it includes the kinetic energy density and Hartree-Fock exchange. The meta-GGA functional VS98 was constructed based on the density matrix expansion. VS98 was found to perform well for atomization energies, and in some tests,[53] it even performs slightly better than the popular B3LYP functional, which is a significant accomplishment because—unlike B3LYP—VS98 has no Hartree-Fock exchange. VS98 is also reviewed by Scuseria and Staroverov.[85]

In order to provide a good overview of the capabilities of meta-GGAs and hybrid meta-GGAs, we also include three more meta-GGAs, namely TPSS, TPSSKCIS, and M06-L, and four more hybrid meta-GGAs, namely TPSSh, TPSS1KCIS, M05, and M06. TPSS includes the kinetic energy density τ into the exchange and correlation functional forms in way designed to satisfy a chosen set of constraints and improve the equilibrium geometries of molecules.[58] TPSSKCIS is a combination of TPSS exchange and the earlier KCIS correlation that was based on a model electron gas with a HOMO-LUMO gap.[59] TPSSh[60] and TPSS1KCIS[62] are obtained by including 10% and 13% Hartree-Fock exchange into TPSS and TPSSKCIS, respectively. M05, M06-L, and M06 represent the recent Minnesota family of density functionals that were developed using a combination of constraint satisfaction and parameter optimization and were designed to be broadly accurate[86] (the other Minnesota functionals[6,36,87] are not recommended for transition metals and other systems with high multireference character and so are not included here, even though they perform better for transition metals than some of the functionals included here).

A recent trend in density functional theory is adding an empirical molecular mechanics term to account for dispersion; this is indicated by "-D" or "plus D". We will test two such functionals here: B97-D and ωB97X-D. B97-D[66] includes empirical damped atom-pairwise dispersion terms into the GGA functional form used in B97. The functional ωB97X-D introduces empirical damped atom-pairwise dispersion terms into a functional containing range-separated Hartree-Fock exchange.[70] In the particular kind of range separation used in ωB97X-D, the long-range exchange is treated as Hartree-Fock exchange, and the short-range part is treated by a hybrid density functional approximation; this is sometimes called a long-range-corrected hybrid.

Another long-range-corrected hybrid that we test is LC-ωPBE,[67] which does not contain empirical dispersion terms; this functional may be considered to be yet another

way to improve PBE. The short-range exchange is PBE exchange; the long-range exchange is Hartree-Fock exchange, and the correlation is PBE correlation.

An alternative kind of range separation is to treat long-range exchange by a density functional approximation and short-range exchange as Hartree-Fock exchange. This is sometimes called screened exchange, and it is the method used for exchange in the HSE functional,[71,72] We examine the recommended form of this functional, which includes the modifications of Henderson et al.;[72] the HSE functional uses the PBE functional for correlation. Several range-separated-hybrid functionals were tested for geometric and energetic properties of transition metal complexes in a recent study.[88] Here we tested three range-separated-hybrid functionals (LC-ωPBE, ωB97X-D, and HSE) against databases for more diverse bond energies and barrier heights. Since several of the functionals use the PBE correlation functional, it is worthwhile mentioning that the PBE correlation functional is very similar to the earlier PW91 correlation functional.

MOHLYP and MPWLYP1M are selected for study here because of their previously demonstrated[4] relatively high accuracy for transition metal bond energies. MOHLYP was constructed by modifying the OptX exchange functional[89] to satisfy the uniform electron gas limit and optimizing against transition metal systems. The correlation part of MOHLYP uses half-LYP correlation (HLYP) instead of LYP correlation. MPWLYP1M was obtained by mixing 5% Hartree-Fock exchange to the mPWLYP functional, which is a combination of the mPW exchange and LYP correlation functionals. A recent paper[5] indicated that MOHLYP barrier heights are very accurate; but the functional called MOHLYP in that reference is not the same as the original (true) MOHLYP functional. The correct mean errors for MOHLYP barrier heights are given in the present article, along with the errors for bond energies.

III. DATABASES

We consider eight databases, in particular seven databases selected to make them representative[2] of larger databases plus the ABDE4 database to include some larger molecules. All eight databases were presented in detail previously.[2-5, 29, 42, 90] AE6 has six atomization energies, all for main-group compounds, in particular, glyoxal, propyne, cyclobutane, SiH_4, SiO_2, and S_2.[2] ABDE4 contains four alkyl bond dissociation energies, in particular the dissociation energies of the following bonds: $H_3C–CH_3$, $H_3C–CH(CH_3)_2$, $H_3CO–CH_3$, and $CH_3O–CH(CH_3)_2$.[29,42] TMAE4 has four transition metal atomization energies; it consists of the bond energies of four diatomic molecules, Cr_2, Cu_2, V_2, and Zr_2.[3] MLBE4 has four metal-ligand bond energies, all involving transition metals, in particular, $CrCH_3^+ \rightarrow Cr^+ + CH_3$, $Fe(CO)_5 \rightarrow Fe + 5CO$, $NiCH_2^+ \rightarrow Ni^+ + CH_2$, and $VS \rightarrow V + S$.[4] HATBH6 contains six barrier heights for heavy-atom transfer reactions (here "heavy atom" is used with the usual quantum-chemistry-literature meaning of "heavier than helium");[5,90] NSBH6 contains six barrier heights for nucleophilic substitution reactions;[5,90] UABH6 contains six barrier heights for unimolecular and association reactions;[5,90] and HTBH6 contains six barrier heights for hydrogen transfer reactions.[2] For each of these four component databases, the reactions were selected as described elsewhere[2,90] to be statistically representative of a larger database.

The four bond energy databases are combined into a merged database DBE18, which contains 18 diverse bond energies. The mean errors for DBE18, which is newly formed in the present article, consist of a 6/18:4/18:4/18:4/18 weighting of those for AE6, ABDE4, TMAE4, and MLBE4 (alternatively, it can be considered to be an unweighted combination of the 18 molecules in these four representative databases). The four barrier height databases are combined into DBH24,[5, 90] which contains 24 diverse barrier heights. Each of the 24 barrier heights has a weight of 1/24. We use version 08[5] of DBH24.

IV. COMPUTATIONAL DETAILS

All calculations were carried out with *Gaussian03*,[74] locally modified versions of *Gaussian03*,[91] and *Gaussian09*.[75]

We used the spin-restricted formalism for closed-shell molecules and atoms and the spin-unrestricted formalism for open-shell systems with one exception, namely singlet Cr_2, for which the spin-unrestricted formalism is used to describe the antiferromagnetic interaction between two Cr atoms. In some cases, we were able to obtain lower energies by allowing the orbitals of metal atoms to break symmetry by requesting the HOMO and LUMO be mixed to destroy spatial symmetries. Ultrafine grids were used for all DFT calculations.

The TZQ (triple zeta quality) basis set[3, 4] was used for TMAE4 and MLBE4, and the geometries were optimized for the given density functional in every case. For AE6 we used QCISD/MG3 geometries.[2] The MG3 basis set[92] is the same as 6-311++G(3d2f,2df,2p) for H-Si and is an improved version of the basis for P-Ar. For ABDE4, single-point calculations were done with 6-311+G(3df, 2p) basis set at B3LYP/6-31G(d) geometries. These calculations of DBH24 were all carried out with the MG3S basis set[93] at QCISD/MG3 geometries. The MG3S basis set is the same as the MG3 basis set except that diffuse functions are removed on hydrogen atoms.

For WC06, the bond energies of V_2, VS, and $NiCH_2^+$ were obtained by post-SCF calculations with PBEsol densities due to convergence problems for V(S = 5/2) and Ni^+(S = 1/2). This approach was validated by applying the same procedure to SOGGA, and the difference between the SCF and post-SCF energies for SOGGA averaged only 0.01 kcal/mol. All calculations presented in this paper are full SCF calculations except for the WC06 calculations of the atomic states V(S = 5/2) and Ni^+(S = 1/2) and the associated bond energies of V_2, VS, and $NiCH_2^+$.

Spin-orbit energies were added as post-SCF corrections for species with first-order spin-orbit effects.[3,4,90] Note that the spin-orbit contributions vanish for closed-

shell species, atoms in *S* states, molecules in Σ states, and singlet and doublet molecules in *A* and *B* states. Thus, for example, there are no spin-orbit contributions in the calculations on the ABDE4 database (the ground state of CH_3O is $^2A'$).

V. RESULTS

All functionals predict the ground states of Cr, Fe, Cu, Cr^+, Ni^+ correctly ($S = 3$, 2, 1/2, 5/2 and 1/2, respectively). The experimental ground state of the V atom is $S = 3/2$ ($4s^2 3d^3$), and the experimental ground state of the Zr atom is $S = 1$ ($4s^2 3d^2$), but these are not predicted correctly by all functionals; the ground states of V and Zr atoms predicted by the various functionals are shown in Table S2 in the supporting information.[94] This means that there are two choices for computing the bond energy (V_2, Zr_2, or VS) where breaking a bond yields V or Zr; one can compute it relative to the calculated energy of the experimental atomic ground state or one may compute it relative to the calculated atomic ground state. And we test both choices.

Mean errors for bond energies are given in Table II. For this table, we computed the bond energies of V_2, Zr_2, and VS and calculated the mean signed error (MSE) and mean unsigned error (MUE) for TMAE4 and MLBE4 databases in both of the ways mentioned in the previous paragraph. The MSE and MUE of each functional calculated in both ways are presented in Table II. The values before "/" are calculated by using the calculated atomic ground states; the values after "/" are calculated by using the experimental atomic ground states (when the MSE and MUE calculated by these two methods are the same, only one value is presented), and the final results for DBE18 are averages over the two methods.

VI. DISCUSSION

The performance of the various functionals is judged by their mean unsigned errors (MUEs), which represent the average absolute deviations from the best estimates in the databases. To illustrate whether there is a systematic trend of overestimating or underestimating bond energies and barrier heights, the tables also show mean signed errors (MSEs).

Table II shows the results for bond energies. For AE6, about half of the functionals considered here have mean unsigned errors per bond of one kcal/mol or less, a target often labeled as "chemical accuracy," with best accuracy of 0.4 kcal/mol achieved by BMK, M05, B97-D, and ωB97X-D. The other three bond energy databases provide harder tests.

For the ABDE4 database, most functionals underestimate alkyl bond dissociation energies. The MUE of B3LYP, the most widely used functional, is 8.6 kcal/mol, while that of B3V5LYP is 9.0 kcal/mol, even larger. The WC06, PBEsol, and SOGGA functionals, all GGAs that are correct to the second order in exchange (SOGGA is also accurate to second order in correlation), overestimate the alkyl bond dissociation energies and give MUEs of 2.3, 4.2, and 5.2 kcal/mol, respectively. These three functionals perform much better than several more widely used functionals, such as B3LYP, B3PW91, and BLYP. The MUEs of revPBE and RPBE for ABDE4 are quite large, 10.5 and 11.1 kcal/mol, respectively; these values are much larger than that of the unmodified PBE functional (4.0 kcal/mol). Only four functionals have MUEs below 3.7 kcal/mol for ABDE4: BMK, 1.7; M06, 1.9; ωB97X-D, 2.2; and WC06, 2.3.

The MUEs of different functionals for the ABDE4 database suggest the importance of the second order term in the expansion of the exchange functional in powers of the reduced density gradient s, as discussed previously.[69] Zupan et al. showed that most atomic and molecular properties depend on s values in the range of $0 \leq s \leq 3$.[95] We drew the gradient enhancement factors F_X as a function of the reduced density

gradients *s* in Figure 1. It is noteworthy that the correlation functionals of the GGAs in Figure 1 are the same or quite similar to one another, so the performance of the different GGAs will mainly reflect the character of the exchange functionals. The MSEs of different GGA functionals correlate with the magnitude of the gradient enhancement factors in the range of $0 \leq s \leq 3$. For example, RPBE, which gives the largest gradient enhancement factor, has the most negative MSE (-11.1 kcal/mol), and SOGGA, which gives the smallest gradient enhancement factor, has the most positive MSE (5.2 kcal/mol). For the rest of the tested GGA functionals, the relative order of gradient enhancement factors is very similar to the relative order of MSEs for the ABDE4 database. From Figure 1, we can see that the gradient enhancement factor of a GGA functional should fall between those of PBE and WC06 if we want it to perform well for the ABDE4 database.

For meta-GGA functionals, we also drew the gradient enhancement factors as a function of the reduced density gradients *s* (see Figure S1 to Figure S3 in the supporting information).[94] However, no simple correlation between the gradient enhancement factors and the MSEs for the ABDE4 database was observed. This might be a consequence of the more flexible functional structure of the meta-GGAs. Another possible reason is that the correlation functionals in the meta-GGAs are quite different from one another, so the MSEs will not reflect only the behavior of exchange functionals.

For TMAE4 and MLBE4, hybrid functionals tend to underestimate the bond energies, while the local functionals (GGAs and meta-GGAs as well as B97-D) tend to overestimate the bond energies. Comparison of our results for these two databases to the results for the 3d reaction energy database of Furche and Perdew[96] in Ref. 88 shows that, for the functionals that the two studies have in common, reasonably consistent conclusions are drawn about the relative merits of the functionals for metal–metal and metal-ligand bonds, that is, about which functionals perform better for predicting transition metal bond energies. This is very encouraging for the validity of the

conclusions drawn in both studies. We have used the 3d reaction energy database in the past, and in those cases, we found[36, 97] that it led to similar conclusions as can be drawn from our older, larger databases.[3, 4] Here we find that similarity for the representative databases and for a greater variety of types of functionals.

Averaging the unsigned errors on all 18 bond energies (which results in DBE18), the best performance is obtained from three hybrid meta-GGAs (M06, 3.6; τ-HCTHhyb, 3.8; M05, 4.4—with all values in kcal/mol) and the M06-L meta-GGA functional, 4.0 kcal/mol. The best performance for a functional without kinetic energy density is obtained with MPWLYP1M, with an MUE of 4.8 kcal/mol. Other functionals that perform exceptionally well are the meta-GGA, VS98 (5.2), and the hybrid meta-GGA, TPSS1KCIS (5.5). RPBE and revPBE, with MUEs of 6.7 and 6.8 kcal/mol, surpass PBE (7.5), PBE0 (6.9), PBEhole (7.9), and PBEsol (12.2). The popular B3LYP has an MUE of 6.7 kcal/mol, and all other functionals in the table have MUEs of 5.2 to 9.9, except SOGGA with a MUE of 12.3 kcal/mol. It is noteworthy to mention that PBEhole, which involves modeling the exchange hole to reproduce the exchange energy of PBE, gives a MUE for DBE18 that is very similar to the MUE of PBE. We note that SOGGA was not designed to be a broadly accurate functional but rather to illustrate the performance of a functional with a tight Lieb-Oxford bound that satisfies exactly the second-order gradient expansion. We also note that PBEsol was not designed to be broadly accurate.

Table III gives mean errors for barrier heights. Again RPBE is very similar to revPBE, and PBEhole is very similar to PBE. Both revPBE and RPBE improve over PBE, but neither performs as well as the very simple MOHLYP. The best performance is by BMK (1.2), followed in order by B97-3 (1.8), ωB97X-D (1.8), LC-ωPBE (2.1), M06 (2.3), M05 (2.5), B98 (3.4), PBE0 (3.6), B3PW91 (3.7), HSE (3.8), and M06-L (4.1), where M06-L has the best performance of any functional that does not have any Hartree-Fock exchange.

Table IV averages the MUEs over DBE18 and DBH24, weighting them 1:1. Whereas Tables 1–3 are in chronological order of the development of the functionals, Table IV is in order of performance. It is encouraging that the recent functionals from the Minnesota suite show great accuracy for a broad set of databases. It is surprising how well the very simple MOHLYP functional does. The performance of τ-HCTHhyb, ωB97X-D, and B97-3 is particularly good, and for that reason we included the two best of them in the title of the article, along with RPBE and revPBE, which motivated this study, and MOLHYP, because of its surprisingly good performance. It is disappointing that RPBE and revPBE do not improve on B3LYP and also have inferior performance to MOHLYP, which also has no Hartree-Fock exchange and no kinetic energy density. Although Table IV is a useful database for judging some of the merits of density functionals for catalytic applications involving transition metals, the reader should keep in mind that other properties such as noncovalent interactions, ionization potentials, and so forth may also be important, and many such properties are tested for these functionals in previous papers.[36, 42]

As a final item of interest we examine the sensitivity to basis sets. We selected the five best performing density functionals (of this study) for barrier heights and we reran the calculations with the maug-cc-pV(T+d)Z[98] basis set. This basis set is comparable in size and quality to the MG3S basis set, but is also very different with essentially no basis functions in common. The results (with those for two other functionals mentioned at the end of the paragraph) are in Table V. The table shows that the MUEs for DBH24 obtained by the MG3S and maug-cc-pV(T+d)Z basis sets are very close to each other, with the largest deviation of 0.3 kcal/mol. The most important aspect of this table though is to show that the results are not overly sensitive to the choice of basis set. For comparison, Table V also shows two other density functionals not recommended for transition metals, M06-2X[36] and M08-SO,[87] that give particularly good performance for main-group barrier heights.

VII. Conclusions

A good density functional for catalysis should perform well for both bond energies and barrier heights. In this article, thirty-four density functional approximations are tested against two diverse databases, one with 18 bond energies and one with 24 barriers; 14 of the bond energies and all of the barrier heights were selected as statistically representative of larger databases, and the other four bond energies test how the performance changes when bond breaking produces larger radicals. The tested density functionals include GGAs, meta-GGAs, hybrid GGAs, and hybrid meta-GGAs. The final overall assessment, called average error for catalytic energies, AECE (given in kcal/mol), is averaged over the bond energies and barrier heights in order to provide a validation and quality test for applications to catalysis involving both transition metal catalysts and main-group reactants. Of the GGAs named as modified PBE functionals, RPBE and revPBE each have lower AECE, 6.5 and 6.6, respectively, than PBE (7.8); and PBEhole (8.0) and PBEsol (11.3) have higher average errors. The best performing GGA is MOHLYP, with an AECE of 6.0. Functionals found to perform better than the best GGA are five hybrid meta-GGAs (M06, 2.9; M05, 3.4; τ-HCTHhyb, 4.1; TPSS1KCIS, 5.1; and BMK, 5.8), two meta-GGAs, (M06-L, 4.0; VS98, 4.8), one range-separated-hybrid GGA with empirical dispersion (ωB97X-D, 4.1), six hybrid GGAs (B97-3, 4.3; B98, 4.7; B3PW91, 5.2; PBE0, 5.2; B3LYP, 5.4; and B3V5LYP, 5.6) and two range-separated-hybrid GGAs (HSE, 5.5; LC-ωPBE, 6.0). Among all the tested functionals, the Minnesota functionals, M06, M05, and M06-L, give the best overall performance, suggesting that they should receive more consideration for applications to catalysis.

It is observed that the performance of GGAs for the alkyl bond dissociation energy database (ABDE4) correlates with the magnitude of the gradient enhancement factor in the exchange functional.

A test of sensitivity to basis sets shows that the quality of the results for barrier heights is about the same for two very different multiply polarized triple zeta basis sets with minimal sets of diffuse functions.

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Table I. Tested density functionals

Functional	Year	Ref(s).	*X*	τ?
BP86	1988	43,44	0	no
BVP86	1988	43–45	0	no
BLYP	1988	44,46	0	no
PW91	1991	47	0	no
B3PW91	1993	44,47,48	20	no
B3LYP	1994	44,46,48,49	20	no
B3V5LYP	1994	44,46,48,50	20	no
PBE	1996	51	0	no
B98	1998	52	21.98	no
revPBE	1998	7	0	no
VS98	1998	53	0	yes
PBEhole	1998	54	0	no
PBE0	1999	55,56	25	no
RPBE	1999	8	0	no
τ-HCTH	2002	57	0	yes
τ-HCTHhyb	2002	57	15	yes
TPSS	2003	58	0	yes
TPSSKCIS	2003	58,59	0	yes
TPSSh	2003	60	10	yes
BMK	2004	61	42	yes
TPSS1KCIS	2005	58,59,62	13	yes
MOHLYP	2005	4	0	no
MPWLYP1M	2005	4	5	no
B97-3	2005	63	26.93	no
M05	2005	64	28	yes
WC06	2006	65	0	no
B97-D	2006	66	0	no
M06-L	2006	42	0	yes
LC-ωPBE	2006	67	0–100[a]	no
M06	2008	36	27	yes
PBEsol	2008	68	0	no
SOGGA	2008	69	0	no
ωB97X-D	2008	70	22.2–100[a]	no
HSE	2009	71,72	0–25[a]	no

[a]The percentage of HF exchange in these functionals is distance-dependent.

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

Functional	AE6		ABDE4		TMAE4		MLBE4		DBE18	
	MSE	MUE	MSE	MUE	MSE[c]	MUE[c]	MSE[c]	MUE[c]	AMSE[d]	AMUE[d]
BP86	3.3	3.3	-6.1	6.1	7.4/13.8	7.4/13.8	12.5/15.7	12.5/15.7	5.2	7.9
BVP86	2.6	2.6	-7.2	7.2	3.9/10.6	5.1/11.9	10.9/14.3	10.9/14.3	3.7	7.1
BLYP	-0.5	1.4	-10.5	10.5	6.6/9.5	7.0/9.9	9.6/11.1	9.6/11.1	1.6	7.0
PW91	2.7	3.2	-3.7	3.7	5.8/13.8	6.8/14.6	13.0/16.7	13.0/16.7	5.5	7.5
B3PW91	-0.2	0.6	-7.3	7.3	-20.7/-12.5	20.7/12.5	-2.6/1.0	5.7/4.2	-5.5	6.6
B3LYP	-0.6	0.7	-8.6	8.6	-16.6/-14.3	16.6/14.3	-1.6/-0.5	5.5/4.4	-5.8	6.7
B3V5LYP	-0.9	0.9	-9.0	9.0	-17.1/-14.9	17.1/14.9	-2.0/-0.9	5.7/4.7	-6.2	7.0
PBE	2.4	3.0	-4.0	4.0	5.4/13.2	6.8/14.6	12.6/16.3	12.6/16.3	5.2	7.5
B98	-0.4	0.6	-4.9	4.9	-10.5	10.5	0.0	5.3	-4.8	6.0
revPBE	-1.2	1.8	-10.5	10.5	-2.8/4.7	5.3/12.2	7.0/10.5	7.0/10.5	-0.6	6.8
VS98	0.0	0.6	-7.9	7.9	4.1/7.6	6.8/10.3	5.4/7.2	5.4/7.2	0.9	5.2
PBEhole	1.9	2.6	-4.8	4.8	4.4/12.2	8.0/15.8	12.8/16.6	12.8/16.6	4.7	7.9
PBE0	-0.1	1.1	-5.0	5.0	-22.6/-15.7	22.6/15.1	-3.3/-0.1	6.4/4.0	-5.8	6.9
RPBE	-1.7	2.0	-11.1	11.1	-2.1/4.1	4.9/10.9	6.6/9.7	6.6/9.7	-1.0	6.7
τ-HCTH	-0.3	0.7	-7.9	7.9	22.3	22.3	7.9	7.9	4.9	8.7
τ-HCTHhyb	-0.3	0.8	-4.2	4.2	4.3	5.7	2.6	5.9	0.5	3.8
TPSS	0.7	1.1	-9.4	9.4	0.2/6.4	3.3/9.5	8.6/11.7	8.6/11.7	1.1	6.1
TPSSKCIS	0.9	1.0	-8.3	8.3	1.1/6.9	3.6/9.3	9.5/12.4	9.5/12.4	1.8	6.0
TPSSh	0.0	1.3	-9.4	9.4	-10.5/-4.7	10.5/4.7	0.3/3.2	7.1/8.7	-3.4	5.9
BMK	0.1	0.4	-1.4	1.7	-38.0/-29.6	38.0/29.6	-5.3/-1.2	9.9/10.3	-8.5	10.3
TPSS1KCIS	0.0	0.7	-8.1	8.1	-13.3/-8.0	13.3/8.0	1.5/4.2	4.5/5.2	-3.5	5.5
MOHLYP	-2.1	2.2	-13.9	13.9	-2.6/0.0	5.1/7.8	4.6/5.9	4.6/5.9	-2.9	6.4
MPWLYP1M	0.1	1.0	-8.6	8.6	1.4/3.4	1.9/3.8	8.1/9.05	8.1/9.05	0.6	4.8
B97-3	-0.2	0.6	-4.6	4.6	-17.3	17.3	-3.1	8.1	-5.6	6.8

M05	0.0	0.4	-5.8	5.8	-5.9	8.3	-1.6	4.9	-3.0	4.4
WC06	5.2	5.5	1.5	2.3	8.4/19.8	8.4/19.8	17.2/22.0	17.2/22.0	9.5	9.9
B97-D	-0.1	0.4	-7.7	7.7	17.9	17.9	7.4	7.4	3.9	7.5
M06-L	0.5	0.7	-5.5	5.5	0.5	4.2	7.0	7.0	0.6	4.0
LC-ωPBE	-0.4	0.9	-4.7	4.7	-33.6/-26.5	33.6/26.5	-8.1/-4.8	10.1/6.8	-9.3	9.9
M06	0.4	0.6	-1.9	1.9	-8.9	8.9	-1.4	4.4	-2.6	3.6
PBEsol	7.3	7.3	4.2	4.2	13.6/22.9	13.6/22.9	19.4/23.6	19.4/23.6	12.2	12.2
SOGGA	7.0	7.3	5.2	5.2	10.8/21.4	11.76/22.5	19.9/24.5	19.9/24.5	12.0	12.3
ωB97X-D	-0.2	0.4	-2.2	2.2	-20.5/-19.8	20.4/19.8	-2.5/-2.2	6.1/5.8	-5.5	6.4
HSE	-0.6	0.9	-5.7	5.7	-21.9/-15.1	21.9/15.1	-4.7/-1.5	8.0/5.6	-6.3	7.2

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

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

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

[d] AMSE and AMUE are the average of MSEs and MUEs for AE6, ABDE4, TMAE4, and MLBE4 databases weighted 6/18:4/18:4/18:4/18; for TMAE4 and MLBE4 databases, the MSEs and MUEs used to compute AMSE and AMUE are chosen to be the average of the MSEs obtained by using calculated atomic ground states or using experimental atomic ground states. As explained in footnote *b*, the mean errors averaged to obtain the final average values of this table are all on a per bond basis before we average them.

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

Functional	HATBH6		NSBH6		UABH6		HTBH6		DBH24/08	
	MSE	MUE	MSE	MUE	MSE	MUE	MSE	MUE	AMSE[b]	AMUE[b]
BP86	-14.0	14.0	-7.1	7.1	-3.4	3.4	-9.2	9.2	-8.4	8.4
BVP86	-14.2	14.2	-7.0	7.0	-3.6	3.6	-9.3	9.3	-8.5	8.5
BLYP	-12.4	12.4	-7.5	7.5	-3.1	3.1	-7.8	7.8	-7.7	7.7
PW91	-13.9	13.9	-7.5	7.5	-2.8	2.8	-9.6	9.6	-8.5	8.5
B3PW91	-6.2	6.2	-2.6	2.6	-0.8	1.9	-4.4	4.4	-3.5	3.7
B3LYP	-6.7	6.7	-3.7	3.7	-1.2	1.7	-4.7	4.7	-4.1	4.2
B3V5LYP	-6.8	6.8	-3.6	3.6	-1.3	1.7	-4.6	4.6	-4.1	4.2
PBE	-13.6	13.6	-7.0	7.0	-2.9	2.9	-9.3	9.3	-8.2	8.2
B98	-4.8	4.8	-3.2	3.2	0.1	1.8	-3.9	3.9	-2.9	3.4
revPBE	-10.9	10.9	-5.8	5.8	-2.3	2.3	-6.5	6.5	-6.4	6.4
VS98	-6.9	6.9	-4.0	4.0	-0.1	1.5	-4.9	4.9	-4.0	4.3
PBEhole	-13.6	13.6	-7.4	7.4	-2.8	2.8	-9.1	9.1	-8.2	8.2
PBE0	-5.8	5.8	-2.1	2.1	-0.6	1.9	-4.6	4.6	-3.3	3.6
RPBE	-10.8	10.8	-5.9	5.9	-2.3	2.3	-6.3	6.3	-6.3	6.3
τ-HCTH	-9.2	9.2	-5.8	5.8	-0.6	2.0	-6.1	6.1	-5.4	5.8
τ-HCTHhyb	-6.2	6.2	-4.7	4.7	0.0	1.8	-4.8	4.8	-3.9	4.4
TPSS	-13.0	13.0	-7.9	7.9	-3.6	3.6	-8.2	8.2	-8.2	8.2
TPSSKCIS	-11.6	11.6	-7.7	7.7	-2.2	2.2	-7.0	7.0	-7.1	7.1
TPSSh	-10.1	10.1	-5.9	5.9	-2.8	2.9	-6.7	6.7	-6.4	6.4
BMK	-1.0	1.0	0.6	0.8	1.0	2.1	-1.1	1.1	-0.1	1.2
TPSS1KCIS	-7.8	7.8	-5.0	5.0	-1.2	1.6	-4.9	4.9	-4.7	4.8
MOHLYP	-10.2	10.2	-3.8	3.8	-3.1	3.1	-5.5	5.6	-5.6	5.7
MPWLYP1M	-11.9	11.9	-7.1	7.1	-2.8	2.8	-7.8	7.8	-7.4	7.4

B97-3	-2.3	2.5	-0.5	1.0	0.7	1.6	-2.2	2.2	-1.1	1.8
M05	-3.3	4.8	0.0	1.0	1.0	2.5	-0.6	1.7	-0.7	2.5
WC06	-15.7	15.7	-7.6	7.6	-3.4	3.4	-11.5	11.5	-9.5	9.5
B97-D	-9.4	9.4	-6.2	6.2	-1.3	1.7	-6.0	6.4	-5.7	5.9
M06-L	-5.9	6.9	-3.4	3.4	0.5	1.8	-4.1	4.2	-3.2	4.1
LC-ωPBE	1.1	2.4	2.8	2.8	1.3	2.1	-1.0	1.2	1.0	2.1
M06	-3.6	4.1	-1.6	1.6	0.5	1.9	-1.5	1.7	-1.6	2.3
PBEsol	-17.5	17.5	-7.4	7.4	-3.9	3.9	-12.7	12.7	-10.4	10.4
SOGGA	-17.0	17.0	-7.1	7.1	-3.9	3.9	-12.9	12.9	-10.2	10.2
ωB97X-D	-1.3	2.2	0.1	0.7	1.0	2.0	-2.0	2.2	-0.6	1.8
HSE	-6.1	6.1	-2.6	2.6	-0.7	1.9	-4.6	4.6	-3.5	3.8

[a] Single-point calculations with MG3S basis set based on QCISD/MG3 geometries.
[b] AMSE and AMUE are the average of MSEs and MUEs for the HATBH6, NSBH6, UABH6, and HTBH6 databases.

Table IV. Average error for catalytic energies (AECE), weighting DBE18 and DBH24 equally

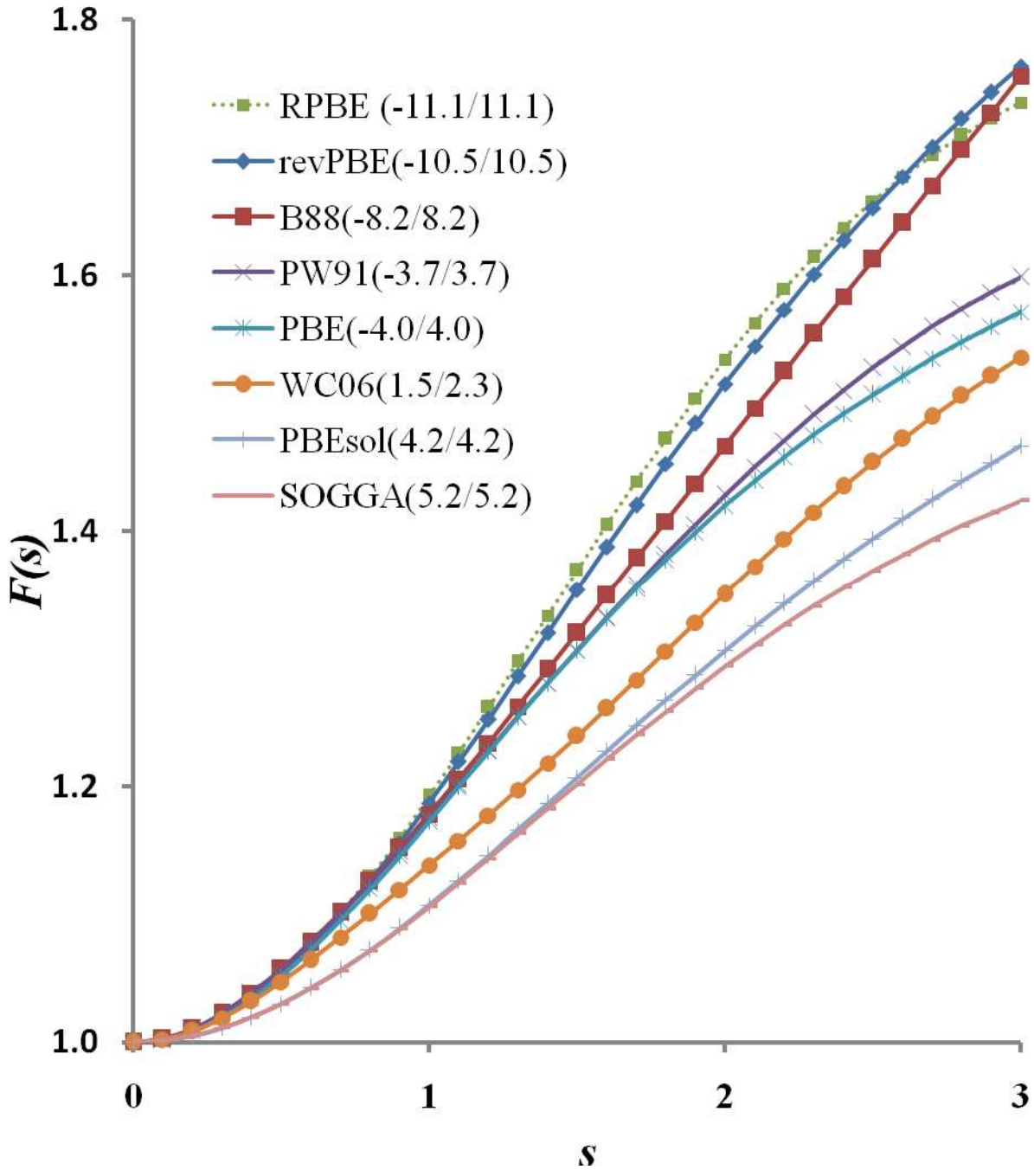
Functional	AECE	Type
M06	2.9	hybrid meta-GGA
M05	3.4	hybrid meta-GGA
M06-L	4.0	meta-GGA
τ-HCTHhyb	4.1	hybrid meta-GGA
ωB97X-D	4.1	range-separated-hybrid GGA plus D
B97-3	4.3	hybrid GGA
B98	4.7	hybrid GGA
VS98	4.8	meta-GGA
TPSS1KCIS	5.1	hybrid meta-GGA
B3PW91	5.2	hybrid GGA
PBE0	5.2	hybrid GGA
B3LYP	5.4	hybrid GGA
HSE	5.5	range-separated-hybrid GGA
B3V5LYP	5.6	hybrid GGA
BMK	5.8	hybrid meta-GGA
LC-ωPBE	6.0	range-separated-hybrid GGA
MOHLYP	6.0	GGA
MPWLYP1M	6.1	hybrid GGA
TPSSh	6.2	hybrid meta-GGA
RPBE	6.5	GGA
TPSSKCIS	6.6	meta-GGA
revPBE	6.6	GGA
B97-D	6.7	GGA plus D
TPSS	7.2	meta-GGA
τ-HCTH	7.3	meta-GGA
BLYP	7.3	GGA
BVP86	7.8	GGA
PBE	7.8	GGA
PW91	8.0	GGA
PBEhole	8.0	GGA
BP86	8.2	GGA
WC06	9.7	GGA
SOGGA	11.3	GGA
PBEsol	11.3	GGA

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

Method	HATBH6		NSBH6		UABH6		HTBH6		DBH24/08
	MSE	MUE	MSE	MUE	MSE	MUE	MSE	MUE	AMUE
MG3S									
M06-2X	0.0	0.7	0.6	0.9	0.4	1.1	-0.5	1.2	1.0
M08-SO	-0.6	1.1	0.2	0.7	0.2	1.4	-0.8	1.0	1.1
BMK	-1.0	1.0	0.6	0.8	1.0	2.1	-1.1	1.1	1.2
ωB97X-D	-1.3	2.2	0.1	0.7	1.0	2.0	-2.0	2.2	1.8
B97-3	-2.3	2.5	-0.5	1.0	0.7	1.6	-2.2	2.2	1.8
LC-ωPBE	1.1	2.4	2.8	2.8	1.3	2.1	-1.0	1.2	2.1
M06	-3.6	4.1	-1.6	1.6	0.5	1.9	-1.5	1.7	2.3
maug-cc-pV(T+d)Z									
M06-2X	-0.2	0.4	0.8	0.8	0.2	1.1	-0.5	1.3	0.9
M08-SO	-0.6	0.7	0.8	0.8	0.2	1.3	-0.8	0.9	0.9
BMK	-1.4	1.4	0.7	0.9	0.8	1.9	-1.1	1.5	1.5
ωB97X-D	-1.3	1.7	0.7	0.8	0.9	2.0	-1.9	2.3	1.7
B97-3	-2.7	2.7	-0.1	1.3	0.5	1.6	-2.2	2.3	2.0
LC-ωPBE	1.0	2.2	3.4	3.4	1.1	2.1	-0.9	1.2	2.2
M06	-3.6	4.0	-0.9	1.3	0.5	1.8	-1.4	1.7	2.2

Figure captions:

FIG. 1. The gradient enhancement factors F_X for popular GGA exchange functionals. (Note: the numbers in the parentheses are the MSEs and MUEs of GGA functionals for the ABDE4 database in units of kcal/mol; the MSE and MUE of B88 are the values of the BPW91 functional)


1.8
1.6
1.4
1.2
1.0
F(s)
0
1
2
3
s
RPBE (-11.1/11.1)
revPBE(-10.5/10.5)
B88(-8.2/8.2)
PW91(-3.7/3.7)
PBE(-4.0/4.0)
WC06(1.5/2.3)
PBEsol(4.2/4.2)
SOGGA(5.2/5.2)