Representative Benchmark Suites for Barrier Heights of Diverse Reaction Types and Assessment of Electronic Structure Methods for Thermochemical Kinetics

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Abstract

We propose three small sets of barrier heights for heavy-atom transfer, nucleophilic substitution, and unimolecular and association reactions as benchmarks for comparing and developing theoretical methods. We choose the data sets to be statistically representative subsets of the NHTBH38/04 database. Each data set consists of 6 barrier heights; we call these small benchmark suites HATBH6, NSBH6, and UABH6. Benchmark values are tabulated for 205 combinations of theory level and basis set. The theory levels studied include single-level wave function theory like Hartree-Fork, Møller-Plesset perturbation theory, quadratic configuration interaction, and coupled cluster theory; they also include multicoefficient correlation methods, local and hybrid density functional theory, and semiempirical molecular orbital methods. The three new representative data sets are combined with a previous representative data set for hydrogen-transfer reactions to form a new compact but diverse and representative data set called DBH24. Comparison of a large number of methods for their performance on DBH24 leads us to recommend the following methods for barrier height calculations, in order of decreasing cost: G3SX, BMC-CCSD, PWB6K, BB1K, M06-L, MPW1K, HF/MIDI!, and PM3.

1   Introduction

Data sets composed of experimental and high-level electronic structure results are very useful for assessing the performance of new theoretical methods. Examples of such data sets are G2/97,[1–3] G3/99,[2–4] Database/3,[5] and NHTBH38/04.[6] These databases usually contain a large number of data to ensure diversity. But a disadvantage of using them to test new methods is that it requires a burdensomely large number of calculations, which is not always affordable. Hence, it is useful to develop a smaller set of data that is representative of the larger database and can be used more conveniently as a benchmark. With this motivation, our group has developed small representative benchmarks suites[7] for the atomization energies and hydrogen-transfer (HT) reactions in Database/3. These benchmark suites have been widely used because of their efficiency. In this paper we develop new small benchmark suites for non-hydrogen-transfer (non-HT) reactions.

The non-HT database NHTBH38/04 contains 38 barrier heights (BH) for heavy-atom transfer (HAT), nucleophilic substitution (NS), and unimolecular and association (UA) reactions. Because it can be expensive to use this suite, we present here a subset of data that has statistical errors close to those exhibited by the entire set, in particular, the small set adequately reproduces the mean signed error (MSE), mean unsigned error (MUE), and root-mean-square error (RMSE) of the full set.

A modern theorist has many quantum chemistry methods available for calculating thermochemical kinetics. In general, high level *ab initio* wave function theory (WFT) methods can give very accurate results, but they are very time-consuming. Semiempirical molecular orbital methods are computationally inexpensive, but less accurate and less reliable. Density-functional

theory (DFT) has proven to be very efficient with an excellent performance-to-cost ratio. Multilevel methods can also achieve high accuracy with low computational cost by extrapolating the results of some low-level methods. In the present work a wide variety of methods covering various kinds of theory and basis sets has been tested against barrier heights for both the full data sets and the representative subsets for both non-HT and HT reactions. These methods are assessed according to their mean errors for calculating barrier heights and their computational scaling and costs in order to allow one to choose the theory level and basis set according to the required performance-to-cost ratio for applications of thermochemical kinetics. In addition, the mean errors presented here can be used to estimate the reliability limits of various methods of calculation.

Section 2 describes the methods and the database used in the present work, Section 3 describe the strategies for selecting a representative subset, Section 4 gives the results and discussion, and Section 5 gives our conclusions.

2   Methods and Databases

2.1   Theoretical Methods

In order to develop the new test sets, we used 205 methods (where a method is a combination of theory level and basis set) to calculate the barrier heights in the NHTBH38/04[6] database. For DFT, theory "level" means choice of density functional.

The single-level methods include local DFT (BB95,[8] BLYP,[9,10] BP86,[9,11] G96LYP,[10,12,13] HCTH,[14] M06-L,[15] mPWKCIS,[16–21] mPWLYP,[10,16] mPWPW,[16] OLYP,[10,22] PBE,[23] PBE1W,[23,24] PW91,[25–29] TPSS,[20,21] TPSSKCIS,[17–21] SPL,[30] SPWL,[31,32] VSXC,[33] and τHCTH[34]), hybrid

DFT (B1B95,[8,9] B1LYP,[8,36] B3LYP,[8,35,37] B3LYP*,[38] B97-1,[39] B97-2,[39] B97-3,[40] B98,[41] BB1K,[42] BHandHLYP,[9,10,35] BMK,[43] HFLYP,[44] M05,[45] M05-2X,[45] M06-HF,[46] MPW1B95,[47] MPW1KCIS,[6,8,17–19] mPW1PW,[16] MPW1K,[16,17,48] MPW3LYP,[10,16,47] MPWB1K,[47] MPWKCIS1K,[6,8,17–19] O3LYP,[10,22,49] PBE1KCIS,[17–19,23,50] PBE1PBE,[23] PW6B95,[51] PWB6K,[51] TPSS1KCIS,[17–21,52] TPSSh,[20,21] X3LYP,[9,10,26,53] and τHCTHh[34]), and single-level WFT (Hartree-Fock (HF), Møller-Plesset second-, third-, and fourth-order perturbation theory (MP2,[54] MP2(full), MP3,[55] MP4[55]), Møller-Plesset fourth-order perturbation theory without triple excitations[55] (MP4SDQ), coupled cluster theory (CCSD,[56] CCSD(T)[57]), and quadratic configuration interaction (QCISD[58] and QCISD(T)[58])). Note that the local DFT methods include strictly local ones (SPWL and SPL), GGAs (BP86, BLYP, HCTH, G96LYP, mPWLYP, mPWPW, OLYP, PBE, PBE1W, and PW91), and meta GGAs (BB95, M06-L, mPWKCIS, TPSS, TPSSKCIS, VSXC, and τHCTH), where GGA denotes generalized gradient approximation. In single-level WFT methods, core electrons are uncorrelated (i.e., doubly occupied in all configurations, sometimes called frozen) except for MP2(full) calculations.

We also tested some semiempirical molecular orbital methods such as AM1,[59] PM3,[60] PDDG/PM3,[62] PM6,[61] RM1[63] and SCC-DFTB.[64] The first five of these methods are based on neglect of diatomic differential overlap (NDDO), whereas SCC-DFTB is a self-consistent-field nonorthogonal tight-binding method.

In addition to the above single-level methods, we also used WFT-based multilevel methods (CBS-4M,[65,66] CBS-Q,[65] CBS-q,[67] CBS-QB3,[66,68] G3SX,[74] G3SX(MP3),[74] MCCM/3,[81] BMC-CCSD,[69] MLSEn+d (n=1-4),[78] and the scaling all correlation method[79–81] (SAC-MP2 including SAC/3)). Within the MCCM/3 suite, we considered MCG3/3, MC-QCISD/3, MC-UT/3, MC-CO/3. Finally we studied multicoefficient extrapolated DFT methods (MC3BB,[82] MC3MPW,[82]

MC3MPWB,[52] MC3TS,[52] MCG3-MPW, -MPWB and -TS,[52] MCCO-MPW, -MPWB and -TS,[52] MCUT-MPW, -MPWB and -TS,[52] MCQCISD-MPW, and MCQCISD-MPWB and -TS[52]). Note that multicoefficient extrapolated DFT methods are examples of fifth-rung[83] DFT.

2.2   Basis Sets

The theoretical levels are combined with one or more of the following basis sets: 6-31B(d),[69] 6-31+B(d,p),[69] 6-31G(d),[55] 6-31G(d,p),[55] 6-31G(2df,p),[55] 6-311G(2d,p),[55] 6-311G(2df,2p),[55] 6-31+G(d),[55] 6-31+G(d,p),[55] 6-31+G(d,2p),[55] 6-31+G(2df,p),[55] 6-31++G(d,p),[55] 6-31++G(2df,2pd),[55] 6-311++G(d,p),[55] 6-311++G(2df,2pd),[55] aug-cc-pV(D+d)Z,[70] aug-cc-pVTZ,[71] aug-pc1,[72] aug-pc2,[72] cc-pV(D+d)Z,[70] cc-pV(T+d)Z,[70] cc-pVTZ,[70] G3Large,[73] G3XLarge,[74] MG3,[75,76] MG3S,[77] MG3T,[77] MIDI!,[84] MIDIX+,[84,85] and MIDIY.[84,85] Note that 6-31+G(d,p) is abbreviated to DIDZ in some of our previous papers. We also note that MG3 is also known as G3LargeMP2 and identical to 6-311++G(3d2f,2df,2p) for H through Si and very similar to 6-311+G(3d2f) for P, S, and Cl. The MG3S basis set is identical to MG3 except that diffuse functions on hydrogen have been removed. The MG3T basis set removes all diffuse functions from the MG3 basis set.

2.3   Geometries, Spin-Orbit Coupling, and Software

All calculations in the present work used structures optimized at the QCISD/MG3 level with the spin-restricted formalism for closed-shell and the spin-unrestricted formalism for open-shell systems. The effect of spin-orbit coupling was added to the energies of the Cl, F, and the OH radicals, which lowers their energies by 0.84, 0.38, and 0.20 kcal/mol, respectively.[80]

All single-level and CBS electronic structure calculations in this work were performed using

the *Gaussian03* package[86] except that B97-3, M05, M05-2X, M06-HF, M06-L, PW6B95, and PWK6B were carried out with a locally modified version of *Gaussian03*, four of semiempirical molecular orbital methods (AM1, PM3, PDDG/PM3, RM1) were calculated by MOPAC 5.012mn[87] program, which is available from the Truhlar group's web page,[88] PM6 method was calculated by MOPAC 7.2[61] program, SCC-DFTB calculations were performed by the DFTB[64,89] program, and single-level CCSD(T) calculations were carried out by the MOLPRO[90] program. All multilevel methods except the CBS ones were carried out with the MLGAUSS[91] program in conjunction with *Gaussian03* except that the MLSE multilevel methods were calculated with *Gaussian03* and a Fortran code. For all single-point energies except CCSD(T), we used the spin-restricted formalism for closed-shell calculations and the spin-unrestricted formalism for open-shell calculations. For CCSD(T), we used a spin-restricted calculation to obtain the orbitals, but a spin-unrestricted correlated calculation.

2.4   NHTBH38/04 Database

The NHTBH38/04[6] database for non-hydrogen-transfer reactions consists of 6 heavy-atom transfer reactions, 4 bimolecular nucleophilic substitution reactions, 4 unimolecular nucleophilic substitution reactions of ion-dipole complexes that produce product ion-dipole complexes, and 5 non-nucleophilic-substitution unimolecular or association reactions. This database is repeated in Supporting Information. The details of the database are presented in Ref. 6. As explained in more detail in Ref. 6, three of the 19 forward barrier heights are semi-experimental (meaning that they are derived by correcting calculated rate constants to agree with experimentally observed ones), and the other 16 are based on Weizmann-1,[6,92] and Weizmann-2[92,93] calculations. The reverse barrier heights are obtained from the forward barrier height and the energy of

reaction. All barrier heights, in both directions, are zero-point-exclusive.

3 Strategies for Selecting a Representative Subset

Since the NHTBH38/04 database contains three different types of reactions, we should select a subset that can represent all the reaction types, e.g., the reactions of the subset should not come from only one or two of these types. Here, we used two strategies to select the representative subset.

3.1 Strategy A

In this strategy, we selected a small subset that represents the *whole* database with the minimum root-mean-square deviation (RMSD) between three error measures, mean signed error, mean unsigned error, and root-mean-square error (MSE, MUE and RMSE) calculated using NHTBH38/04 and the same error measures calculated using the subset (SS), e.g., the deviation between the MSE using NHTBH38/04 (MSE(NH38)) and the MSE using the small subset (MSE(SS)). In this strategy, all the subsets must contain at least one reaction from each reaction type. This restriction guarantees that the representative subset is meaningful for whole database. The RMSD is calculated by using Eq. 1.

$$RMSD = [\frac{1}{3n} \sum_{i=1}^{n} [(MSE_i(NH38) - MSE_i(SS))^2 + (MUE_i(NH38) - MUE_i(SS))^2$$
$$+ (RMSE_i(NH38) - RMSE_i(SS))^2]]^{1/2} \tag{1}$$

where n is the number of methods used to generate representative test sets, in particularly n=154. The mean error (ME) is then defined by

$$ME = \frac{1}{3n} \sum_{i=1}^{n} (|MSE_i(NH38)| + MUE_i(NH38) + RMSE(NH38)) \tag{2}$$

which is calculated only once for whole database. Finally, we calculated the percentage error in representation (PEIR) using

$$PEIR = 100\% \times \frac{RMSD}{ME} \tag{3}$$

Note that although the present study includes 204 methods, we used n=154 in the above statistical analysis, because we excluded the six semiempirical molecular orbital methods at this stage because they increase PEIR significantly, and the other 44 methods were only used to calculate the representative subsets.

This choice of 154 methods yields ME=5.26 kcal/mol. The value of RMSD and PEIR were calculated for each possible subset of reactions in the NHTBH38/04 database, and the subset for a given number of reactions is the one with the smallest PEIR.

3.2   Strategy B

An alternative strategy of generating a representative subset is to consider the three types of reactions (HAT, NS, and UA) as *independent* data sets and calculate the corresponding subset's RMSD and PEIR for each reaction type (HAT, NS, and UA) by using equations analogous to Eq. 1, 2, and 3, respectively, and then select the most representative subset for each reaction type.

4 Results and Discussion

4.1 The Large Non-Hydrogen-Transfer Database

Table 1 contains mean signed and unsigned errors for NHTBH38/04 for 160 methods.

4.2 Representative Databases

In order to select a representative subset of NHTBH38/04 database, at least three reactions are required, which represent the three reaction types in the database. Hence, we calculated a series of the most representative subsets consisting of 3 to 9 reactions according to strategy A (see Fig. 1(a)). The 9-reaction representative subset gives the lowest PEIR, namely 12.8%, and it consists of 3 reactions for each reaction type. Encouragingly, strategy B also selected the same reactions for the representative subset, so the results of strategy A and B are consistent with each other. The 3-reaction subsets for HAT, NS, and UA reactions according to strategy B have similar PEIR, which are 12.4%, 9.2%, and 11.1%, respectively (see Fig. 1(b)). We call these representative subsets HATBH6, NSBH6, and UABH6, respectively. In a previous paper,[7] we have identified a representative data set for hydrogen-transfer reactions, namely BH6. We may label this BH6 database more explicitly as HTBH6 in the present paper. The combined set of these four representative databases is called DBH24, where D denotes diverse, and it is given in Table 2. As explained more fully in Ref. 5 and 6, four of the 12 forward barrier heights in DBH24 are semi-experimental (defined in Sect 2.4), six are from Weizmann-1 calculations, and two are from Weizmann-2 calculations. The reverse barrier heights are obtained from the forward barrier height and the energy of reaction. All barrier heights in the database, in both directions, are zero-point-exclusive.

(a)

(b)
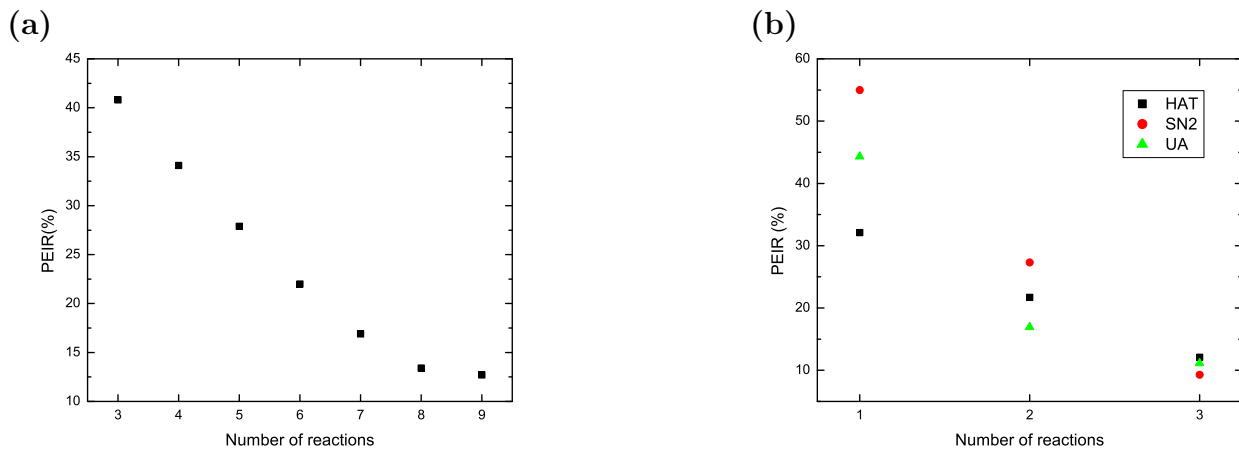
Figure 1: Percentage error in representation vs. number of reactions. (a) is for strategy A and (b) is for strategy B.

The HATBH6 data set is based on three reactions involving nitrogen, fluorine, and chlorine transfer. It represents the six heavy-atom transfer reactions in NHTBH38/04 database not only by having the smallest PEIR but also by covering all the heavy-atom transfer types in the whole database. NSBH6 is also appealing in that not only is it statistically representative, but also it involves all the three anion OH^-, F^-, and Cl^- that appear in NHTBH38/04. UABH6 includes two open-shell systems and one closed-shell system. Fortunately, the most time-consuming reaction $CH_3 + C_2H_4 \longrightarrow CH_3CH_2CH_2$ is not involved in this subset.

The subsets of non-hydrogen-transfer and hydrogen-transfer barrier heights yield errors that are representative of their respective errors using NHTBH38/04 and Database/3, respectively. Table 3 gives the errors calculated using the HATBH6, NSBH6, and UABH6 subsets. The size of the representative subsets is less than half of the whole NHTBH38/04 and using these subsets can significantly reduce the computational cost for testing and developing new theoretical methods.

11

4.3 Assessment of Methods

We have tested 160 methods against the full NHTBH38/04 database and 153 methods against both the non-hydrogen-transfer and hydrogen-transfer representative barrier height databases. All the mean errors (MSE and MUE) by these methods are given in Table 1 for non-hydrogen-transfer full data set and in Table 3 for both non-hydrogen-transfer and hydrogen-transfer representative subsets. We also tabulated a value for MMUE (mean MUE) as defined,

$$MMUE = \frac{1}{3}[MUE(HAT) + MUE(NS) + MUE(UA)] \tag{4}$$

in Table 1 or

$$MMUE = \frac{1}{4}[MUE(HAT) + MUE(NS) + MUE(UA) + MUE(HT)] \tag{5}$$

in Table 3. In the two tables, all methods are sorted by MMUE and the scaling order σ, where a method's computational cost, in the limit of a large number N of atoms, scales[94] as N^{σ}.

The computational costs in Table 1 and 3 are the computer time for calculating an energy gradient of the molecule phosphinomethanol divided by the time for an MP2/6-31+G(d,p) energy gradient calculation with the same computer program on the same computer. For calculations where the energy was calculated with *Gaussian03* or MOLPRO we calculated the MP2/6-31+G(d,p) gradient with the same program. For semiempirical molecular orbital methods calculated with MOPAC or DFTB, we take the ratio to the MP2/6-31+G(d,p) computer time with *Gaussian03* on the same computer. We used a gradient calculation to illustrate the cost because gradients are important for geometry optimization and dynamics calculations. When analytic gradients are available in the computer programs specified in Section 2.3, we used them. Otherwise, we used numerical gradients. In *Gaussian03* the cost for a numerical gradient of phosphinomethanol is 49 times the cost of a single-point energy, whereas in

MOLPRO it is 19 times the cost of a single-point energy. For local DFT methods, we give two costs corresponding to carrying out the calculation with and without density fitting. The density fitting method[95,96] (sometimes called resolution of the identity) employs auxiliary basis functions to represent the electron density; in this way, the four-center two-electron repulsion integrals are decomposed into three- and two-center integrals, reducing the formal scaling from N^4 to N^3.

4.3.1 Non-Hydrogen-Transfer Reactions

Among the tested multilevel methods, G3SX gives the lowest mean errors. The MMUEs of G3SX(MP3) and BMC-CCSD are identical and a little bit higher than that of G3SX, and the MMUE of BMC-CCSD is only 13% higher than that of G3SX(MP3). But the computational cost of BMC-CCSD is about 6 times smaller than that of G3SX(MP3) and 9 times smaller than that of G3SX. The MLSEn+d methods give good performance for neutral systems, but are not as good for general charged systems since they lack diffuse functions in their basis sets.

Among the *ab initio* WFT methods in Table 1, CCSD(T)/aug-cc-pVTZ gives a very high accuracy with 0.61 kcal/mol MMUE, and underestimates non-hydrogen-transfer BHs slightly. But it is very time-consuming. The QCISD(T)/MG3S method has a slightly higher MMUE for non-hydrogen-transfer reactions but with smaller cost than the CCSD(T)/aug-cc-pVTZ method. MP4, MP4SDQ, MP3, MP2, and HF systematically overestimate the BHs of HAT and UA reactions as shown by their high positive MSE.

Among the hybrid DFT methods in Table 1, BMK, PWB6K, BB1K and MPWB1K are the best performing methods with regards to their MMUE, and they give even higher accuracy than some multilevel methods for calculating BHs of non-HT reactions. M05 gives the lowest MUE

for NS reactions, and B1B95 gives the lowest MUE for UA reactions. The B3LYP* functional improves upon the B3LYP functional (see Table 3) by reducing HF exchange energy from 20% to 15%.

Among the local DFT methods in Table 1, our recently developed M06-L functional shows very good performance even with a double-ζ basis set. All the local DFT methods systematically underestimate the BHs of non-HT reactions as shown by their negative MSE, except that M06-L overestimates barrier heights of UA reactions with a small positive MSE.

The five NDDO semiempirical methods tested, AM1, PM3, PM6, RM1, and PDDG/PM3, all underestimate the BHs of HAT reactions and significantly overestimate the BHs of NS and UA reactions. But they are faster than MP2/6-31+G(d,p) by about five order of magnitude for phosphinomethanol gradients and by even more for larger system.

4.3.2   The Diverse DBH24 Database

For 108 of the 160 methods in Table 1 plus 44 new methods, we list mean unsigned errors for DBH24 in Table 3. The mean errors of HATBH6, NSBH6, and UABH6 shown in Table 3 are consistent with those of the full data set shown in Table 3. This illustrates the representative quality of these subsets. Table 3 also gives the mean errors of hydrogen-transfer reactions with the HTBH6 data set. Table 3 shows that the quality of all the tested methods in Table 3 for calculating hydrogen-transfer barrier heights correlates well with their quality for calculating non-hydrogen-transfer barrier heights. Mean errors of non-hydrogen-transfer representative data sets for the methods shown in Table 1 but not in Table 3 are given in Table S2 of Supporting Information.

In Table 3 we compare several basis sets for DFT methods. We found that the MG3S basis

set is both less expensive and more accurate than the aug-pc2 basis set for DFT methods, although aug-pc2 was specially designed[72] for use with DFT methods. The aug-pc1 basis set is 16 times less expensive than aug-pc2, but its MMUE is higher than that of aug-pc2 by only about 0.6 kcal/mol (2.00 vs. 1.43 kcal/mol). Hence aug-pc1 has a better performance-to-cost ratio than aug-pc2. But it is still less accurate than the 6-31+G(d,p) basis set, at least for the MPWB1K functional. We also tested the 6-31+G(d,p) basis set with several other functionals, and we found that it is competitive with MG3S because, although its computational costs are about 7-10 times faster, its MMUEs are slightly higher than those of MG3S. But 6-31G(d,p) gives much higher MMUEs, in particular for NS reactions, due to its lack of diffuse functions, a subject we have discussed previously.[77] According to our calculations, MG3S gives the best performance for barrier heights among the tested basis sets for DFT methods.

Since the SCC-DFTB method lacks parameters for halogens, we only calculated barrier heights for UA reactions, HTBH6 reactions, and two HAT reactions ($H + N_2O \longrightarrow OH + N_2$ and its reverse) with this method. SCC-DFTB gives better results than the NDDO semiempirical molecular orbital methods for UA reactions with a 9.78 kcal/mol MUE, and it overestimates the barrier heights for UA reactions on average by only 1.00 kcal/mol. But the MSE of full UA reaction barrier heights (see Table 1) becomes -3.47 kcal/mol. The MSEs of full data set and representative subset are not consistent with each other because DBH24 doesn't have the representative quality for semiempirical methods since these methods were not used to select the representative subset as we discussed in Section 3.1. Nevertheless the small test sets are instructive even for semiempirical methods. The SCC-DFTB MUEs for hydrogen-transfer barrier heights and for the one heavy-atom-transfer reaction are 30.53 and 23.02 kcal/mol, respectively, which are much larger than those of the NDDO semiempirical molecular orbital

methods. Since the SCC-DFTB method is parameterized against the B3LYP method, it is interesting to compare them. If we take B3LYP/MG3S barrier heights as the standards, the MUE of SCC-DFTB is improved to 8.37 kcal/mol for UA reactions, and the MSE relative to B3LYP/MG3 is 2.35 kcal/mol. We conclude that SCC-DFTB might be improved if it is reparameterized against more accurate functionals.

Table 4 summarizes the best methods when methods are judged solely on the basis of the accuracy of the predicted barrier heights, the cost of the method, and its scaling. Any method not in Table 4 performs less well for DBH24 than at least one method in Table 4 that has the same or lower cost or better scaling. This table, though, is not a replacement for careful consideration when choosing a basis set. For example, BB1K is better than MPWB1K and M05-2X, on average, for barrier heights, but only slightly so, but MPWB1K and M05-2X are better as all-purpose functionals, especially for noncovalent interactions.[52,97] Therefore Table 5 lists some additional recommended methods with performance for barrier heights almost as good as those in Table 4 and with good overall quality on a performance-for-a-given-cost basis.

5   Conclusions

Three small but representative data sets, HATBH6, NSBH6, and UABH6, are identified for the barrier heights of heavy-atom transfer, nucleophilic substitution, and unimolecular and association reactions, respectively. They are representative of the full data set within 12% (HAT), 9% (NS), and 11% (UA), respectively. We combine these data sets with a previous small representative data set for hydrogen-transfer reactions to create a diverse representative data set of zero-point-exclusive barrier heights called DBH24. Assessment of methods with

DBH24 shows that DFT and multilevel methods have much better performance-to-cost ratios than single-level WFT methods. The best N^6 method is BMC-CCSD, and its cost is an order of magnitude smaller than the best N^7 methods, although it is almost as accurate. The two best N^4 methods, PWB6K and BB1K, outperform the best N^5 method MC3BB. The best local DFT method is M06-L. The MG3S basis set gives the best performance for DFT methods among the tested basis sets.

Supporting Information Available: Tables of NHTBH38/04 data base, mean unsigned and signed errors of HATBH6, NSBH6, UABH6 for 52 methods that are not included in Table 3, geometries of species in DBH24 data base and phosphinomethanol, and T1[98] diagnostic values of species in DBH24 data base. This information is available free of charge via the Internet at http://pubs.acs.org.

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Table 1: Calculated errors and costs of various methods for non-hydrogen-transfer reactions in NHTBH38/04.

Methods	HAT(12)		NS(16)		UA(10)		MMUE^a	cost^b
	MSE	MUE	MSE	MUE	MSE	MUE		
N^7 Methods								
G3SX	-0.59	0.74	-0.50	0.50	-0.16	0.56	0.60	246
CCSD(T)/aug-cc-pVTZ	-0.34	0.71	-0.71	0.71	-0.18	0.41	0.61	12898
G3SX(MP3)	-0.47	0.76	0.13	0.88	-0.21	0.85	0.75	175
MCG3-MPW	-0.82	1.16	-0.40	0.58	-0.22	0.73	0.82	113
MCG3-MPWB	-0.94	1.15	-0.16	0.65	-0.26	0.76	0.85	114
QCISD(T)/MG3S	1.04	1.21	-0.62	1.08	0.30	0.53	0.94	5076
MCG3-TS	-0.74	1.35	-0.91	0.91	-0.04	0.59	0.95	108
MCG3/3	-0.61	1.17	-0.35	0.94	-0.48	0.91	1.01	102
MLSE4+d	-0.44	1.04	-3.64	4.47	-0.36	0.55	2.02	186
MLSE3+d	0.05	1.09	-3.80	4.64	-0.20	0.45	2.06	186
MLSE2+d	-0.35	1.02	-4.37	5.65	-0.38	0.64	2.44	186
MLSE1+d	-0.15	1.22	-4.77	5.90	-0.33	0.53	2.55	186
QCISD(T)/cc-pV(D+d)Z	2.14	3.04	-4.32	7.87	0.00	1.63	4.18	160
QCISD(T)/6-31G(d)	1.84	5.66	-3.30	7.77	0.96	2.95	5.46	63
MP4/6-31+G(d)	8.53	9.14	-0.95	2.72	3.56	5.03	5.63	84
MP4/6-31G(2df,p)	8.01	8.01	-5.03	9.13	3.74	4.18	7.11	699
MP4/6-31G(d)	8.64	9.24	-3.57	8.08	3.70	5.54	7.62	37
N^6 Methods								
BMC-CCSD	-0.27	1.14	-0.02	0.42	-0.39	0.69	0.75	27
MC-QCISD/3	1.26	1.53	-0.15	0.53	0.44	0.61	0.89	23

Table 1: Continued.

Methods	HAT(12)		NS(16)		UA(10)		MMUE[a]	cost[b]
	MSE	MUE	MSE	MUE	MSE	MUE		
MCQCISD-MPW	−1.16	1.38	−0.17	0.51	−0.11	0.85	0.91	34
MCQCISD-MPWB	−0.94	1.27	0.07	0.78	−0.09	0.85	0.97	35
MCQCISD-TS	−1.37	1.51	−0.98	0.98	−0.02	0.70	1.06	31
MCUT-MPWB	1.36	2.15	−0.07	0.58	1.04	1.31	1.35	34
CCSD/aug-cc-pVTZ	2.44	2.44	1.70	1.70	0.76	0.80	1.65	3868
MCUT-MPW	1.31	2.72	−0.74	0.75	1.16	1.48	1.65	33
MCUT-TS	0.90	2.71	−1.43	1.43	1.12	1.24	1.79	28
QCISD/MG3S	3.43	3.43	1.26	1.32	1.04	1.08	1.94	152
CCSD/6-31+G(d,p)	4.31	4.59	1.88	1.92	2.03	2.03	2.85	12
CCSD/6-31+B(d,p)	4.53	6.48	0.68	1.97	2.19	2.19	3.55	11
MC-UT/3	7.47	7.47	0.23	0.33	3.02	3.02	3.61	22
MP4SDQ/aug-cc-pVTZ	7.24	7.24	1.07	1.07	2.62	2.62	3.64	673
MP4SDQ/MG3S	8.60	8.60	1.42	1.44	3.08	3.12	4.39	95
CCSD/6-31B(d)	4.49	7.09	−0.39	4.70	1.98	2.73	4.84	2.3
MP4SDQ/6-31+G(p,d)	9.55	9.55	1.18	1.86	4.05	4.05	5.15	3.4
MP3/aug-cc-pVTZ	9.24	9.24	3.09	3.09	3.69	3.69	5.34	530
MP4SDQ/6-31+B(d,p)	9.36	9.78	0.07	2.34	4.16	4.16	5.43	3.3
QCISD/6-31G(d)	3.43	5.93	−2.37	7.53	1.53	2.89	5.45	1.7
MP3/MG3S	10.59	10.59	3.62	3.62	4.14	4.14	6.12	71
MP3/6-31+B(d,p)	11.35	11.50	2.54	2.86	5.21	5.21	6.52	2.8
MP4SDQ/cc-pV(D+d)Z	9.23	9.23	−2.44	6.95	2.81	3.79	6.66	2.8
MP3/6-31+G(d)	11.05	11.05	3.55	3.55	4.78	5.37	6.66	1.4

Table 1: Continued.

Methods	HAT(12)		NS(16)		UA(10)		MMUE[a]	cost[b]
	MSE	MUE	MSE	MUE	MSE	MUE		
MP3/6-31+G(d,p)	11.49	11.49	3.66	3.66	5.08	5.08	6.74	2.7
MP4SDQ/6-31G(2df,p)	8.68	8.68	−2.73	7.73	3.86	3.98	6.80	14
MP4DQ/6-31B(d)	11.20	11.48	1.14	4.98	4.92	5.55	7.34	0.83
MP4SDQ/6-31G(d)	9.07	9.34	−1.94	7.58	3.86	5.23	7.38	0.87
MP3/6-31G(2df,p)	10.64	10.64	−0.81	6.90	4.91	4.91	7.48	12
MP3/6-31G(d)	10.97	10.97	0.02	6.93	4.89	5.81	7.90	0.73
N^5 Methods								
MCCO-MPWB	0.60	1.86	1.29	1.60	0.95	1.14	1.53	33
MC3BB	1.18	2.44	0.55	0.66	1.53	1.53	1.54	14
MC3MPWB	1.23	2.55	0.18	0.67	1.57	1.57	1.60	14
MCCO-TS	0.78	2.75	−0.92	1.32	1.34	1.52	1.86	27
MC3MPW	1.50	2.69	0.17	0.89	2.14	2.20	1.93	13
MC3TS	1.35	2.82	−0.90	1.05	2.09	2.16	2.01	7.4
MCCO-MPW	2.13	2.97	0.63	1.48	1.75	1.85	2.10	32
MP2/aug-cc-pVTZ	10.46	10.46	0.37	0.67	4.29	4.88	5.34	140
MC-CO/3	10.61	10.61	0.08	1.37	4.04	4.04	5.34	21
MP2/aug-cc-pV(D+d)Z	10.28	10.28	−0.95	1.27	3.80	4.74	5.43	4.3
MP2/6-31++G(2df,2pd)	11.07	11.07	0.55	0.65	4.64	5.15	5.62	13
MP2/6-311++G(2df,2pd)	11.07	11.07	0.55	0.65	4.64	5.15	5.62	18
MP2/MG3	11.46	11.46	0.70	0.73	4.65	5.40	5.86	14
MP2(full)/6-31G(2df,p)	11.41	11.41	0.91	0.91	4.72	5.46	5.93	3.6
MP2/MG3S	11.76	11.76	0.74	0.74	4.71	5.44	5.98	13

Table 1: Continued.

Methods	HAT(12)		NS(16)		UA(10)		MMUE[a]	cost[b]
	MSE	MUE	MSE	MUE	MSE	MUE		
MP2/6-31++G(d,p)	11.19	11.19	1.12	2.18	5.28	5.87	6.41	1.1
MP2/6-31+G(d,2p)	12.04	12.04	0.97	2.21	4.96	5.31	6.52	1.5
SAC/3[c]	11.55	11.55	0.26	2.84	5.27	5.81	6.73	2.5
MP2/6-31+B(d,p)	12.15	12.15	−0.22	2.62	5.57	5.76	6.84	1.0
MP2/6-31+G(d,p)	12.56	12.56	1.14	2.21	5.49	5.93	6.90	1.0
SAC-MP2/6-31+G(d,p)	12.06	12.06	0.32	2.95	5.93	6.44	7.15	1.7
MP2/cc-pV(T+d)Z	11.75	11.75	−2.14	4.42	4.49	5.30	7.16	15
MP2/6-311++G(d,p)	12.57	12.57	3.28	3.28	4.71	5.89	7.25	2.0
MP2/6-311+G(d,p)	12.57	12.57	3.28	3.28	4.71	5.89	7.25	1.7
MP2/6-31+G(d)	12.14	12.54	1.08	2.32	5.31	7.07	7.31	0.60
MP2/6-31B(d)	12.00	12.76	−1.45	4.99	5.57	7.10	8.28	0.41
MP2/cc-pV(D+d)Z	12.09	12.09	−2.75	7.29	4.23	5.95	8.44	1.4
MP2/cc-pVDZ	12.20	12.20	−2.97	7.45	4.23	5.95	8.53	0.92
MP2/6-31G(2df,p)	11.63	11.63	−3.47	8.28	5.34	6.23	8.71	3.0
MP2/6-31G(d)	12.00	12.43	−2.22	8.02	5.37	7.54	9.33	0.41
SAC-MP2/6-31G(d)	11.51	13.32	−3.64	8.85	6.11	8.69	10.29	0.56
N^4 Methods								
BMK/MG3S	−1.21	1.49	0.75	0.91	0.80	1.58	1.33	13
PWB6K/MG3S	−0.24	1.61	0.94	1.10	0.65	1.53	1.41	12
BB1K/MG3S	−0.69	1.58	1.23	1.30	0.53	1.44	1.44	12
MPWB1K/MG3S	−0.77	1.69	1.08	1.19	0.52	1.61	1.50	12
PWB6K/aug-pc2	−0.68	1.59	1.48	1.48	0.53	1.51	1.53	64
MPWB1K/aug-pc2	−1.19	1.81	1.66	1.66	0.40	1.58	1.68	64

Table 1: Continued.

Methods	HAT(12)		NS(16)		UA(10)		MMUE[a]	cost[b]
	MSE	MUE	MSE	MUE	MSE	MUE		
BB1K/6-31+G(d,p)	−0.68	1.86	1.02	1.17	0.84	2.10	1.71	2.0
M05-2X/MG3S	1.15	2.00	−0.79	1.48	0.91	1.77	1.75	13
MPW1K/MG3S	−0.83	1.89	1.12	1.28	0.96	2.42	1.86	12
MPWB1K/aug-pc1	−1.78	2.92	0.20	1.15	0.02	1.95	2.01	3.7
M05-2X/6-31+G(d,p)	1.06	2.53	−0.63	1.68	1.00	1.90	2.04	2.2
BHandHLYP/MG3S	0.07	3.04	0.95	1.39	0.76	1.98	2.14	10
M05/MG3S	−2.84	3.79	0.00	0.80	0.69	2.24	2.28	13
B97-2/MG3S	−3.13	3.52	−1.43	1.47	0.62	1.91	2.30	11
B1B95/MG3S	−4.73	4.73	−0.95	1.08	−0.58	1.21	2.34	12
MPW1B95/MG3S	−4.62	4.62	−0.81	1.21	−0.52	1.31	2.38	12
MPWKCIS1K/MG3S	−1.94	2.82	1.69	1.69	0.95	2.97	2.49	13
M05/6-31+G(d,p)	−2.73	4.29	−0.74	1.14	0.81	3.06	2.83	2.1
PW6B95/MG3S	−5.36	5.36	−2.05	2.05	−0.76	1.43	2.95	12
mPW1PW/MG3S	−5.99	5.99	−1.81	1.94	−0.38	2.00	3.31	11
B98/6-311+G(3df,2p)	−5.19	5.19	−2.93	2.93	−0.39	1.96	3.36	10
B98/MG3S	−5.18	5.18	−2.96	2.96	−0.31	1.97	3.37	11
B97-1/MG3S	−5.18	5.18	−3.21	3.21	−0.23	1.83	3.41	11
PBE1PBE/MG3S	−6.62	6.62	−1.87	2.05	−0.58	2.16	3.61	10
PBE1KCIS/MG3	−8.56	8.56	−1.77	1.88	−0.86	2.64	4.36	12
X3LYP/MG3S	−8.48	8.48	−2.89	2.90	−1.43	2.06	4.48	11
B3LYP/MG3S	−8.49	8.49	−3.25	3.25	−1.42	2.02	4.59	9.4
τHCTHh/MG3S	−6.73	6.73	−4.53	4.53	−0.23	2.65	4.64	11
MPWB1K/cc-pVDZ	−2.06	3.14	−5.79	9.40	0.01	1.74	4.76	1.6

Table 1: Continued.

Methods	HAT(12)		NS(16)		UA(10)		MMUE[a]	cost[b]
	MSE	MUE	MSE	MUE	MSE	MUE		
O3LYP/MG3S	−8.27	8.27	2.61	4.42	−1.02	2.27	4.99	11
B3LYP/6-31+G(d,p)	−8.79	8.79	−3.59	3.59	−1.27	2.65	5.01	1.4
MPW3LYP/MG3S	−9.29	9.29	−4.29	4.29	−1.61	2.21	5.26	11
MPW1KCIS/MG3S	−9.89	9.89	−3.46	3.46	−1.27	2.61	5.32	13
TPSS1KCIS/MG3S	−9.26	9.26	−4.88	4.88	−1.39	2.12	5.42	13
B3LYP*/MG3T	−6.02	6.02	−6.92	8.40	1.45	4.00	6.14	7.5
B97-2/6-31G(d)	−4.25	5.85	−7.33	11.03	0.95	2.16	6.35	0.89
TPSSh/MG3S	−11.51	11.51	−5.78	5.78	−2.94	3.23	6.84	13
B3LYP/6-311G(2df,2p)	−8.92	8.92	−8.97	11.05	−1.71	1.98	7.32	5.2
B3LYP/6-311G(2d,p)	−8.89	8.89	−9.68	11.65	−1.85	1.98	7.51	1.5
BB1K/MIDIY	−6.80	6.90	−11.71	16.40	0.03	1.83	8.38	1.4
HF/aug-cc-pV(D+d)Z	14.23	16.34	5.23	5.23	2.35	3.77	8.45	0.55
B3LYP/6-31G(d,p)	−9.99	9.99	−9.71	12.92	−1.51	2.49	8.47	0.92
HF/cc-pV(T+d)Z	15.03	16.97	4.18	5.04	2.49	3.75	8.59	1.9
HF/cc-pV(D+d)Z	14.19	16.50	1.20	5.64	2.22	3.80	8.65	0.45
HF/6-31+B(d,p)	14.55	17.73	4.15	4.34	3.23	3.99	8.69	0.87
HF/cc-pVDZ	14.25	16.57	0.93	5.80	2.22	3.80	8.72	0.28
HF/6-31G(d)	13.63	15.47	2.52	6.74	2.95	4.23	8.81	0.15
HF/aug-cc-pVTZ	14.43	16.39	6.76	6.76	2.53	3.72	8.96	45
HF/6-31B(d)	13.93	17.34	3.22	5.16	3.43	4.40	8.97	0.17
HF/6-31+G(d,2p)	15.33	17.44	5.66	5.66	2.86	3.91	9.00	0.97
HF/6-31+G(d,p)	15.29	17.38	5.72	5.72	3.03	3.95	9.02	0.67
HF/MG3	14.64	16.67	6.67	6.67	2.67	3.79	9.04	9.2

Table 1: Continued.

Methods	HAT(12)		NS(16)		UA(10)		MMUE[a]	cost[b]
	MSE	MUE	MSE	MUE	MSE	MUE		
HF/G3XLarge	14.62	16.64	6.73	6.73	2.67	3.79	9.05	18
HF/G3Large	14.64	16.66	6.72	6.72	2.67	3.79	9.06	13
HF/MG3S	14.86	16.87	6.67	6.67	2.70	3.82	9.12	7.9
N^3 Methods								
M06-L/MG3S	−5.68	5.93	−3.56	3.56	0.27	2.35	3.95	5.7/8.9[d]
M06-L/6-31+G(d,p)	−5.36	6.22	−4.55	4.55	0.16	2.27	4.35	2.1/2.2
HCTH/MG3S	−8.84	8.84	−2.71	2.71	−0.75	2.20	4.58	3.9/6.7
VSXC/MG3S	−7.44	7.44	−5.30	5.30	−0.91	2.40	5.05	5.2/8.8
VSXC/6-31+G(d,p)	−7.58	7.58	−5.52	5.52	−0.67	2.90	5.33	1.9/2.0
OLYP/MG3S	−11.23	11.23	−2.73	2.73	−1.92	2.53	5.50	3.7/6.8
τHCTH/MG3S	−9.21	9.21	−5.71	5.71	−1.04	2.82	5.91	5.4/8.8
G96LYP/MG3S	−13.03	13.03	−5.80	5.80	−2.86	3.04	7.29	3.8/7.3
mPWKCIS/MG3S	−13.65	13.65	−6.66	6.66	−2.67	3.07	7.79	6.1/9.7
BB95/MG3S	−13.88	13.88	−6.36	6.36	−3.22	3.40	7.88	5.4/8.7
TPSSKCIS/MG3S	−13.37	13.37	−7.64	7.64	−2.56	2.98	8.00	5.7/9.3
MPWPW/MG3S	−14.10	14.10	−7.45	7.45	−2.67	3.10	8.22	3.8/7.1
PBE1W/MG3S	−14.51	14.51	−7.06	7.06	−2.69	3.13	8.23	3.8/7.4
PBE/MG3S	−14.93	14.93	−6.97	6.97	−2.94	3.35	8.42	3.7/7.3
BP86/MG3S	−15.51	15.51	−6.91	6.91	−3.41	3.87	8.76	3.9/6.9
PW91/MG3S	−15.42	15.42	−7.75	7.75	−2.78	3.22	8.80	3.8/6.9
TPSS/MG3S	−14.65	14.65	−7.75	7.75	−3.84	4.04	8.81	5.5/8.8
BLYP/MG3S	−14.66	14.66	−8.40	8.40	−3.38	3.51	8.86	3.8/7.3
mPWLYP/MG3S	−15.76	15.76	−8.14	8.14	−3.64	3.79	9.23	3.8/7.3

Table 1: Continued.

Methods	HAT(12)		NS(16)		UA(10)			
	MSE	MUE	MSE	MUE	MSE	MUE	MMUE^a	cost^b
SPL/MG3S	-23.36	23.36	-8.58	8.58	-5.08	5.82	12.59	2.5/5.8
SPWL/MG3S	-23.48	23.48	-8.50	8.50	-5.17	5.90	12.63	3.5/5.9
PM6	-18.83	19.37	1.76	6.54	9.61	15.66	13.86	5×10^{-5}
AM1	-8.99	10.60	16.02	19.08	9.04	15.01	14.90	5×10^{-5}
PM3	-13.97	15.88	19.91	20.24	3.53	11.25	15.79	5×10^{-5}
RM1	-14.80	18.34	6.59	18.43	6.72	14.28	17.02	5×10^{-5}
PDDG/PM3	-21.19	21.90	20.53	20.53	3.01	10.52	17.65	5×10^{-5}
SCC-DFTB	-23.02^e	23.02^e			-3.47	9.94	16.48^f	4×10^{-4}

^{a} MMUE is defined as Eq. 4.

^{b} The cost for each method is measured by the computer time for an energy gradient calculation of phosphinomethanol divided by the computer time for an MP2/6-31+G(d,p) energy gradient calculation with the same software (except semiempirical molecular orbital methods, see text) on the same computer. Although such costs depend to some extent (for example, 15%) on the machine, the program, and the computer load, they still provide a useful indication of computer resource demand.

^{c} Also called SAC-MP2/6-31+G(d,2p)

^{d}The double entries for local DFT methods correspond to timings with/without density fitting.

^{e} The forward and reverse barriers of the reaction H + N$_2$O $\longrightarrow$ OH + N$_2$.

^{f} Mean value of MUE for the forward and reverse barriers of the reaction H + N$_2$O $\longrightarrow$ OH + N$_2$ and the MUE for UA(10).

Table 2:   Representative barrier heights database DBH24.

Database	Reaction	$V_f^{\neq a}$	$V_r^{\neq a}$
	$H + N_2O \longrightarrow OH + N_2$	18.14	83.22
HATBH6	$H + ClH \longrightarrow HCl + H$	18.00	18.00
	$CH_3 + FCl \longrightarrow CH_3F + Cl$	7.43	61.01
	$Cl^- \cdots CH_3Cl \longrightarrow ClCH_3 \cdots Cl^-$	13.61	13.61
NSBH6	$F^- \cdots CH_3Cl \longrightarrow FCH_3 \cdots Cl^-$	2.89	29.62
	$OH^- + CH_3F \longrightarrow HOCH_3 + F^-$	-2.78	17.33
	$H + N_2 \longrightarrow HN_2$	14.69	10.72
UABH6	$H + C_2H_4 \longrightarrow CH_3CH_2$	1.72	41.75
	$HCN \longrightarrow HNC$	48.16	33.11
	$OH + CH_4 \longrightarrow CH_3 + H_2O$	6.7	19.6
HTBH6	$H + OH \longrightarrow O + H_2$	10.7	13.1
	$H + H_2S \longrightarrow H_2 + HS$	3.6	17.3

[a] $V_f^{\neq}$ denotes forward BH, and $V_r^{\neq}$ denotes reverse BH (in kcal/mol).

Table 3: Calculated mean errors of various methods for non-hydrogen-transfer and hydrogen-transfer representative databases and for the diverse barrier heights database DBH24.

Methods	HATBH6		NSBH6		UABH6		HTBH6		DBH24	cost[b]
	MSE	MUE	MSE	MUE	MSE	MUE	MSE	MUE	MMUE[a]	
			N^7 Methods							
G3SX	−1.02	1.20	−0.54	0.54	−0.06	0.27	0.31	0.53	0.64	246
CCSD(T)/aug-cc-pVTZ	−0.11	0.84	−0.67	0.68	−0.06	0.40	−0.11	0.64	0.64	12898
G3SX(MP3)	−0.98	1.18	0.00	0.73	−0.15	0.40	0.49	0.51	0.71	175
MCG3-MPW	−1.31	1.40	−0.50	0.67	−0.26	0.71	−0.15	0.36	0.79	113
MCG3-TS	−1.14	1.16	−0.99	0.99	−0.02	0.60	−0.30	0.46	0.80	108
MCG3-MPWB	−1.31	1.35	−0.26	0.79	−0.29	0.72	−0.39	0.52	0.85	114
MCG3/3	−1.16	1.65	0.43	0.90	−0.44	0.68	0.58	0.76	1.00	102
QCISD(T)/MG3S	0.94	1.29	−0.59	1.14	0.51	0.52	1.02	1.12	1.02	5076
CBS-QB3	−1.26	1.76	−0.51	0.59	−2.21	2.47	−1.42	1.42	1.56	363[c]
CBS-Q	−2.52	2.52	−1.43	1.48	−2.61	2.67	−0.87	0.88	1.89	369[c]
CCSD(T)/cc-pV(T+d)Z	1.12	1.12	−2.91	4.93	0.18	0.49	0.68	1.26	1.95	1761
CCSD(T)/cc-pVTZ	1.26	1.35	−3.05	5.10	0.18	0.49	0.80	1.30	2.06	1660
CBS-q	−1.95	2.72	−0.32	1.58	−3.25	3.68	−1.00	1.18	2.29	180[c]
CBS-4M	0.50	3.59	1.94	2.48	−2.38	2.85	−0.40	0.57	2.37	173[c]

Table 3: Continued.

Methods	HATBH6		NSBH6		UABH6		HTBH6		DBH24	cost[b]
	MSE	MUE	MSE	MUE	MSE	MUE	MSE	MUE	MMUE[a]	
CCSD(T)/6-311G(2df,2p)	1.24	2.16	−3.81	7.98	0.43	0.66	1.15	1.71	3.13	1080
QCISD(T)/6-311G(2df,2p)	1.13	2.25	−4.13	8.20	0.42	0.65	1.08	1.62	3.18	2269
QCISD(T)/6-31G(d)	3.61	4.68	−2.63	7.89	1.31	2.94	4.68	5.53	5.26	63
MP4/6-311G(2df,2p)	7.36	7.36	−4.48	8.47	3.07	3.72	2.27	2.36	5.48	1608
MP4/6-311G(2d,p)	8.49	8.49	−4.90	8.71	2.94	4.00	2.90	3.39	6.15	458
MP4/6-31G(d)	10.09	10.09	−2.78	8.27	4.08	5.31	5.94	6.38	7.51	37
N^6 Methods										
BMC-CCSD	−0.12	1.36	0.09	0.54	−0.38	0.40	0.00	0.57	0.72	27
MC-QCISD/3	0.84	1.22	−0.10	0.46	0.36	0.61	0.81	0.91	0.80	23
MCQCISD-MPW	−1.46	1.46	−0.24	0.70	−0.28	0.99	−0.50	0.50	0.91	34
MCQCISD-MPWB	−1.14	1.25	0.02	0.96	−0.22	0.95	−0.61	0.64	0.95	35
MCUT-MPWB	0.89	1.03	−0.11	0.81	0.96	1.42	−0.60	0.66	0.98	34
MCQCISD-TS	−1.45	1.45	−1.02	1.02	−0.07	0.70	−0.73	0.73	0.98	31
MCUT-MPW	0.74	1.43	−0.79	0.83	1.03	1.53	−0.62	0.62	1.10	33
MCUT-TS	0.54	1.35	−1.45	1.45	1.14	1.22	−0.67	0.67	1.17	28
QCISD/MG3S	3.76	3.76	1.29	1.29	1.17	1.17	2.27	2.27	2.12	152
CCSD/MG3S	3.54	3.54	2.03	2.03	1.48	1.51	2.50	2.50	2.40	242

Table 3: Continued.

Methods	HATBH6		NSBH6		UABH6		HTBH6		DBH24	cost[b]
	MSE	MUE	MSE	MUE	MSE	MUE	MSE	MUE	MMUE[a]	
MC-UT/3	6.38	6.38	0.36	0.36	2.98	2.98	2.25	2.25	2.99	22
MP4SDQ/MG3S	8.31	8.31	1.51	1.51	3.24	3.24	3.48	3.48	4.14	95
QCISD/6-31B(d)	5.76	8.63	−0.62	5.01	2.13	2.31	4.78	5.09	5.26	1.7
CCSD/6-31B(d)	6.10	8.76	0.42	5.26	2.43	2.58	4.91	5.11	5.43	2.3
QCISD/6-31G(d)	5.54	5.84	−1.65	7.78	1.84	2.61	5.36	5.81	5.44	1.7
MP3/MG3S	10.06	10.06	3.44	3.44	4.31	4.31	4.21	4.21	5.51	71
MP4SDQ/6-31G(2df,p)	8.41	8.41	−2.02	7.92	4.19	4.19	4.62	4.62	6.29	14
MP3/6-31+G(d)	11.72	11.72	3.76	3.76	5.09	5.09	7.05	7.05	6.91	1.4
MP4SDQ/6-31G(d)	10.53	10.53	−1.19	7.91	4.24	4.97	6.54	6.55	7.49	0.87
MP4DQ/6-31B(d)	12.20	12.39	1.96	6.17	5.49	5.49	6.81	6.81	7.72	0.83
MP3/6-31G(d)	12.21	12.21	0.62	7.29	5.29	5.54	7.26	7.26	8.08	0.73
N^5 Methods										
MC3BB	1.05	2.25	0.52	0.59	1.47	1.47	−0.51	0.72	1.26	14
MC3MPWB	1.14	2.42	0.25	0.63	1.58	1.58	−0.61	0.84	1.37	14
MC3TS	1.38	2.10	−0.80	0.82	2.15	2.15	−0.30	0.44	1.38	7.4
MCCO-MPWB	0.46	1.39	1.09	1.63	0.98	1.16	−1.35	1.35	1.38	33
MC3MPW	1.27	2.24	0.16	0.78	2.06	2.06	−0.54	0.72	1.45	13

Table 3: Continued.

Methods	HATBH6		NSBH6		UABH6		HTBH6		DBH24	
	MSE	MUE	MSE	MUE	MSE	MUE	MSE	MUE	MMUE[a]	cost[b]
MCCO-TS	0.52	1.84	−1.05	1.46	1.49	1.49	−1.00	1.00	1.45	27
MCCO-MPW	1.52	2.38	0.38	1.84	1.76	1.76	−0.73	1.18	1.79	32
MC-CO/3	8.80	8.80	−0.01	1.24	4.66	4.66	2.58	2.67	4.34	21
MP2/aug-cc-pV(D+d)Z	9.73	9.73	−0.48	1.00	4.06	4.96	2.74	3.27	4.74	4.3
MP2/MG3	10.79	10.79	0.72	0.80	5.15	5.65	3.88	3.88	5.28	14
MP2/MG3S	10.95	10.95	0.80	0.81	5.12	6.00	3.91	3.91	5.42	13
MP2(full)/6-31G(2df,p)	10.55	10.55	0.94	0.94	5.11	6.04	4.74	4.74	5.57	3.6
SAC/3	10.53	10.53	0.62	2.99	5.36	6.25	2.62	2.62	5.60	2.5
MP2/6-31+G(d,2p)	11.44	11.44	1.27	2.52	5.14	5.56	3.98	3.98	5.88	1.5
SAC-MP2/6-31+G(d,p)	11.35	11.35	0.75	3.09	6.13	6.09	4.13	4.13	6.17	1.7
MP2/6-31+G(d,p)	11.44	11.44	1.27	2.52	5.14	5.56	5.49	5.49	6.25	1.0
MP2/6-31++G(d,p)	11.87	11.87	1.46	2.53	5.53	6.22	5.42	5.42	6.51	1.1
MP2/6-31G(2df,p)	10.87	10.87	−2.78	8.29	5.91	6.80	4.98	4.98	7.74	3.0
MP2/6-31B(d)	12.47	12.58	−0.94	5.03	6.20	7.40	6.14	6.14	7.79	0.41
MP2/6-31G(d)	13.22	13.22	−1.48	8.31	6.05	7.83	6.81	6.81	9.04	0.41
N^4 Methods										
PWB6K/MG3S	−0.06	1.05	0.96	0.96	0.71	1.59	−0.99	1.22	1.21	12
BB1K/MG3S	−0.60	1.09	1.07	1.17	0.42	1.57	−1.03	1.14	1.24	12
MPWB1K/MG3S	−0.69	1.16	1.01	1.01	0.46	1.63	−1.32	1.32	1.28	12

Table 3: Continued.

Methods	HATBH6		NSBH6		UABH6		HTBH6		DBH24	
	MSE	MUE	MSE	MUE	MSE	MUE	MSE	MUE	MMUE[a]	cost[b]
BMK/MG3S	−1.58	1.58	0.72	0.86	0.85	2.06	−1.20	1.20	1.43	13
MPWB1K/aug-pc2	−0.93	1.17	1.57	1.57	0.28	1.61	−1.37	1.37	1.43	64
MPW1K/MG3S	−0.79	1.36	0.91	1.15	0.82	2.42	−1.14	1.40	1.58	11
MPWB1K/MG3	−1.15	1.56	0.97	1.97	0.78	2.46	−1.34	1.34	1.58	13
M05-2X/MG3S	0.72	1.96	−0.94	1.48	1.25	1.60	−0.36	1.40	1.61	13
M05-2X/MG3	0.33	1.58	−0.96	1.50	1.50	2.25	−0.36	1.42	1.69	14
BB1K/6-31+G(d,p)	−0.95	1.92	0.92	1.26	0.70	2.20	−1.03	1.42	1.70	2.0
PWB6K/6-31+G(d,p)	−0.45	2.05	0.79	1.23	0.99	2.30	−1.02	1.35	1.73	2.0
MPWB1K/6-31+G(d,p)	−1.05	1.99	0.86	1.24	0.75	2.37	−1.33	1.43	1.76	2.0
MPW1K/6-31+G(d,p)	−1.14	1.55	0.60	1.50	1.15	3.21	−1.05	1.42	1.92	1.4
M05-2X/6-31+G(d,p)	0.07	2.44	−0.80	1.72	1.32	1.90	−0.64	1.60	1.92	2.1
B97-3/MG3S	−2.93	2.93	−0.39	1.07	0.57	1.63	−2.22	2.29	1.98	11
MPWB1K/aug-pc1	−1.27	2.60	0.36	1.32	−0.31	1.92	−2.17	2.17	2.00	3.7
BHandHLYP/MG3S	1.06	2.79	0.81	1.50	0.88	2.35	0.10	1.98	2.16	10
MPWKCIS1K/MG3S	−1.93	2.20	1.48	1.48	0.81	3.35	−1.97	1.97	2.25	13
BB1K/6-31+B(d,p)	−2.13	4.06	0.13	1.48	0.91	2.23	−1.29	1.29	2.27	2.3
M06-HF/MG3S	3.69	4.11	−0.79	1.74	0.98	1.69	1.14	1.95	2.37	16

40

Table 3: Continued.

Methods	HATBH6		NSBH6		UABH6		HTBH6		DBH24	cost[b]
	MSE	MUE	MSE	MUE	MSE	MUE	MSE	MUE	MMUE[a]	
M06-HF/6-31+G(d,p)	2.93	4.49	−0.09	1.56	1.25	1.56	0.82	2.34	2.49	2.7
B1B95/MG3S	−4.46	4.46	−1.12	1.22	−0.69	1.12	−3.14	3.14	2.49	12
M05/MG3S	−3.89	5.09	0.13	1.00	0.87	2.48	−0.76	1.64	2.55	13
MPW1B95/MG3S	−4.37	4.37	−0.56	1.26	−0.57	1.23	−3.38	3.38	2.56	12
B97-2/MG3S	−3.68	4.46	−1.63	1.63	0.79	1.81	−2.88	3.21	2.78	11
PW6B95/MG3S	−4.92	4.92	−2.08	2.08	−0.68	1.17	−3.46	3.46	2.91	12
M05/6-31+G(d,p)	−4.37	5.59	−0.47	1.02	0.75	3.28	−0.91	2.09	3.00	2.1
MPW1K/MIDIX+	−3.86	3.86	−2.30	2.30	1.72	3.16	−2.73	3.09	3.10	1.0
MPWB1K/MG3T	−1.52	1.65	−3.68	7.09	0.69	2.27	−1.64	1.64	3.16	8.8
mPW1PW/MG3S	−5.73	5.73	−2.00	2.00	−0.53	1.93	−3.95	3.95	3.40	11
M05-2X/MG3T	0.00	1.79	−5.56	8.53	1.41	2.04	−0.54	1.60	3.49	11
BB1K/6-31B(d)	−0.91	5.20	−1.97	4.67	1.11	1.90	−0.90	2.35	3.53	1.3
B98/MG3S	−5.39	5.39	−3.05	3.05	−0.05	1.84	−4.00	4.00	3.57	11
B97-1/MG3S	−5.45	5.45	−3.21	3.21	0.05	1.68	−4.14	4.14	3.62	11
MPW1K/6-31B(d)	−0.96	4.75	−2.22	4.55	1.64	3.21	−0.92	2.13	3.66	0.80
PBE1PBE/MG3S	−6.45	6.45	−1.99	1.99	−0.77	1.96	−4.62	4.62	3.76	10
mPW1PW/6-31+G(d,p)	−6.20	6.20	−2.17	2.19	−0.30	2.76	−3.94	3.94	3.77	1.4
MPWB1K/6-31G(d,p)	−1.32	2.17	−3.63	9.35	0.71	2.09	−1.55	2.13	3.94	1.3

41

Table 3: Continued.

Methods	HATBH6		NSBH6		UABH6		HTBH6		DBH24	cost[b]
	MSE	MUE	MSE	MUE	MSE	MUE	MSE	MUE	MMUE[a]	
B1LYP/6-31+G(d,p)	−6.28	6.28	−3.03	3.03	−0.92	2.49	−3.79	4.13	3.98	1.2
M05-2X/6-31G(d,p)	−0.21	2.08	−5.34	10.88	1.38	1.75	−0.79	2.06	4.19	1.5
PBE1PBE/6-31+G(d,p)	−6.90	6.90	−2.16	2.16	−0.53	2.75	−4.61	4.61	4.11	1.4
MPWB1K/cc-pVDZ	−1.93	3.14	−5.07	8.86	−0.31	1.58	−2.84	2.84	4.11	1.6
X3LYP/MG3S	−7.36	7.36	−2.85	2.85	−1.33	1.75	−4.91	4.91	4.22	11
MPW1K/6-31G(d)	−1.24	2.15	−3.54	9.11	1.50	3.11	−0.66	2.70	4.27	0.80
B3LYP/MG3S	−7.38	7.38	−3.44	3.44	−1.35	1.69	−4.73	4.73	4.31	9.4
M05-2X/6-31G(d)	−0.02	2.89	−5.26	10.84	1.77	1.77	−0.28	2.74	4.56	1.5
B97-3/6-31G(d)	−3.53	4.43	−5.51	10.29	1.08	1.89	−1.82	2.44	4.76	0.89
B3LYP*/6-31+G(d,p)	−6.52	6.52	−2.44	2.85	1.72	4.84	−3.81	4.17	4.60	1.4
PBE1KCIS/MG3S	−8.21	8.21	−1.90	1.90	−1.01	2.80	−5.71	5.71	4.66	12
B3LYP/6-31+G(d, p)	−8.08	8.08	−3.73	3.73	−1.30	2.59	−4.99	5.03	4.86	1.4
O3LYP/MG3S	−7.98	7.98	3.41	5.14	−1.42	2.19	−4.45	4.45	4.94	11
MPW3LYP/MG3S	−8.17	8.17	−4.55	4.55	−1.48	1.81	−5.27	5.27	4.95	11
TPSS1KCIS/MG3S	−8.45	8.45	−4.95	4.95	−1.29	1.66	−4.99	4.99	5.01	13

Table 3: Continued.

Methods	HATBH6		NSBH6		UABH6		HTBH6		DBH24	cost[b]
	MSE	MUE	MSE	MUE	MSE	MUE	MSE	MUE	MMUE[a]	
B97-2/6-31G(d)	−4.27	6.27	−6.71	11.02	1.25	2.05	−2.40	3.30	5.66	0.89
MPW1KCIS/MG3S	−9.45	9.45	−4.44	4.44	−1.38	2.61	−6.36	6.36	5.72	13
HFLYP/MG3S	11.17	11.17	5.28	5.28	3.51	4.20	5.44	5.44	6.52	10
TPSSh/MG3S	−10.75	10.75	−5.82	5.82	−2.94	2.94	−6.72	6.72	6.56	13
M05-2X/MIDI!	−5.80	6.22	−12.34	18.14	1.26	2.75	−3.44	3.85	7.74	1.20
MPW1K/MIDI!	−7.44	7.44	−11.08	16.24	0.90	3.26	−3.92	4.93	7.97	0.66
HF/MIDI!	11.10	11.10	−2.15	10.28	3.39	4.84	8.90	9.69	8.98	0.10
HF/6-31G(d)	16.98	16.98	2.78	6.17	4.18	4.18	12.20	12.20	9.88	0.15
HF/6-31+G(d,p)	17.50	17.50	5.63	5.63	3.97	3.97	12.42	12.42	9.88	0.67
HF/G3Large	17.50	17.50	6.41	6.41	3.48	3.57	12.33	12.33	9.95	13
HF/MG3S	17.65	17.65	6.38	6.38	3.52	3.62	12.34	12.34	10.00	9.2
N^3 Methods										
M06-L/MG3S	−6.72	7.22	−3.25	3.25	0.78	2.58	−4.21	4.32	4.34	5.7/8.9
M06-L/6-31+G(d,p)	−6.90	7.62	−4.13	4.13	0.29	2.36	−4.09	4.09	4.55	2.1/2.2
VSXC/MG3S	−7.53	7.53	−4.90	4.90	−0.19	1.49	−4.98	4.98	4.73	5.2/8.8
HCTH/MG3S	−9.46	9.46	−2.78	2.78	−0.79	1.74	−5.25	5.25	4.81	3.9/6.7
VSXC/6-31+G(d,p)	−8.06	8.06	−4.52	4.52	−0.12	2.16	−5.05	5.05	4.95	2.0/1.9

43

Table 3: Continued.

Methods	HATBH6		NSBH6		UABH6		HTBH6		DBH24	
	MSE	MUE	MSE	MUE	MSE	MUE	MSE	MUE	MMUE[a]	cost[b]
OLYP/MG3S	−10.81	10.81	−3.10	3.10	−2.35	2.35	−5.88	5.88	5.54	3.7/8.6
τHCTH/MG3S	−9.83	9.83	−6.01	6.01	−0.71	2.09	−6.21	6.21	6.04	5.4/8.8
M06-L/6-31G(d)	−6.95	8.86	−8.41	11.84	0.57	1.84	−3.21	3.33	6.47	1.7/1.6
G96LYP/MG3S	−11.57	11.57	−6.25	6.25	−2.88	2.88	−6.60	6.60	6.83	3.8/7.3
TPSSKCIS/MG3S	−12.27	12.27	−7.56	7.56	−2.36	2.36	−7.08	7.08	7.32	5.7/9.3
mPWKCIS/MG3S	−12.62	12.62	−6.69	6.69	−2.59	2.59	−7.56	7.56	7.37	6.1/9.7
BB95/MG3S	−13.21	13.21	−6.49	6.49	−3.20	3.20	−8.02	8.02	7.73	5.4/8.7
mPWPW/MG3S	−13.35	13.35	−7.32	7.32	−2.72	2.72	−8.47	8.47	7.97	3.8/7.1
BLYP/MG3S	−13.01	13.01	−8.64	8.64	−3.19	3.19	−7.83	7.83	8.17	3.8/7.3
TPSS/MG3S	−13.67	13.67	−7.43	7.43	−3.76	3.76	−8.30	8.30	8.29	5.5/8.8
PBE/MG3S	−14.25	14.25	−6.90	6.90	−3.01	3.01	−9.33	9.33	8.37	3.7/7.3
mPWLYP/MG3S	−14.09	14.09	−8.08	8.08	−3.37	3.37	−8.85	8.85	8.60	3.8/7.3
BLYP/6-31+G(d, p)	−13.88	13.88	−7.54	7.54	−3.31	3.31	−8.26	8.26	8.25	1.4/1.3
BP86/MG3S	−14.64	14.64	−7.02	7.02	−3.54	3.54	−9.29	9.29	8.62	3.9/6.9
M06-L/MIDI!	−11.88	13.07	−16.46	18.81	0.62	2.87	−6.20	6.20	10.24	1.6/1.4

Table 3: Continued.

Methods	HATBH6		NSBH6		UABH6		HTBH6		DBH24	cost[b]
	MSE	MUE	MSE	MUE	MSE	MUE	MSE	MUE	MMUE[a]	
PM3	−13.45	16.86	13.93	14.80	5.97	13.92	−3.63	5.82	12.85	5×10^{-5}
AM1	−9.08	11.83	10.53	15.56	13.06	18.88	−0.22	5.25	12.88	5×10^{-5}
SPL/MG3S	−23.05	23.05	−8.33	8.33	−5.21	5.21	−17.75	17.75	13.59	2.5/5.8
SPWL/MG3S	−23.16	23.16	−8.25	8.25	−5.34	5.34	−17.97	17.97	13.68	3.5/5.9
PDDG/PM3	−16.86	18.32	15.56	15.56	5.25	13.54	−4.00	12.47	14.97	5×10^{-5}
RM1	−20.05	20.93	0.27	15.46	10.47	19.83	−5.79	7.35	15.89	5×10^{-5}
PM6	−21.65	22.73	−0.79	4.13	13.97	22.04	−9.10	18.57	16.87	5×10^{-5}
SCC-DFTB	−23.02[d]	23.02[d]			1.00	9.78	−30.53	30.53	19.34[e]	4×10^{-4}

[a] MMUE is defined as Eq. 5.

[b] The cost for each method is measured by the computer time for an energy gradient calculation with the same software (except semiempirical molecular orbital methods, see text) on the same computer. The double entries of local DFT methods correspond to with/without density fitting.

[c] Although CBS methods are defined to use a lower-level geometry and are not normally employed in gradient calculations, we include a timing here so that the reader can judge their approximate cost on the same basis as the other methods. This timing is estimated as 49 times the cost of a single-point energy, since that is the cost of a numerical gradient for phosphinomethanol when using the *Gaussian03* program.

[d] These values are only for reaction H + N$_2$O → OH + N$_2$ and its reverse.

[e] It is the mean value of MUEs for HAT (H + N$_2$O → OH + N$_2$ and its reverse), UABH6, and HTBH6.

45

Table 4: Best methods for barrier height calculations as judged by performance for a given cost and scaling.

Method	Scaling	Cost	MMUE/DBH24 (kcal/mol)
G3SX	7	246	0.64
BMC-CCSD	6	27	0.72
PWB6K/MG3S	4	12	1.21
BB1K/6-31+G(d,p)	4	2.0	1.70
MPW1K/6-31+G(d,p)	4	1.4	1.92
MPW1K/MIDIX+	4	1.0	3.10
MPW1K/6-31B(d)	4	0.80	3.66
MPW1K/MIDI!	4	0.66	7.97
HF/MIDI!	4	0.10	8.98
M06-L/MG3S	3	5.7	4.34
M06-L/6-31+G(d,p)	3	2.1	4.55
M06-L/6-31G(d)	3	1.6	6.47
BLYP/6-31+G(d,p)	3	1.3	8.25
PM3	3	5×10^{-5}	12.85

Table 5: Other methods to be considered for reaction dynamics calculations based on overall quality.

Method	Scaling	Cost	MMUE/DBH24 (kcal/mol)
G3SX(MP3)	7	175	0.71
MCG3-MPW	7	113	0.79
MCQCISD-MPWB	6	35	0.95
MC3MPWB	5	14	1.37
M05-2X/MG3S	4	13	1.61
M05-2X/6-31+G(d,p)	4	2.1	1.92
PWB6K/6-31+G(d,p)	4	2.0	1.73
AM1	3	5×10^{-5}	12.88